

Mechanical Properties and Testing of Polymers

POLYMER SCIENCE AND TECHNOLOGY SERIES

Volume 3

Series editors

Dr Derek Brewis
Inst. of Surface Science & Technology
Loughborough University of
Technology
Loughborough, Leicestershire
LE11 3TU

Professor David Briggs
Siacon Consultants Ltd
21 Wood Farm Road
Malvern Wells
Worcestershire
WR14 4PL

Advisory board

Professor A. Bantjes
University of Twente
Faculty of Chemical Technology
Department of Macromolecular
Chemistry and Materials Science
PO Box 217, 7500 AE Enschede
The Netherlands

Dr Chi-Ming Chan
Department of Chemical Engineering
The Hong Kong University of Science
and Technology
Room 4558, Academic Building
Clear Water Bay, Kowloon
Hong Kong

Dr John R. Ebdon
The Polymer Centre
School of Physics and Chemistry
Lancaster University
Lancaster LA1 4YA
UK

Professor Robert G. Gilbert
School of Chemistry
University of Sydney
New South Wales 2006
Australia

Professor Richard Pethrick
Department of Pure and Applied
Chemistry
Strathclyde University
Thomas Graham Building
295 Cathedral Street
Glasgow G1 1XL
UK

Dr John F. Rabolt
Materials Science Program
University of Delaware
Spencer Laboratory #201
Newark, Delaware 19716
USA

The titles published in this series are listed at the end of this volume.

Mechanical Properties and Testing of Polymers

An A-Z Reference

Edited by

G.M. SWALLOWE

*Department of Physics,
Loughborough University of Technology,
Leicestershire, United Kingdom*



SPRINGER-SCIENCE+BUSINESS MEDIA, B.V.

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 978-90-481-4024-4 ISBN 978-94-015-9231-4 (eBook)
DOI 10.1007/978-94-015-9231-4

Printed on acid-free paper

All Rights Reserved
© 1999 Springer Science+Business Media Dordrecht
Originally published by Kluwer Academic Publishers in 1999
Softcover reprint of the hardcover 1st edition 1999

No part of the material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without written permission from the copyright owner.

List of Contributors

Dr. M. A. Ansarifar, IPTME, Loughborough University, Leics LE11 3TU, U.K.

Dr. M. Ashton, Dept. of Aeronautical and Automotive Engineering, Loughborough University, LE11 3TU, U.K.

Prof. M. Boyce, Dept. of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts MA02139, USA

Prof. B. J. Briscoe, Dept. of Chemical Engineering, Imperial College, London SW7 2BY, U.K.

Dr. C. Chui, Dept. of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts MA02139, USA

Dr. P. Dawson, Epron Industries Ltd., Ketton, Stamford, Lincs. PE9 3SZ, U.K.

Dr. A. E. Donald, Polymers and Colloids Group, Cavendish Laboratory, Cambridge CB3 0HE, U.K.

Dr. J. Duncan, 38 Bramcote Road, Loughborough, Leics LE11 2SA, U.K.

Prof. K. E. Evans, School of Engineering, University of Exeter, North Park Road, Exeter, EX4 4QF, UK

Prof. N. Fleck, Cambridge University Engineering Dept., Trumpington St., Cambridge CB2 1PZ, U.K.

Dr. C. Gauthier, Institut National des Sciences Appliquées de Lyon, 20 Avenue Albert Einstein, 69621 Villerbaune Cedex, France

Prof. D. J. Hourston, IPTME, Loughborough University, Leics LE11 3TU, U.K.

Prof. H. H. Kausch, Laboratoire de Polymers, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Dr. P. S. Leever, Dept. of Mechanical Engineering, Imperial College, London SW7 2BX, U.K.

Dr. P. Ludovice, School of Chemical Engineering, Georgia Institute of Technology, 778 Atlantic Dr., Atlanta, Georgia 30332, U.S.A.

Dr. D. R. Moore, ICI plc, Research and Technology Centre, PO Box 90, Wilton, Middlesborough, Cleveland, TS90 8JE, U.K

Dr. E. J. Moskala, Eastmann Chemical Company Research Laboratories, Kingsport, Tennessee 37662, U.S.A.

Dr. T. Q. Nguyen, Laboratoire de Polymers, Ecole Polytechnique Federale de Lausanne, CH-1015 Lausanne, Switzerland

Dr. D. J. Parry, Dept. Physics, Loughborough University, LE11 3TU, U.K.

Dr. P. E. Reed, Dept. of Mechanical Engineering, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

Dr. A. Rennie, Chemistry Dept., Kings College London, Strand, London WC2R 2LS, U.K.

Dr. S. K. Sinha, Dept of Chemical Engineering, Imperial College, London SW7 2BY, U.K.

Dr. G. Swallowe, Dept. Physics, Loughborough University, Leics LE11 3TU, U.K.

Dr. S. Walley, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, U.K.

Dr. L. Warnet, Dept. of Mechanical Engineering, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

Alphabetical list of Articles

1:Accuracy and Errors	G. M. Swallowe	1
2:Adhesion of Elastomers	M. A. Ansarifar	5
3:Adiabatic Shear Instability: Observations and Experimental Techniques	S. M. Walley	10
4:Adiabatic Shear Instability: Theory	N. A. Fleck	15
5:Alloys and Blends	D. J. Hourston	20
6:Amorphous Polymers	A. R. Rennie	23
7:Crazing	G. M. Swallowe	25
8:Creep	D. R. Moore	29
9:Crystalline Polymers	A. R. Rennie	32
10:Crystallinity	G. M. Swallowe	34
11:Ductile-Brittle Transition	G. M. Swallowe	40
12:Dynamic Mechanical Analysis Techniques and Complex Modulus	J. Duncan	43
13:Electron Microscopy applied to the Study of Polymer Deformation	A. M. Donald	49
14:Environmental Effects	G. M. Swallowe	52
15:Falling Weight Impact Tests	P. E. Reed	57
16:Falling Weight Impact Testing Equipment	L. Warnet and P. E. Reed	61
17:Falling Weight Impact Testing Principles	L. Warnet and P. E. Reed	66
18:Fast Fracture in Polymers	P. S. Leevers	71
19:Fatigue	E. J. Moskala	75
20:The Finite Element Method	M. Ashton	81
21:Flow Properties of Molten Polymers	P. C. Dawson	88
22:Fracture Mechanics	P. S. Leevers	96
23:Friction	B. J. Briscoe and S. K. Shinha	102
24:Glass Transition	D. J. Hourston	109
25:Hardness and Normal Indentation of Polymers	B. J. Briscoe and S. K. Shinha	113
26:The Hopkinson Bar	D. J. Parry	123

27: <i>Impact Strength</i>	P. S. Leever	127
28: <i>Impact and Rapid Crack Propagation Measurement Techniques</i>	P. S. Leever	130
29: <i>Manipulation of Poisson's Ratio</i>	K. E. Evans	134
30: <i>Measurement of Creep</i>	D. R. Moore	137
31: <i>Measurement of Poisson's Ratio</i>	K. E. Evans	140
32: <i>Molecular Weight Distribution and Mechanical Properties</i>	T. Q. Nguyen and H. H. Kausch	143
33: <i>Molecular Weight Distribution: Characterisation by GPC</i>	T. Q. Nguyen and H. H. Kausch	151
34: <i>Monte Carlo Techniques</i>	C. Chiu and M. Boyce	156
35: <i>Monte Carlo Techniques applied to Polymer Deformation</i>	C. Chiu and M. Boyce	163
36: <i>Neutron Scattering</i>	A. R. Rennie	171
37: <i>Non Elastic Deformation during a Mechanical Test</i>	C. Gauthier	174
38: <i>Plasticisers</i>	G. M. Swallowe	179
39: <i>Poisson's Ratio</i>	K. E. Evans	183
40: <i>Polymer Models</i>	D. J. Parry	187
41: <i>Recovery of Glassy Polymers</i>	C. Gauthier	191
42: <i>Relaxations in Polymers</i>	G. M. Swallowe	195
43: <i>Sensors and Transducers</i>	G. M. Swallowe	199
44: <i>Slow Crack Growth and Fracture</i>	P. S. Leever	204
45: <i>Slow Crack Growth and Fracture: Measurement Techniques</i>	P. S. Leever	208
46: <i>Standards for Polymer Testing</i>	G. M. Swallowe	211
47: <i>Strain Rate Effects</i>	G. M. Swallowe	214
48: <i>Stress and Strain</i>	G. M. Swallowe	219
49: <i>Structure-Property Relationships: Glassy Polymers</i>	P. J. Ludovice	225
50: <i>Structure-Property Relationships: Large Strain</i>	P. J. Ludovice	233
51: <i>Structure-Property Relationships: Rubbery Polymers</i>	P. J. Ludovice	238
52: <i>Tensile and Compressive Testing</i>	G. M. Swallowe	242
53: <i>Thermoplastics and Thermosets</i>	A.R. Rennie	248

54: <i>Time-Temperature Equivalence</i>	G. M. Swallowe	249
55: <i>Torsion and Bend Tests</i>	G. M. Swallowe	252
56: <i>Toughening</i>	G. M. Swallowe	257
57: <i>Ultrasonic Techniques</i>	G. M. Swallowe	260
58: <i>Viscoelasticity</i>	G. M. Swallowe	265
59: <i>Wear</i>	B. J. Briscoe and S. K. Shinha	270
60: <i>X-Ray scattering Methods in the Study of Polymer Deformation</i>	A. M. Donald	278
61: <i>Yield and Plastic Deformation</i>	G. M. Swallowe	281
Appendix 1: <i>Further Reading-Selected Bibliography</i>		286
Appendix 2: <i>Glossary</i>		290
Appendix 3: <i>Table of mechanical properties</i>		294
Index		296

Classified list of Articles

MODELING

20:	<i>The Finite Element Method</i>	M. Ashton	81
34:	<i>Monte Carlo Techniques</i>	C. Chiu and M. Boyce	156
35:	<i>Monte Carlo Techniques applied to Polymer Deformation</i>	C. Chiu and M. Boyce	163
40:	<i>Polymer Models</i>	D. J. Parry	187

PROPERTIES AND GENERAL

2:	<i>Adhesion of Elastomers</i>	M. A. Ansarifar	5
5:	<i>Alloys and Blends</i>	D. J. Hourston	20
6:	<i>Amorphous Polymers</i>	A. R. Rennie	23
7:	<i>Crazing</i>	G.M. Swallowe	25
8:	<i>Creep</i>	D. R. Moore	29
9:	<i>Crystalline Polymers</i>	A. R. Rennie	32
10:	<i>Crystallinity</i>	G. M. Swallowe	34
11:	<i>Ductile-Brittle Transition</i>	G. M. Swallowe	40
14:	<i>Environmental Effects</i>	G. M. Swallowe	52
18:	<i>Fast Fracture in Polymers</i>	P. S. Leever	71
19:	<i>Fatigue</i>	E. J. Moskala	75
21:	<i>Flow Properties of Molten Polymers</i>	P. C. Dawson	88
23:	<i>Friction</i>	B. J. Briscoe and S. K. Shinha	102
24:	<i>Glass Transition</i>	D. J. Hourston	109
25:	<i>Hardness and Normal Indentation of Polymers</i>	B. J. Briscoe and S. K. Shinha	113
27:	<i>Impact Strength</i>	P. S. Leever	127
29:	<i>Manipulation of Poisson's Ratio</i>	K. E. Evans	134

32:	<i>Molecular Weight Distribution and Mechanical Properties</i>	
	T. Q. Nguyen and H. H. Kausch	143
36:	<i>Neutron Scattering</i>	A. R. Rennie 171
37:	<i>Non Elastic Deformation during a Mechanical Test</i>	C. Gauthier 174
38:	<i>Plasticisers</i>	G. M. Swallowe 179
39:	<i>Poisson's Ratio</i>	K. E. Evans 183
41:	<i>Recovery of Glassy Polymers</i>	C. Gauthier 191
42:	<i>Relaxations in Polymers</i>	G. M. Swallowe 195
44:	<i>Slow Crack Growth and Fracture</i>	P. S. Leevers 204
47:	<i>Strain Rate Effects</i>	G. M. Swallowe 214
53:	<i>Thermoplastics and Thermosets</i>	A.R. Rennie 248
54:	<i>Time-Temperature Equivalence</i>	G. M. Swallowe 249
56:	<i>Toughening</i>	G. M. Swallowe 257
58:	<i>Viscoelasticity</i>	G. M. Swallowe 265
59:	<i>Wear</i>	B. J. Briscoe and S. K. Shinha 270
61:	<i>Yield and Plastic Deformation</i>	G. M. Swallowe 281

TESTING

3:	<i>Adiabatic Shear Instability: Observations and Techniques</i>	S. M. Walley 10
12:	<i>Dynamic Mechanical Analysis Techniques and Complex Modulus</i>	J. Duncan 43
13:	<i>Electron Microscopy applied to the Study of Polymer Deformation</i>	A. M. Donald 49
15:	<i>Falling Weight Impact Tests</i>	P. E. Reed 57
16:	<i>Falling Weight Impact Testing Equipment</i>	L. Warnet and P. E. Reed 61
26:	<i>The Hopkinson Bar</i>	D. J. Parry 123
28:	<i>Impact and Rapid Crack Propagation Measurement Techniques</i>	P. S. Leevers 130
30:	<i>Measurement of Creep</i>	D. R. Moore 137
31:	<i>Measurement of Poisson's Ratio</i>	K. E. Evans 140
33:	<i>Molecular Weight Distribution: Characterisation by GPC</i>	T. Q. Nguyen and H. H. Kausch 151

43:	<i>Sensors and Transducers</i>	G. M. Swallowe	199
45:	<i>Slow Crack Growth and Fracture: Measurement Techniques</i>	P. S. Leever	208
46:	<i>Standards for Polymer Testing</i>	G. M. Swallowe	211
52:	<i>Tensile and Compressive Testing</i>	G. M. Swallowe	242
55:	<i>Torsion and Bend Tests</i>	G. M. Swallowe	252
57:	<i>Ultrasonic Techniques</i>	G. M. Swallowe	260
60:	<i>X-Ray scattering Methods in the Study of Polymer Deformation</i>	A. M. Donald	278

THEORY

1:	<i>Accuracy and Errors</i>	G. M. Swallowe	1
4:	<i>Adiabatic Shear Instability: Theory</i>	N. A. Fleck	15
17:	<i>Falling Weight Impact Testing Principles</i>	L. Warnet and P. E. Reed	66
22:	<i>Fracture Mechanics</i>	P. S. Leever	96
48:	<i>Stress and Strain</i>	G. M. Swallowe	219
49:	<i>Structure-Property Relationships: Glassy Polymers</i>	P. J. Ludovice	225
50:	<i>Structure-Property Relationships: Large Strain</i>	P. J. Ludovice	233
51:	<i>Structure-Property Relationships: Rubbery Polymers</i>	P. J. Ludovice	238

Preface

This volume represents a continuation of the Polymer Science and Technology series edited by Dr. D. M. Brewis and Professor D. Briggs. The theme of the series is the production of a number of stand alone volumes on various areas of polymer science and technology. Each volume contains short articles by a variety of expert contributors outlining a particular topic and these articles are extensively cross referenced. References to related topics included in the volume are indicated by **bold text** in the articles, the bold text being the title of the relevant article. At the end of each article there is a list of bibliographic references where interested readers can obtain further detailed information on the subject of the article.

This volume was produced at the invitation of Derek Brewis who asked me to edit a text which concentrated on the mechanical properties of polymers. There are already many excellent books on the mechanical properties of polymers, and a somewhat lesser number of volumes dealing with methods of carrying out mechanical tests on polymers. Some of these books are listed in Appendix 1. In this volume I have attempted to cover basic mechanical properties and test methods as well as the theory of polymer mechanical deformation and hope that the reader will find the approach useful. However, rather than concentrating solely on topics which are well covered by previous authors, I have also attempted to cover areas of polymer science which have been relatively neglected in non-specialised texts but which I feel are of some importance. These are, in particular, the areas of high strain rate behaviour, anelastic deformation, adiabatic shearing, rapid fracture, friction and wear as well as the predictive areas of structure-property relationships. I have also included articles on more exotic techniques such as neutron diffraction and computer modeling which are increasingly being used to advance polymer science as well as on the much neglected topic of the Poisson's ratio of polymers. I am indebted to the contributors who produced such clear expositions of these topics in their articles.

The volume departs from the pattern set in previous volumes of the series in that the articles are, in general, considerably longer than those found in the earlier books. This is so that a somewhat more detailed description of the topics can be given by the contributors. I believe that this will provide a more useful introduction to the topics and enable the reader to move with confidence to the specialist references listed at the end of each article and also enable the links between the different aspects of polymer mechanical properties to be more clearly seen.

I am extremely grateful to the individual authors for their cooperation and the patience that was required in the preparation of the text. Any errors that may have crept into the final version of the articles are entirely my responsibility.

G. M. Swallowe
Loughborough University
May 1999

1: Accuracy and errors

G. M. Swallowe

Tests give rise to numerical results for properties such as modulus, flow stress etc. but quoting a result without an estimate of its accuracy is only of limited use. For example a specimen may be measured and its length quoted as 10 mm. Conventionally this may be taken to mean that the length falls between 9 and 11 mm i.e. the specimen length is 10 ± 1 mm. However the measurement may have been taken to either greater or lesser accuracy than convention suggests. It could have been measured to 0.1 mm giving a result 10.0 ± 0.1 mm or alternatively taken very roughly as 'about 10 mm' meaning anything between 8 and 12 mm. If the accuracy is not quoted a user of the measurement is unaware of the measurement accuracy and can only guess that the measurement has been made to an accuracy of ± 1 in the last figure. It is common practice to call the accuracy estimate 'the error' and although this may carry the implications of 'a mistake' the terminology is commonly used and will be used here.

SYSTEMATIC AND RANDOM ERRORS

Errors may conveniently be classified into two groups, systematic and random. Random errors and an outline of their treatment will be discussed below. Systematic errors, which are harder to deal with, are discussed first. A systematic error is often due to inaccuracy or incorrect operation of an instrument and will usually not be discovered unless a calibration of the instrument is carried out or an operator fully conversant with the instruments operation re-measures a sample. However systematic errors can arise from a wide variety of other sources. For example a series of measurements that depend on viscosity which are made on a Monday morning while the laboratory is heating up after a weekend shut down will lead to inaccuracies because viscosity falls rapidly with temperature. The slow uptake of water by a sample of nylon will lead to changes in mechanical properties which may be wrongly attributed to other reasons if the moisture content is not monitored. The use of an incorrect theory to derive a result from a set of measurements can also be considered to be a systematic error. Humans are often biased in their reading of a scale and will frequently 'round' to the nearest graticule mark even if accurate between mark estimates can be made. They are also prone to bias reading in the direction they wish them to go, and may tend to underestimate values if they feel that the results are coming out higher than is desired or expected or visa versa.

It is very difficult to be sure that systematic errors have been eliminated in a set of measurements since by their very nature one is often not aware of their presence. The chance of a systematic error arising can however be considerably reduced by frequent calibration of equipment, careful design of experiments, and conscious effort to be unbiased when taking readings. The use of a control experiment where the same quantity

is measured using alternative equipment or another operator also greatly assists in the elimination of systematic errors.

RANDOM ERRORS

Suppose a specimen of true length x_0 is measured by a number of experimenters and they obtain values x_1, x_2, x_3 etc. for the length of the specimen. It is assumed that the measurements x_1, x_2, x_3 etc. will be randomly distributed about the true value x_0 with a distribution which peaks at x_0 . The distribution of the measurements about the true value is assumed to follow the Gaussian distribution, this is also called the Normal distribution, and it is frequently met in practice. The value quoted is the mean of the values x_1, x_2, x_3 etc. and the error is taken to be the standard deviation σ of the distribution of measurements. The same is true if a single operator makes repeated measurements on one specimen and by extension if a single operator makes many measurements on a number of samples drawn from what is nominally an identical batch. The latter case may in fact give rise to a distribution which is not Gaussian either due to a bias on one side or other of the true mean in the samples selected, this can be eliminated by choosing a greater number of samples. However it must be borne in mind that it is possible that the distribution of lengths is not in fact Gaussian. Non Gaussian distributions are quite common but from the point of view of getting a value of some quantity together with an estimate of the accuracy of this value the Gaussian assumption is normally a reasonable one.

Quoting a value to $\pm\sigma$ means that there is a 68% chance that the true value will lie in the range quoted, quoting to $\pm 2\sigma$ means a 95% chance and to $\pm 3\sigma$ a 99.7% chance. It is usual to quote $\pm\sigma$ but 2σ is sometimes used and it is important that if anything other than $\pm\sigma$ is quoted that this is made clear. Most scientific pocket calculators now have in built programmes to enable the mean and standard deviation of a series of measurements to be calculated.

COMBINATIONS OF ERRORS

It is frequently the case that a quantity is determined from a formula relating it to other more easily measurable quantities. A simple example would be the density of a cylindrical specimen. This could be obtained by weighing and measuring its length and radius then calculating the density from the expression $\rho = M/\pi r^2 l$. In this case the errors in the measured quantities radius r , length l and mass M must be combined to yield the error in density. Rules to determine the errors in a derived quantity q where the measured quantities are a, b, c etc. and the errors in these quantities are $\Delta a, \Delta b, \Delta c$ etc. are:

For sums and differences: $q = a + b + c \dots$ add the squares

$$\Delta q^2 = \Delta a^2 + \Delta b^2 + \Delta c^2 + \quad (1)$$

For products: $q = abc\dots$ add the squares of fractional errors

$$(\Delta q/q)^2 = (\Delta a/a)^2 + (\Delta b/b)^2 + (\Delta c/c)^2 + \quad (2)$$

For power relationships: $q = a^r b^s c^t \dots$ add the squares of the fractional errors multiplied by the powers

$$(\Delta q/q)^2 = r^2(\Delta a/a)^2 + s^2(\Delta b/b)^2 + t^2(\Delta c/c)^2 \quad (3)$$

Rules for other functional relationships as well as the derivation of these relationships can be found in the standard texts listed in the references. For trigonometric functions it is simple to calculate the errors associated with θ (the angle) and take the range of the trigonometric function including $\pm\Delta\theta$ as the error.

If a single specimen is measured n times and the measurements each have an accuracy of σ the error in the mean of these measurements, i.e. the error in the assumed true value of the quantity being measured, is given by $\sigma/\sqrt{n}$. Therefore by measuring a quantity many times the error in the mean is reduced. However this is a situation of diminishing returns, the error only decreases as the square root on the number of measurements.

PRACTICAL CONSIDERATIONS

It is frequently the case that only a small number n of repeat measurements are made (typically between 3 and 10) in order to determine a quantity such as a yield stress and that the mean of these measurements is then quoted as the value of the quantity under investigation. In these cases simple estimates of errors will give values of the error which are just as valid as those derived from detailed calculations of a standard deviation. A useful rule of thumb is to take the error as $1/\sqrt{n}$ of the range (i.e. difference between the greatest and smallest) of the measured values of the quantity of interest.

In the case of a functional relationship between the quantity to be determined and a number of measured quantities (such as r , l and M in the density example above) it is often the case that one error dominates the calculation. It may be for example that there is a 10% error in r ($\Delta r/r = 0.1$) but only 1% in l and 0.1% in M . In cases like these there, where one error dominates all the others, there is little point carrying out a full error calculation and the error in ρ can immediately be quoted to be $\pm 20\%$ (square root of $2^2(\Delta r/r)^2$).

Limits of error, rather than standard deviations are frequently quoted when the value is the result of a single measurement, e.g. reading the scale on a meter stick. Thus a value of a length may be quoted as 40.5 ± 0.5 mm meaning that the value lies between 40 and 41 mm but that it is almost certain not to be outside this range. Recalling that $\pm$ a

standard deviation encompasses a 68% chance of including the true value it can be seen that a “limit of error” is a more conservative estimate than a standard deviation and may be taken to be approximately equal to two standard deviations.

In the case of polymers in particular, the variability of the properties of notionally the same material between different batches can be quite high. If all the measurements combined in the error calculation for a particular property are made on samples from the same batch the quoted error may be exceeded by the batch to batch variability of the property. Care should therefore be taken when quoting (or using) error estimates that it is clear to what population the value and its quoted error applies i.e. is the error estimate applicable only to a particular batch of material or representative of the range of properties observed over a large number of batches of notionally the same material.

REFERENCES

1. Barford, C. (1985) *Experimental Measurements: Precision, Error and Truth*, Wiley and Sons
2. Turner, S. (1983) *Mechanical Testing of Plastics 2nd ed.*, George Godwin.

2: Adhesion of Elastomers

M. A. Ansarifar

Joining an elastomer to itself or to dissimilar elastomers is a feature widely utilised in the manufacture of elastomer-based products such as conveyor belts and hoses. The strength of the joint depends mainly on the intimate contact time between the surfaces. Other factors such as polarity, molecular weight and intimate contact temperature are found to influence the strength of the interfacial adhesion and the time needed for the attainment of full joint strength.

EFFECTS OF CONTACT TIME AND TEMPERATURE, AND MOLECULAR WEIGHT ON JOINT STRENGTH

In joining an elastomer to itself (self-adhesion) or to dissimilar elastomers (mutual adhesion), it is essential to bring the surfaces into intimate contact under pressure. Provided that the surfaces are kept under pressure for a sufficient length of time, the interfacial adhesion may increase with time, eventually reaching its maximum possible attainable strength (see also **Friction**). There are at least two main processes occurring at the interface which contribute to the development of interfacial adhesion. The first is an increase in the area of real intimate contact at molecular level¹. Often elastomer surfaces are uneven and contain craters and asperities which reduce the area available for interfacial contact between the participating surfaces. Furthermore, contaminants such as grease or gases can be trapped at the interface further reducing the contact area; however provided that a sufficient pressure is applied to the joint and enough time is allowed, these inhibitors may diffuse away from the region of the interface into the bulk of the elastomer facilitating complete actual contact at molecular level.

Secondly, following the attainment of actual molecular contact, elastomer chains may diffuse across the interface into the opposite mass² and entangle themselves physically with other chains. This mechanism enhances the strength of interfacial adhesion. The process of chain interdiffusion is influenced by the mobility and freedom of molecular chains to diffuse across the interface and is fundamentally governed by the diffusion coefficient of the elastomer³. Increasing the intimate contact temperature or decreasing the molecular weight of the elastomer reduces the viscosity of the material and either assists the surfaces in wetting more effectively at the interface or speeds up the process of chain interdiffusion.

INFLUENCE OF POLARITY ON INTERFACIAL JOINT STRENGTH

In order for two polymers to be miscible, the Gibb's free energy of mixing (ΔG_{mix}) given by expression (1) must be negative

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \quad (1)$$

where the enthalpy term ΔH_{mix} is essentially independent of molecular weight and is a measure of the energy change associated with intermolecular interactions and the entropy term ΔS_{mix} is associated with the change in molecular arrangements. The magnitude of the entropy change is essentially an inverse function of the molecular weight of the polymers being mixed, and is likely to be small. ΔH_{mix} is thus the parameter determining the miscibility of high molecular weight polymers (see **Alloys and Blends**). For two non-polar polymers with solubility parameters δ_1 and δ_2 , ΔH_{mix} can be expressed as

$$\Delta H_{mix} \propto (\delta_1 - \delta_2)^2 \quad (2)$$

Miscibility on a molecular scale is possible when the difference in the solubility parameters of the two polymers is very small. However, this is seldom the case so that ΔH_{mix} is greater than $T\Delta S_{mix}$ and therefore non-polar polymer pairs are generally unable to satisfy the conditions for miscibility. For polar polymers, which allow specific interactions to occur, ΔH_{mix} may be negative so that mixing may take place at the interface between the polymers creating good joint strength.

TEST METHOD AND RECENT FINDINGS

Adhesion tests can be carried out by bringing the surfaces into contact and leaving them under a constant applied pressure at a fixed temperature for various lengths of time. Subsequently the samples are peeled apart at ambient temperature and at an angle of 180° , and the peel force recorded. The peel energy, P , is calculated from the average peel force, F , using the relation

$$P = 2F/w \quad (3)$$

where w is the width of the test-piece.

More recent studies⁴, as summarised in the following, are typical of the procedure used in adhesion tests. In these studies the self-adhesion and mutual-adhesion of various unvulcanised elastomers with different molecular weights and chemical compositions have been measured. The surfaces were brought into contact and left under a constant applied pressure at either ambient temperature 23°C or at 60°C for various lengths of time. The elastomers selected for these studies were chemically incompatible and hence

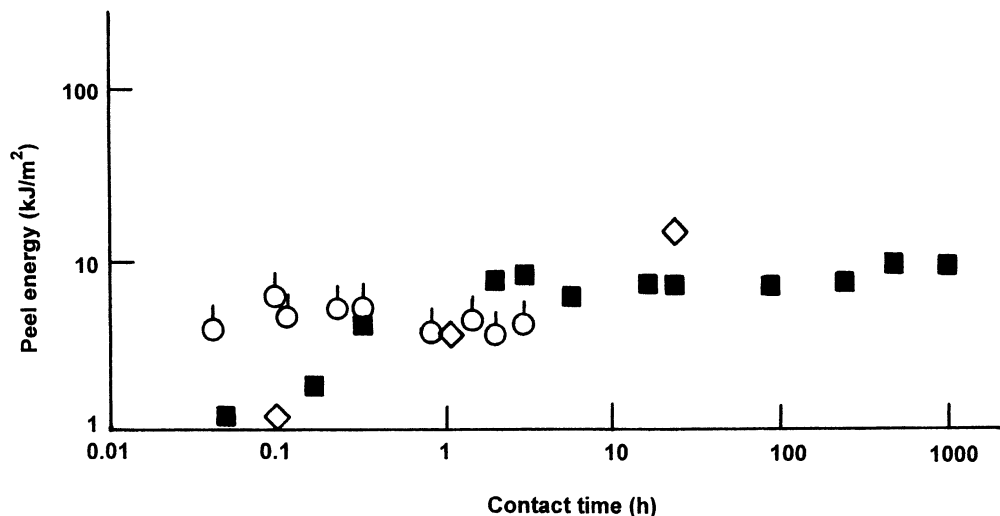


Figure 1: Variation of self-adhesion of ENR and IR with time of contact. ENR ■ IR ($M_w \sim 1000k$) ◇ and IR ($M_w \sim 477k$) O; contact temperature 23 °C.

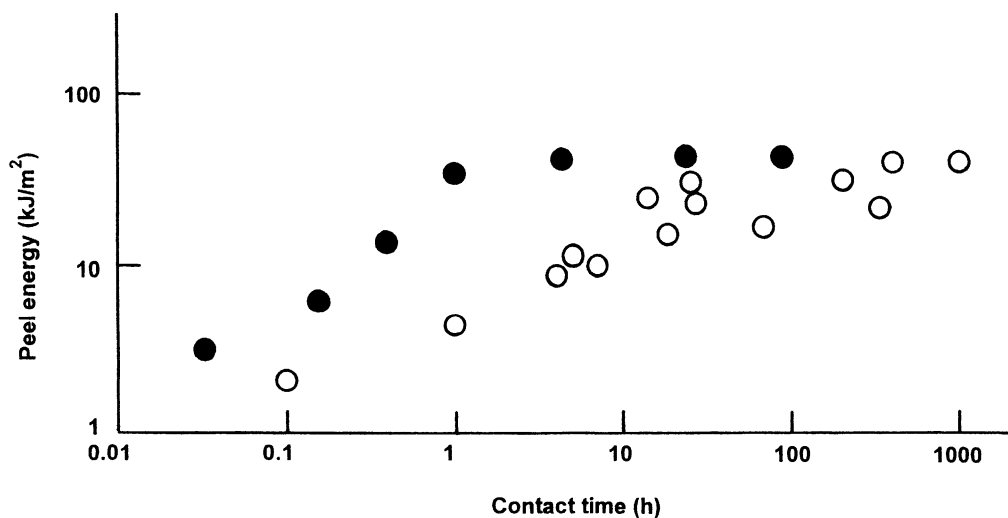


Figure 2: Variation of self-adhesion of NBR with time of contact. Contact temperature 23 °C O, contact temperature 60 °C ●.

any mutual chain interdiffusion at the interface was limited to short segments of chains and strong joints were not formed. The self-adhesion of some elastomers such as polar nitrile rubber (NBR)($M_w \sim 250k$), polar epoxidised natural rubber (ENR 50)($M_w \sim 270k$), non-polar synthetic polyisoprene (IR)($M_w \sim 1000k$) and non-polar ethylene-

propylene rubber (EPR)(MW ~ 180k) was found to be time-dependent over the time scales studied reaching a plateau energy for some of the materials.

Other systems such as non-polar natural rubber (NR)(MW ~ 430k), non-polar polybutadiene (BR)(MW ~ 274k), and IR (MW ~ 477k) attained their full joint strengths almost immediately after the surfaces were brought into intimate contact under pressure. Some examples are shown in figure 1. Interestingly, when the self adhesion strength of NBR was measured, after the surfaces were brought into intimate contact at either 23 °C or 60 °C and then peeled at 23 °C, a similar maximum joint strength was recorded in both cases (figure 2). It also emerged that increasing the intimate contact temperature shortened the time needed for adhesion to start to increase and advanced noticeably the rate of development of the joint strength towards reaching a plateau. In similar studies, the mutual-adhesion between these elastomers was measured. Surprisingly, the adhesion of ENR/NBR, IR/ENR, IR/EPR and NR/NBR pairs was found to improve with intimate contact time, in some cases reaching the cohesive strength of the weakest adherent, provided that the surfaces were kept in full intimate contact for sufficient length of time in each test. The highest and the lowest joint strengths were recorded for the NBR/ENR and NBR/NR pairs respectively (figure 3). In contrast, the adhesion of the ENR/BR pair showed no sign of improving with time, remained low over the time scale studied and produced a weak joint similar to the NBR/NR combination. Similar tests with the ENR/NBR pair at 60 °C contact temperature, showed a substantial shortening of the time needed for the onset of increase in the strength of the adhesion between the elastomers (figure 4). Moreover, a noticeable increase in the rate of development of the strength of the joint was recorded.

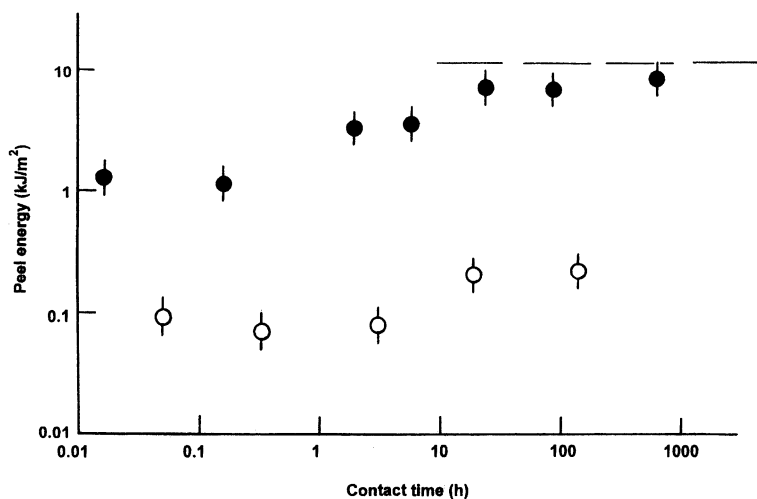


Figure 3: Variation of mutual adhesion of NBR/ENR and NBR/NR with time of contact at 23 °C. NBR/ENR ●, NBR/NR ○ and cohesive strength ENR —

SUMMARY

The phenomenon of interfacial adhesion between elastomers may be attributed mainly to an increase in the area of actual intimate contact between the surfaces and an interdiffusion mechanism at the interface. Admittedly, the exact extent or nature of the contributions made by these sources is not immediately known. Other factors which may be governing the adhesion process are not yet fully understood. It remains to be seen to what extent exactly the aforementioned factors may be influencing the phenomena measured in the adhesion tests and how the unexpected increases in the strength of interfacial adhesion between chemically incompatible elastomers can be explained.

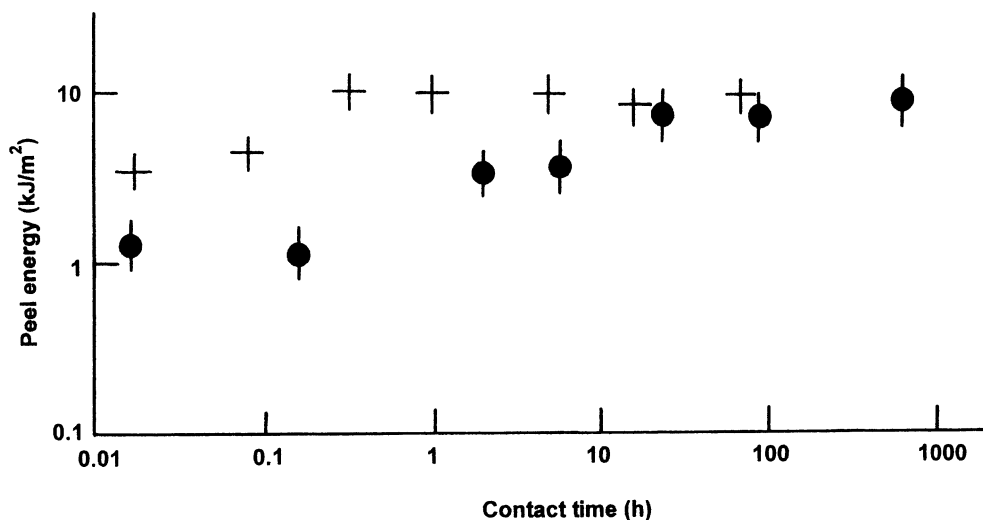


Figure 4: Variation of mutual adhesion of NBR/ENR with time of contact.
Contact temperature 23 °C ●, contact temperature 60 °C +

REFERENCES

1. Hamed, G.R. (1981) Tack and green strength of elastomeric materials. *Rubber Chem. Technol.*, **54**, 576-595.
2. Klein, J. (1990) The interdiffusion of polymers. *Science*, **250**, 640-646.
3. Skewis, J.D. (1966) Self-adhesion coefficients and tack of some rubbery polymers. *Rubber Chem. Technol.*, **39**, 217-225.
4. Ansarifar, M.A., Fuller, K.N.G., Lake, G.L. and Raveendran, B. (1993) Adhesion of vulcanised elastomers. *Int. J. Adhesion and Adhesives*, **13**, 105-110.

3: Adiabatic Shear Instability: Observations and Experimental Techniques

S.M. Walley

INTRODUCTION

Although an extensive literature exists on experimental studies of adiabatic shear banding in metals¹ and shear bands have been studied in polymers at low rates of deformation² very little has been published on adiabatic shear bands (ASBs) in polymers at high rates of deformation (see **Adiabatic Shear Instability: Theory**). Most studies on polymer failure during impact have largely been concerned with fracture³, ballistic impact⁴, and sensitisation of energetic materials⁵. As ASBs are often precursors to fracture, it is not always clear from *post-mortem* examination of a specimen whether shear-bands were present before fracture took place, particularly if the fracture was partially or entirely mode III. The rubbing together of the free surfaces can destroy crucial evidence of the nucleation and growth of the bands.

EXPERIMENTAL METHODS

ASBs are distinguished from other forms of shear-banding by being formed at high rates of deformation. A pre-requisite for studying them are machines for subjecting specimens to impact loading. Such machines may be designed primarily to simulate 'real-life' impacts (e.g. hemispherically-nosed **drop-weights**, laboratory gas-guns, exploding tubes) or to generate 'pure' states of stress and strain, to generate strength data for validating constitutive models (e.g. hydraulically operated mechanical testing machines, dropweights with flat anvils, **Hopkinson pressure bars**, exploding rings, plate impact). It is generally easier to make and interpret observations made with the latter types of machines.

In addition to the mechanical testing machines themselves, instrumentation capable of recording data on microsecond timescales is required if it is desired to study the nucleation and growth of ASBs rather than just perform *post-mortem* studies. Strain can easily (and relatively cheaply) be measured on these timescales using gauges and various optical techniques (see **Transducers**), but direct visual information requires specialised (and expensive) high-speed cameras⁶. A major and general problem with the study of ASBs is that it is not possible to predict in advance precisely when and where they will form, even if the experiment has been designed to give simple states of pure loading. The reason for this is that although a necessary condition for ASBs to form is that the load displacement curve has a maximum, it is not a sufficient condition: a period of

nucleation and growth is required. As this nucleation and growth phase takes place in a mechanically unstable regime (negative stress-strain curve), no analysis exists at present to predict how long this period will last. This does not matter too much for strain or force transducers coupled to modern storage oscilloscopes, but it is great problem for high-speed photography. So far, only one paper has been published with a high-speed photographic sequence of an ASB forming, and that was of a steel specimen deforming in a torsional Hopkinson bar⁷.

Temperature measurements of ASBs are bedevilled by emissivity problems, short timescales, and electrical discharges due to charging of the surfaces. Nevertheless there do exist some measurements in the literature for ASBs in metals⁷, and measurements have been made of temperature rises due to failure in polymers^{8,9}.

As ASBs typically form on timescales of tens to hundreds of microseconds, they do not fully form during the timescale of a typical plate impact shock experiment. So in what follows, we will only describe results obtained with dropweights and Hopkinson bars.

EXPERIMENTAL OBSERVATIONS

A schematic diagram of a dropweight machine that has been extensively used to study failure mechanisms in polymers and energetic materials is given in figure 1.

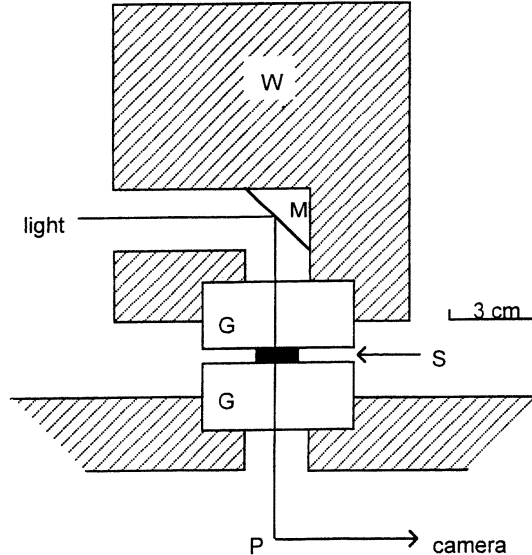


Figure 1. High-speed photography drop-weight apparatus. W weight, M mirror, G glass anvil, S specimen, P prism. Mass of dropweight = 5.545 kg. Maximum drop height 1.3 m.

In its normal configuration, a disc of the material under study is placed on the lower anvil. It is then impacted by the dropweight. Just before impact, a simple mechanical switch is operated which triggers the discharge of a capacitor bank through a xenon flash tube. The deformation of the specimen is recorded using a rotating mirror camera of the continuous access type capable of taking 140 pictures with an interframe time of 5 μ s. The dropweight can be used in another configuration where a rectangular specimen is confined between glass blocks. A metallic slider rests on the upper surface of the specimen and transfers the impact load from the dropweight to the polymer (see figure 2).

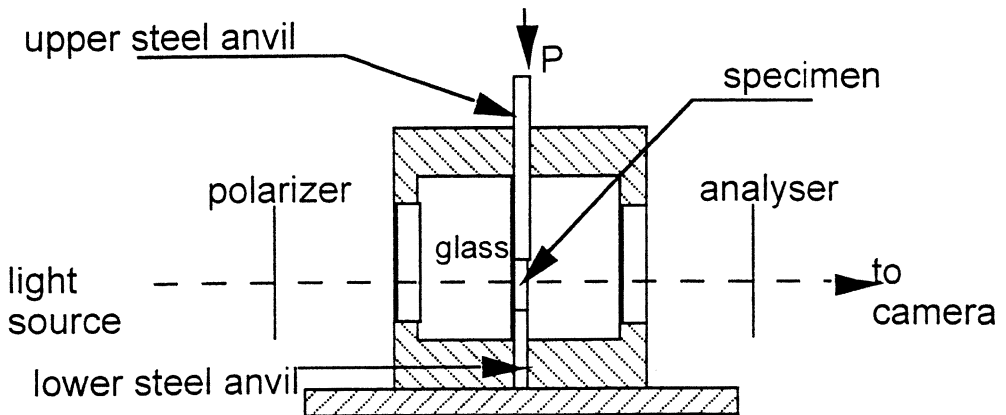


Figure 2. Schematic diagram of apparatus used to dynamically load polymer specimens in plane strain in the dropweight apparatus of figure 1.

Three transparent polymers were studied using this apparatus: polymethylmethacrylate (PMMA), polystyrene (PS), and polycarbonate (PC). Firstly, quasistatic sequences were obtained in conjunction with a load cell to measure the force applied (figure 3). It can be clearly seen that full localisation into shear bands only starts after the stress maximum for PS. The other two polymers did not exhibit a stress maximum in the quasistatic test and did not develop shear bands. However, when the tests were repeated dynamically in the dropweight, PMMA also showed mode III failure. Unfortunately, force measurements were not obtained in the dynamic plane strain case, but dynamic experiments carried out in plane stress showed that failure was associated with load drops in all three polymers. Fuller details may be found in the section by Walley, Xing and Field of reference 4.

These observations hint at the necessity of obtaining mechanical properties of polymers at high rates of strain under various loading conditions if we are to have any hope of predicting which polymers will exhibit catastrophic failure via ASB formation. Data obtained on the shapes of the stress-strain curves of polymers at room temperature over a wide range of strain rates in plane stress compression show four basic types of

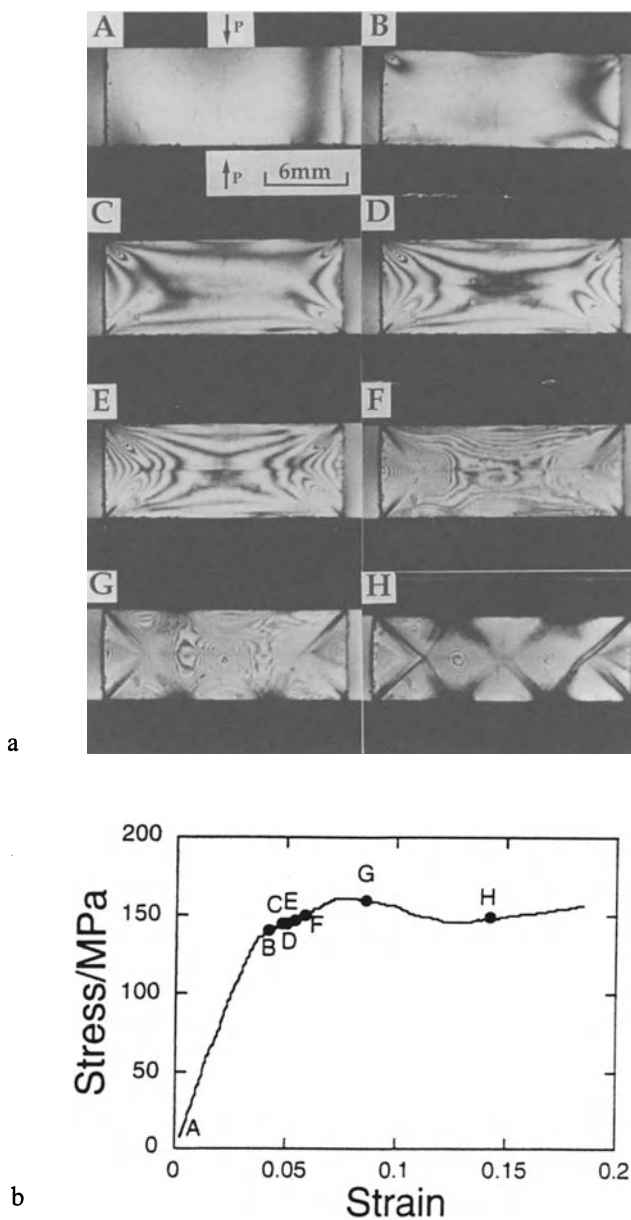


Figure 3. (a) Selected frames from the photographic record of the quasistatic plane strain deformation of a 17.6 x 7.4 x 3 mm PS specimen along with (b) its stress-strain curve.

behaviour: (a) flow at a constant stress which depends on strain rate (nylon 6 and nylon 66); (b) stress maximum at all strain rates (polybutylene terephthalate, polycarbonate, polyethersulphone, polyethylene terephthalate, polyvinyl chloride); (c) change from constant flow stress at low strain rates to showing a stress maximum at high strain rates (polypropylene; polyvinylidene difluoride); and (d) polytetrafluoroethylene which shows a change from flow at constant stress at low strain rates to pronounced strain hardening at high rates of strain. The high strain-rate mechanical behaviour of these polymers does, of course, depend on the temperature at which they are tested. Fuller details may be found in reference 10.

It should be noted that many of the polymers studied in the above work did not fail catastrophically even though they exhibited strain softening. Indeed many showed strain-hardening after an initial period of strain softening. This will suppress any tendency to localisation and must imply that the damage levels reached are not sufficient in these polymers to initiate fracture within any shear bands that may form.

REFERENCES

(A fuller set of references may be obtained from the author).

1. Bai, Y.L. & Dodd, B. (1992) *Adiabatic Shear Localization: Occurrence, Theories and Applications* Pergamon, Oxford
2. Li, J.C.M. (1982) in *Plastic Deformation of Amorphous and Semicrystalline Materials*, ed. Escaig, B. & G'Sell, C., les editions de physique, les Ulis, France, p. 359-373.
3. Williams J.G. & Pavan A., eds, (1995) *Impact and Dynamic Fracture of Polymers and Composites*, Mechanical Engineering Publications Ltd., London
4. Wright S.C., Fleck N.A. & Stronge W.J. (1993) *Int. J. Impact Engng* 13 1-20
5. Swallowe, G.M. & Field J.E. (1982) *Proc. R. Soc. Lond.* **A379** 389-408
6. Ray S.F., ed. (1997) *High-Speed Photography and Photonics*, Focal Press, Oxford
7. Marchand A. & Duffy J. (1988) *J. Mech. Phys. Solids* **36** 251-283
8. Fuller K.N.G., Fox P.G. & Field J.E., (1975) *Proc. R. Soc. Lond.* **A341** 537-557
9. Swallowe G.M., Field J.E. & Horn L.A., (1986) *J. Mater. Sci.* **21** 4089-4096
10. Walley S.M. & Field J.E., (1994) *DYMATJournal* **1**, 211-228

4: Adiabatic Shear Instability: Theory

N A Fleck

At sufficiently high strain rates, many polymers undergo localised shear deformation. This material instability is due to *thermal softening* dominating *strain hardening*. Data are sparse in comparison with shear localisation in metals, notably titanium alloys and high strength steels. This article is a summary of theoretical understanding of the subject with references to experimental data as appropriate.

ISOTHERMAL VERSUS ADIABATIC TESTS

The thermal diffusivity of polymers is low ($\kappa = 10^{-7} \text{ m}^2\text{s}^{-1}$) when compared with that for metals ($\kappa = 10^{-4}\text{s}^{-1}$). Consequently, material tests switch from isothermal to adiabatic at much lower strain rates for polymers than for metals. Consider a simple shear test on a polymer specimen of length scale L . Plastic deformation of the specimen results in a temperature rise, and the time t required for heat to diffuse from the centre of the specimen to the environment is given approximately by the random walk equation,

$$L = \sqrt{(\kappa t)} \quad (1)$$

The time of the test can be taken to be $t = 1/\dot{\gamma}$, for a test at constant shear strain rate $\dot{\gamma}$. Thus, the heat generated within the sample is dissipated adequately (the test is isothermal) provided the strain rate $\dot{\gamma}$ satisfies

$$\dot{\gamma} < \frac{\kappa}{L^2} \quad (2)$$

On assuming representative values, $L = 10 \text{ mm}$ and $\kappa \approx 10^{-7} \text{ m}^2\text{s}^{-1}$ for a polymer, we find that the test is isothermal provided $\dot{\gamma} < 10^{-3} \text{ s}^{-1}$. At higher strain rates the test is adiabatic. Typical quasi-static engineering tests on polymers are conducted at strain rates in the range $10^{-5} - 10^{-3}$, and so can be regarded as isothermal. *Adiabatic* tests are performed at higher strain rates (up to 10 s^{-1} in a servo hydraulic test machine; about 10^2 s^{-1} in an instrumented drop weight machine, about 10^3 s^{-1} in a split-**Hopkinson bar** and at about 10^4 s^{-1} in a plate impact test). In these adiabatic tests the specimen heats up significantly during the test due to internal plastic dissipation. Since the flow strength τ of polymers decreases with increasing temperature, the adiabatic temperature increase leads to *thermal softening* and to the possibility of the unstable growth of a localised shear band.

The temperature increase ΔT due to plastic dissipation can be estimated in a

straightforward manner by equating the plastic work per unit volume $\int \tau d\gamma$ with the increase in internal energy $\rho c \Delta T$. For example, a polymer such as PMMA or PC has a shear strength of approximately 50 MPa, a density of $\rho = 1000 \text{ kg m}^{-3}$, and a specific heat capacity $c = 1300 \text{ J kg}^{-1} \text{ K}^{-1}$. Then, on imposing a shear strain of $\gamma = 1$, the computed temperature rise ΔT is about 38 K. This result has two implications:

(i) the temperature in an adiabatic test changes significantly over the test and the measured stress-strain response is softer than that in an isothermal test at the same strain rate;

(ii) the progressive thermal softening in an adiabatic test can lead to shear localisation, whereas in the equivalent isothermal test the response is stable. We demonstrate below that instability initiates at the point of maximum shear stress in a shear test.

A comparison of the isothermal and adiabatic responses is sketched in Fig. 1 to demonstrate the thermal softening associated with an adiabatic test. When the degree of thermal softening is sufficient the adiabatic test shows a maximum in shear stress and an instability, whereas the isothermal test shows continued strain hardening and a stable response.

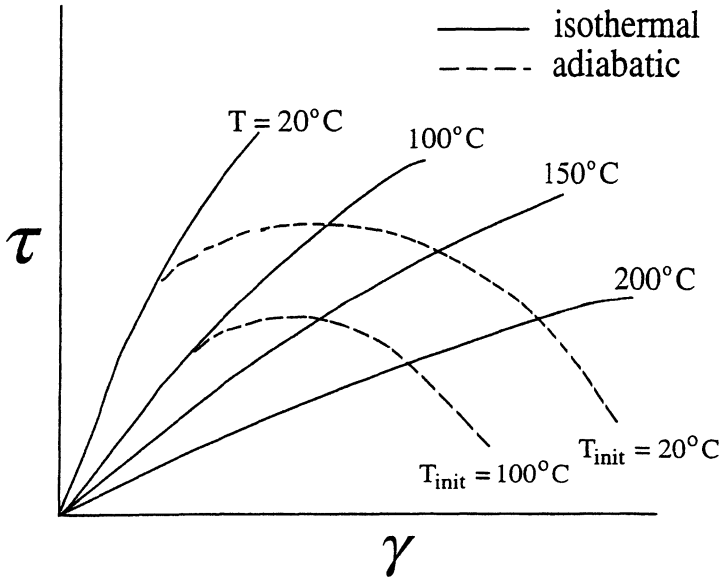


Figure 1: Comparison of isothermal and adiabatic shear responses at fixed strain rate. Thermal softening in the adiabatic test can lead to a maximum load and to shear localisation.

STABILITY ANALYSIS: THE ONSET OF LOCALISATION

The onset of shear localisation can be predicted by imposing a perturbation about the current state in a stress-strain test, and determining whether the perturbation grows

unstably^{1,2}. Consider a shear test with the shear stress related to the shear strain γ , and to the current temperature T in the material by

$$\tau = f(\gamma, T) \quad (3)$$

Then, a perturbation in (γ, T) results in a shear stress perturbation $\delta\tau$ of

$$\delta\tau = \frac{\partial f}{\partial \gamma} \delta\gamma + \frac{\partial f}{\partial T} \delta T \quad (4)$$

But, in an adiabatic test, an increment in shear strain $\delta\gamma$ results in a temperature increase of

$$\delta T = \tau \delta\gamma / \rho c \quad (5)$$

and so relation (4) can be simplified to

$$\delta\tau = \left(\frac{\partial f}{\partial \gamma} + \frac{\partial f}{\partial T} \frac{\tau}{\rho c} \right) \delta\gamma \quad (6)$$

The instability grows when the perturbation $\delta\gamma$ results in a negative value of $\delta\tau$, and so the onset of instability in an adiabatic test occurs according to the criterion:

$$\frac{\partial f}{\partial \gamma} + \frac{\partial f}{\partial T} \frac{\tau}{\rho c} = 0 \quad (7)$$

This corresponds to the peak value of shear stress in an adiabatic test. The criterion (7) remains valid in the presence of strain rate hardening, and when inertial and thermal conductivity are included in the analysis². It simply states that adiabatic shear localisation occurs when the rate of thermal softening outweighs the strain hardening rate. Rapid thermal softening occurs in the vicinity of the **glass transition** temperature T_g for amorphous polymers (and in the vicinity of the softening temperature for semi-crystalline polymers). Thus shear localisation occurs when the initial temperature in an adiabatic test is in the vicinity of T_g . But shear localisation can also occur at lower temperatures, brought about by the negative strain hardening rate induced by **crazing** and microcrack formation. This mechanism has been identified by Fleck, Stronge and Liu³ but does not appear to be appreciated within the general literature.

THE WIDTH OF A SHEAR BAND

The prediction of the width w of a shear band is not fully resolved. There are at least two viewpoints on the main controlling factors for the shear band width:

- (i) the width w is set by the distance over which heat can diffuse during the formation of a shear band⁴. Here, it is assumed that the shear band width is fixed by the transient period of shear band nucleation and growth. On taking the formation time t to be approximately, $t \approx 1/\dot{\gamma}$, heat can diffuse over a distance $w \approx \sqrt{(\kappa t)}$ on making use of relation (1), and so w is given by

$$w = \sqrt{(\kappa / \dot{\gamma})} \quad (8)$$

Substitution of typical values for $\dot{\gamma} = 10^3 \text{ s}^{-1}$ in a high strain rate test, and $\kappa \approx 10^{-7} \text{ m}^2 \text{ s}^{-1}$ for a polymer, gives $w \approx 10 \mu\text{m}$. This value is of the same order of magnitude as the measured value.

- (ii) the width w is set by the distance over which heat is conducted in steady state, after all transients have finished⁵. Consider a simple heat flow balance for a band of material of width w wherein plastic dissipation occurs at a constant rate $\tau \dot{\gamma}$. The temperature at the centre of the band is taken to be elevated by ΔT above that of the material outside the band. On assuming steady state conditions, this power is dissipated by thermal conduction across the band boundary, giving

$$w \tau \dot{\gamma} = \lambda \frac{\Delta T}{w} \quad (9)$$

where λ , is the thermal conductivity of the polymer. Thus, the band width w is given by $w \approx \sqrt{\lambda \Delta T / \tau \dot{\gamma}}$. Note that for steady state conditions to be attained, this band width should be stable with respect to time, and neither increase or diminish in an unstable manner: an additional stability statement is required in addition to the satisfaction of (9). Details are omitted here, but the additional statement reads

$$\left(\frac{w \tau \dot{\gamma}}{\lambda} \right)^2 \frac{\partial^2 f}{\partial T^2} + \frac{2 \dot{\gamma}}{w^2} \frac{\partial f}{\partial \dot{\gamma}} + \left(\frac{\dot{\gamma}}{w} \right)^2 \frac{\partial^2 f}{\partial \dot{\gamma}^2} > 0 \quad (10)$$

where the constitutive law for the solid is written in the form $\tau = f(\dot{\gamma}, T)$. The practical relevance of relation (9) is questioned: shear band formation is a highly transient phenomenon, and steady state conditions are rarely achieved in practice.

REFERENCES

1. Bai, Y.L. (1982) Thermo-plastic instability in simple shear, *J. Mech. Phys. Solids*, **30**(4) 197-207
2. Bai, Y.L. and Dodd, B. (1992) *Adiabatic Shear Localization*, Pergamon Press
3. Fleck, N.A., Stronge, W.J. and Liu, J.H. (1990) High strain-rate shear response of polycarbonate and polymethyl methacrylate, *Proc. Roy. Soc Lond.*, **A429**, 459-479
4. Zhou, M., Needelman, A. and Clifton, R.J., (1994) Finite element simulations of shear localization in plate impact, *J. Mech. Phys. Solids*, **42**(3), 423-458
5. Dodd, B. and Bai, Y.L. (1985) Width of adiabatic shear bands, *Mat. Sci. and Tech.*, **1**, 38-40

5: Alloys and Blends

D. J. HOURSTON

INTRODUCTION

Over the last few decades, polymer blends or alloys have grown from very small beginnings to become a major area of research and commerce¹. This field is driven commercially by the demand for ever-increasing physical, mechanical, thermal and other properties. Faced with this situation, there are two general responses. The first would be to synthesise a new polymer to meet the desired specifications. This approach has two major drawbacks. Firstly, polymer science has yet to reach the state of maturity which allows the design and synthesis of materials with prescribed properties. The other problem is that the cost of developing and manufacturing a new polymer from scratch is very high. The second approach is to blend usually not more than two polymers, which will in combination, but not singly, have the desired properties. This is clearly a vastly less expensive route. It is the case, however, that the vast majority of polymer pairs are immiscible, but even these can have important properties such as markedly enhanced impact strength.

COMPATIBILITY AND MISCIBILITY

The terms compatibility and miscibility must be clearly distinguished. Compatibility is a more technological term referring to the situation where two or more polymers can be blended by, for example, milling or twin-screw extrusion to give commercially useful materials. In other words, the blend has acceptable mechanical properties, but has a phase separated morphology. Miscibility indicates that the polymers mix on the segmental level to give a homogeneous material. For the components to be miscible, a necessary, but not sufficient condition is that ΔG_{mix} in the following equation must be negative.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (1)$$

With polymers, the $-T\Delta S_{mix}$ term, the combinatorial entropy, is very small compared to the situation for the mixing of small molecules, where vastly more combinations of mixing exist than are possible with the linked repeat units in macromolecules. For polymers, the ΔH_{mix} term is generally positive. Therefore, normally, it is the case that pairs of polymers are immiscible as the positive ΔH_{mix} term usually dominates the $T\Delta S_{mix}$ term. If, however, there are specific interactions between the segments of the constituent polymers, then mixing will occur as ΔH_{mix} is negative in this case.

The other necessary condition for polymer-polymer miscibility to occur over the entire composition range is that $\delta^2 \Delta G_{mix} / \delta \phi_2^2 > 0$. See reference 1 for further details.

The following thermodynamic equations have been developed for the mixing of two polymers¹.

$$\Delta H_{mix} = Vz\omega\phi_1\phi_2/V_s \quad (2)$$

$$\Delta S_{mix} = -k[N_1 \ln \phi_1 + N_2 \ln \phi_2] \quad (3)$$

$$\Delta G_{mix}/V = kT[(\phi_1/V_1) \ln \phi_1 + (\phi_2/V_2) \ln \phi_2] + z\omega\phi_1\phi_2/V_s \quad (4)$$

where V is the total volume, z is the lattice co-ordination number, ω is the energy of interaction (exchange energy), ϕ_1 and ϕ_2 are the volume fractions of component i , V_s is the interacting segment volume, k is the Boltzmann constant, N_1 and N_2 are the number of molecules of component i , V_1 and V_2 are the volume per molecule of component i and T is the absolute temperature.

It must be remembered that in any spontaneous mixing or phase separation process it is likely that the kinetics of the process will be relatively slow. Consequently, the observed morphology is not likely to represent a true thermodynamic equilibrium.

CHARACTERISATION OF BLENDS

In the characterisation of a polymer blend, the following are some of the points at issue. Is the blend miscible or phase separated? If the blend is phase separated, what are the compositions, size distribution and extent of connectivity of these phases? There is a battery of characterisation techniques which can be and are applied to such materials. It is true to say that no one technique comes close to answering all these questions. It is often the case that a full characterisation is very difficult or near to impossible, given the limitations of existing techniques. The question regarding miscibility is the first one to tackle in most situations. The basis of the approach here is usually to determine the number of glass transitions that can be detected. If the blend is a miscible one, then a single glass transition, intermediate relative to the Tgs of the constituent polymers, occurs. In the other extreme case, no mixing occurs. The result would be the manifestation of two Tgs at the same temperatures as those of the constituent polymers. There is also the possibility of there being some inward shifting of the Tgs with respect to the constituent polymer values. This indicates a state of partial miscibility. It is often the case that this last situation yields useful materials².

In practice, two techniques predominate in this type of assessment of blend miscibility. They are differential scanning calorimetry, DSC, and **dynamic mechanical thermal analysis**, DMTA. Recently, it has been shown³ that modulated-temperature differential scanning calorimetry, M-TDSC, can be a very sensitive technique for the detection of Tg.

It has to be borne in mind that techniques are not equally sensitive to the glass

transition. Consequently, the polymer blends literature abounds with cases where counter claims as regards miscibility are made. It is the general experience that DMTA is preferable to DSC as a means of detecting T_gs, but the advent of M-TDSC and the consequent ability to achieve readily accurate values of the heat capacity means that this technique⁵ may well become the method of choice in the future.

Questions about phase size, shape and interconnectivity may be addressed by optical, but usually more effectively by scanning and transmission electron microscopies (see **Applications of Electron Microscopy to the Study of Polymer Deformation**).

APPLICATIONS OF POLYMER BLENDS

A major use of polymer blends arises in the field of **toughening** relatively brittle thermosets and thermoplastics such as epoxy resins, polystyrene and the Nylons. These materials are used in a very diverse range of applications including many uses in the aeronautical and automotive industries. It is now true to say that many classes of commercial polymer are available as rubber-toughened grades⁴. The detailed mechanisms by which such materials fail are reviewed in reference 4.

REFERENCES

1. MacKnight, W.J. and Karasz, F.E. in *Comprehensive Polymer Science* (1989) Pergamon, (eds G. Allen and J. C. Bevington). Chapter 4, 111-130.
2. Olabisi, O., Robeson, L.M., Shaw, M.T. (1979) *Polymer-Polymer Miscibility*. Academic Press, New York.
3. Hourston, D.J., Song, M., Hammiche, A., Pollock, H.M., Reading, M. (1997) *Polymer*, **38**, 1
4. Collyer, A. A. (1994) *Rubber Toughened Engineering Plastics*. Chapman and Hall, London.

6: Amorphous Polymers

A. R. Rennie

Amorphous is used as a description of the structure of a material and it implies that there is no long-range order such as that found in crystalline or liquid crystalline substances. Such disordered arrangements are found in melts. In this case the arrangement of polymer molecules will normally be that of randomly arranged, entangled molecules that are mobile. The same structural arrangement might exist as a solid in which there is no long-distance mobility of a molecule due to thermal motion. This is characteristic of a 'glassy' material. Materials that can be cooled from a melt sufficiently rapidly that they do not have the opportunity to reorganise to a regular structure in the form of a crystal will form glassy or amorphous solids. The usual thermodynamic equilibrium state of most materials will be a crystal at sufficiently low temperatures. Many polymers are never observed as crystalline or semi-crystalline solids. This is either as a consequence of the very low gain in free-energy on crystallisation or of the high viscosity near the melting point. Polymers with bulky sidegroups and irregular tacticity are particularly likely to form amorphous solids (see **Crystallinity, Glass Transition**)

Although it is common to describe the difference between an amorphous solid (or glass) and a liquid in terms of the molecular mobility, viscosity or self diffusion coefficient as mentioned in the previous paragraph, this will have some considerable difficulties in practice. The choice of a particular viscosity (or diffusion coefficient) for the boundary will be arbitrary. There is no sharp boundary as the transition between the glass and melt is not first order (for example there is no latent heat only a change in the thermal capacity). The detailed study of the glass transition is still of considerable research interest but the practical materials scientist will recognise the glass as a solid with elastic moduli and a yield stress, and the melt as a liquid that flows. As with most aspects of polymer mechanics and rheology, the amorphous materials will be non-Newtonian and display **visco-elasticity** that depends on the time, temperature and other conditions of test which will usually be described to a first approximation by the WLF equation.

Some examples of glassy, amorphous polymers are atactic polystyrene, polycarbonates (such as bisphenol-A polycarbonate) and polymethylmethacrylate. The physical properties of these materials can be quite varied but good accounts are available¹. The absence of crystallites or other inhomogeneities on the length scale of the wavelength of light means that they are usually transparent. At sufficiently low temperatures, they will behave like most inorganic glasses as brittle solids. If the temperature of the test is sufficiently close to the glass transition or the speed of the deformation is slow, the materials can be plastic. If an amorphous polymer is cross-linked to form a network and is at a temperature above the glass transition, it will behave as an elastomer.

REFERENCES

1. Haward, R. N. (ed.) (1973) *The Physics of Glassy Polymers* Applied Science, London

7: Crazing

G M Swallowe

Failure in tension of all thermoplastic polymers involves the formation of a craze through which a crack then grows. Crazes are most evident in glassy polymers (i.e. amorphous polymers below their **glass transition** temperature). They are an intermediate stage between **yielding** and **fracture**. Crazes may be observed visually as a whitening of the polymer which occurs under stress. This whitening is caused by multiple reflections of light from the polymer/void interfaces in the crazes. Crazes form perpendicular to the applied stress and consist of regions of polymer in which an incipient crack is bridged by highly orientated material in a direction perpendicular to the direction of the crack. A schematic of a craze is illustrated in Figure 1.

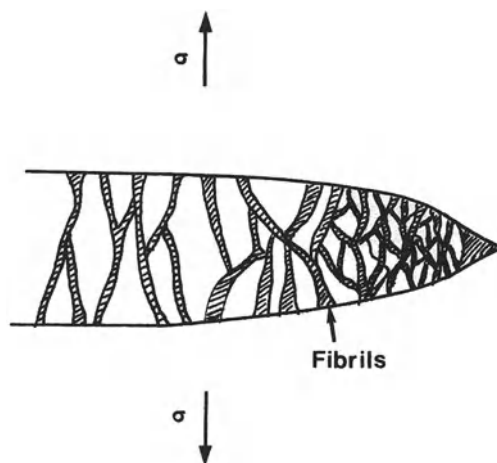


Figure 1: Schematic of a craze; the arrows represent stress in 'good' polymer and the craze appears as a crack whose walls are joined by oriented fibrils of polymer (shaded).

Crazes occur both on the surface and in the interior of a polymer and their occurrence is strongly related to the combination of the presence of defects and the stress state. The initiation of crazes is a statistical process which can be described by a Weibull distribution in the same manner as crack formation in ceramic materials. **Environmental effects** have a strong influence on the formation and growth of surface crazes and the presence of organic liquids will generally greatly accelerate craze formation. Crazes generally have a thickness (parallel to the tensile stress direction) of a few tenths of a μm to a few μm and lengths which can vary from tens of μm to many mm. Their third dimension can also vary from microns to tens of mm. Surface crazes often take on the appearance of a series of parallel surface cracks and form as the result of environmental attack in combination with residual stresses caused by the moulding

process.

Since crazes consist of fibrils bridging an incipient crack they contain a large fraction of voids, percentages up to 80% are possible but of the order of 50 to 60 % more common. Except at the craze tip the voids are interconnected and this provides a pathway for small molecules to diffuse to the craze tip and promote further craze growth. The craze fibrils generally have diameters in the range 5 to 50 nm.

Crazes are most commonly observed in **glassy polymers** but also occur in semi-crystalline polymers, although, since these materials are often used above their **glass transition** temperature, the crazing is less distinct because macroscopic plastic deformation (see **Yield and Plastic Deformation**) is the predominant deformation mode. In semi-crystalline polymers crazes tend to be thicker and shorter than in glassy polymers but essentially have the same structure of voids and oriented fibrils and run through the crystalline as well as the amorphous regions of the material.

CRITERIA FOR CRAZE FORMATION

Crazes only form when the polymer is in tension, shear yielding occurs in compression. Studies by Sternstein and Ongchin¹ among others give rise to a craze yielding criterion in biaxial loading

$$\sigma_1 - \sigma_2 \geq A(T) + \frac{B(T)}{\sigma_1 + \sigma_2} \quad (1)$$

with σ_1 and σ_2 the largest and smallest principle stress components in the polymers and $A(T)$ and $B(T)$ temperature dependent constants. This criterion can be illustrated by the diagram of Figure 2 which shows the competition between shear yielding and crazing. In the first quadrant (σ_1 and σ_2 positive) crazing is the predominant deformation mechanism while in the third quadrant yield follows the von Mises criterion. In quadrants two and four crazing competes with yielding provided the sum of σ_1 and σ_2 is positive.

The above criterion (equation 1) is only valid in the case of plane stresses. Others workers, notably Argon² and Kausch³ have proposed less empirical models based on the formation of microvoids of diameter ~ 10 nm occurring in the polymer due to mechanical stress. These voids then coalesce to leave fibrils connecting the craze structure. The microvoiding is regarded as a stress dependent kinetic process which can be described by an equation of the form

$$\dot{v} = \dot{v}_0 \exp\left(-\frac{\Delta G}{kT} \right) \quad (2)$$

with $\dot{v}$ the rate of voiding, $\dot{v}_0$ a constant, ΔG a stress dependent activation enthalpy, k Boltzmanns constant and T temperature. ΔG is given by

$$\Delta G = kT \left(\frac{A}{\tau} + B \right) \sigma_y \quad (3)$$

with σ_y the uniaxial yield stress, A and B constants and τ the shear stress. Argon's theory leads to a prediction of the stress required to cause microvoids to grow into a craze given by

$$p = \frac{2\sigma_y}{3} \log \left(\frac{1}{v} \right) \quad (4)$$

with p the hydrostatic stress and v the volume fraction of microvoids. Generally the required stress is found to be lower than the value estimated from equation 4.

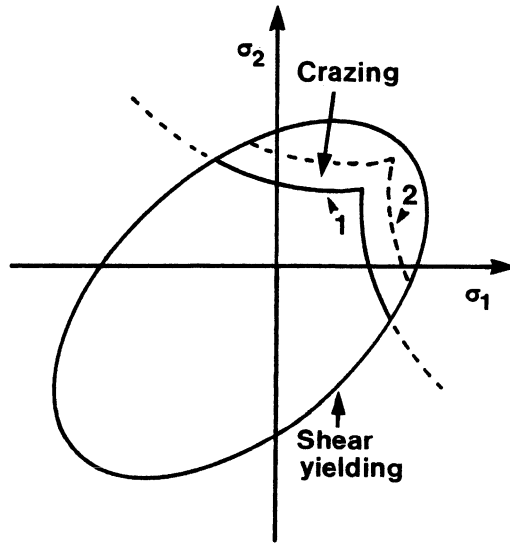


Figure 2: Yield locus under biaxial stress showing competition between crazing and shear yield. The elliptical shape represents the von Mises locus for shear yielding, lines 1 and 2 the locus for crazing. Line 2 shows the shift in crazing locus with reduction in temperature.

Craze thickness and length increases as a function of loading time and this process eventually leads to **fracture**. In general growth occurs in the direction normal to the maximum principle stress. The growth rate (at a constant stress) is generally accepted to be proportional to the logarithm of time and can be written as

$$l = b \log t \quad (5)$$

with l the craze length, t time and b a constant. This expression applies in conditions in which creep deformation can easily occur. Environmentally induced craze growth follows the equation

$$l = Ct^n \quad (6)$$

with C and n constants and $n \sim 0.5$. Environmental craze growth does not occur if the stress intensity factor at the crack tip (see **Fracture Mechanics**) does not exceed a critical value K_C .

MOLECULAR WEIGHT AND STRUCTURE

Crazes are stabilised and can carry a load because the fibrils bridging the craze zone can sustain a stress in a similar way and with a similar modulus to polymer fibres. However the fibrils will creep under load and for a craze to be stable there must be chain entanglements. The possible number of entanglements will depend on chain length and hence molecular weight (see **Molecular Weight Distribution and Mechanical Effects**). If the molecular weight between entanglements M_E is greater than approximately twice M_n (the number average molecular weight) no crazing occurs. If M_n is greater than about twice M_E crazing occurs with no molecular weight dependence on craze formation. M_E can be estimated from the high temperature rubbery modulus (see **Stress and Strain**) using the expression

$$M_E = \frac{\rho RT}{G} \quad (7)$$

with T the temperature, G the modulus, R the gas constant and ρ the density

Crazing is a phenomenon unique to polymers and is a precursor to **fracture**. A more detailed description of crazing can be found in the chapter by Narisawa and Yee⁴ and works such as that of Ward⁵.

REFERENCES

1. Sternstein, S.S. and Ongchin, L. (1969) *Polymer Preprints*, **10**, 1117
2. Argon, A.S. and Hannoosh, J.G. (1977) *Phil. Mag.* **36**, 1195
3. Kausch, K.K. (1976) *Kunststoffe* **66**, 538
4. Narisawa, I. and Yee, A.F. (1993) in *Materials Science and Technology Volume 12* (eds. R.W. Cahn, P. Haasen, E.J. Kramer) VCH Publishers, New York.
5. Ward, I.M (1983) *Mechanical Properties of Solid Polymers* 2nd edition, Wiley

8: Creep

D R Moore

INTRODUCTION

Polymers are non-linear **viscoelastic** materials. This implies that a 'modulus' for a polymer is both time dependent and stress or strain dependent. Even then, it is helpful to consider the material as isotropic (i.e. the properties are the same in all directions within the material). Unfortunately, this simplified condition still leads to an absence of a comprehensive viable theory that describes the deformational behaviour of polymeric systems and consequently it is necessary to use empirical methods to describe 'modulus'. However, there are numerous further simplifications that can be made in practice, particularly when it is required to describe 'modulus' for polymers used in load-bearing engineering applications. Consequently, it is helpful to develop an understanding of creep in polymers from the simplest concepts and to understand where these are accurate and where the limitations exist.

DEFINITIONS OF MODULUS AND COMPLIANCE.

The modulus E of linear elastic materials originates from Hooke's law and is the ratio of stress σ over strain ϵ . This definition is quite inadequate for polymers as we shall see. An alternative set of definitions for time dependent materials is to define a relaxation modulus $E(t, T)$ where stress is varying and strain is held constant and creep compliance $C(t, T)$ where strain is varying and stress is held constant. In both cases, T is temperature, which is known to influence deformational properties for polymers, and t is time. Therefore:

$$E(t, T) = \sigma(t) / \epsilon \quad (1)$$

and
$$C(t, T) = \epsilon(t) / \sigma \quad (2)$$

Unfortunately, $E(t, T)$ does not equal $1/C(t, T)$ unless there is no time dependence, although they are related¹.

THE CREEP FUNCTION.

Equation (2) describes the creep experiment for polymers. In a practical sense a constant load is applied to a specimen with uniform cross section and therefore a constant stress is generated and the time dependent strain is measured at a particular test temperature.

This can be used to describe the simplest form of the creep function for polymers by assuming them to behave as linear viscoelastic materials. Therefore for a single temperature:

$$\varepsilon = \sigma f(t) \quad (3)$$

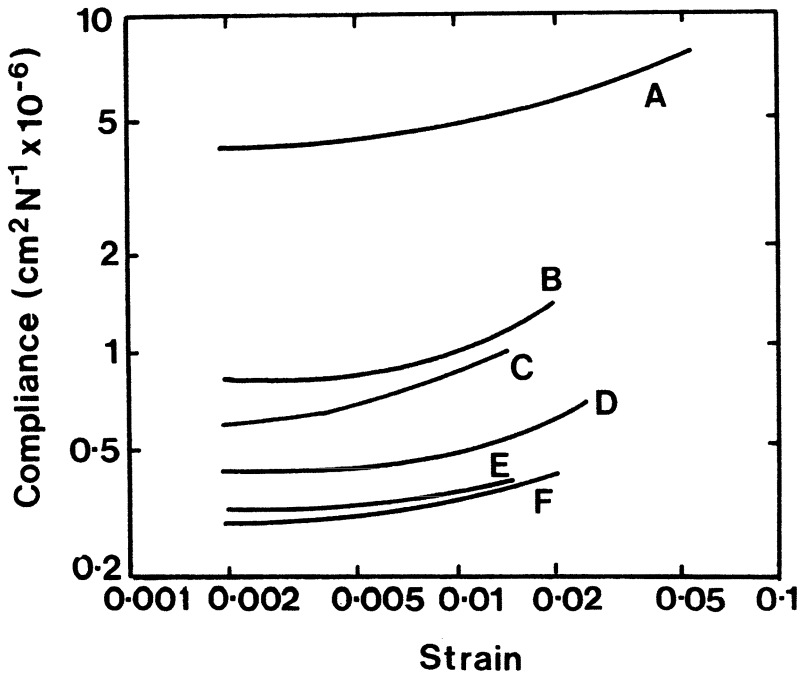


Figure 1: Nonlinear viscoelasticity of: A, polyethylene of density 920 Kg m^{-3} (+18%); B, polypropylene of density 909 Kg m^{-3} (+22%); C, polyethylene of density 980 Kg m^{-3} (+43%); D, polyoxymethylene copolymer (+12%); E, uPVC (+8%). All at 20 °C.

This implies that the ratio of strain to stress (the compliance) should be a constant if the time under load is fixed, at say 100 seconds. This is clearly not the case as shown by the data in Figure 1 for a range of different polymeric materials, where the values in the caption indicate the extent to which this approach is inaccurate at a strain level of 0.01. The dependence of strain on the level of deformation requires a non-linear viscoelastic approach, such as:

$$\varepsilon = g(\sigma) f(t) \quad (4)$$

In this equation, the variables of stress and time are taken to be separable. This can apply up to strains of about 2% for quite a range of polymers. Moreover, this has lead to

a number of empirical creep laws, for example that due to Findley:

$$\varepsilon = h_1 + h_2 t^n \quad (5)$$

Where h_1 and h_2 are functions of applied stress and n is a constant.

Inevitably, there are occasions where the variables of stress and time cannot be separated and further experimental measurement will be required.

COPING WITH NON-LINEAR VISCOELASTIC POLYMERS

The nature of creep behaviour in polymers can be accommodated in practical problems. For example, in using these materials and their deformational properties in engineering design calculations it is a matter of recognising which of the variables can influence compliance. Often, it is convenient to assume that compliance and modulus are inversely related and although this may not be rigorously correct it might be possible to accommodate the assumption if the limits of any inaccuracy are understood. Naturally, the consequences of such assumptions should also be examined.

REFERENCES

1. Gross, B. (1953) *A mathematical structure of the theories of viscoelasticity*, Herman and Co., Paris
2. Turner (1964) Creep in thermoplastics, *British Plast* **37**, 440
3. Findley N. (1994) Creep characteristics of plastics, *Symposium on plastics*, ASTM
4. Moore D.R., Smith J.M, Turner S., (1994) Engineering design properties for injection mouldings based on PEEK, *Plast. Rub. & Comp: Proc. & Appl.* **21**, 19-31.

9: Crystalline Polymers

A. R. Rennie

Many polymers can crystallise to form regular structures despite their large molecular size. The arrangement will often be with the axis of a polymer chain aligned along one of the crystal axes of the unit cell. The unit cell will usually contain only a small fraction of one or more polymer molecules, the repeat unit being a few monomers. The structure of polymer crystals can be determined by the usual techniques of x-ray, electron or **neutron diffraction** (see **X-ray Scattering Methods**). There are several distinctive features of polymer crystals that deserve mention. Very few polymers will crystallise completely, particularly from melts where the molecules are initially highly entangled. The usual structure is referred to as semi-crystalline in which there are some regular crystals separated by amorphous regions. The study of the arrangement and growth of crystals in their distinctive morphologies is particular to polymeric materials¹.

Polymers that crystallise under normal cooling from the melt include polyethylene, polypropylene, polyamides (nylon) and polyoxymethylene. Other materials such as natural rubber may crystallise under strain providing a mechanism by which the material hardens under deformation. In most cases it will be only stereo regular polymers with a low degree of chemical heterogeneity (branching and cross-linking) that will crystallise. In copolymers and blends (see **Alloys and Blends**) one component may crystallise and this can be a useful mechanism for establishing a composite structure of materials with very different properties. In some synthetic elastomers crystalline components will act as cross-links in place of permanent chemical bonds to form a network.

When grown from melts it is common for polymers to crystallise as lamellae where there will be some folding of the molecules to allow re-entry into the crystallite but some molecules will link or tie separate lamellae across amorphous regions. This is shown schematically in the Figure. The crystallites may have a distinctive separation known as the long period, arising from the growth process. They are often arranged in a spherulitic superstructure. The structure resembles in some respects a composite material with phases having different properties. The crystalline regions will usually be denser (about 10 %) and harder than the amorphous polymer. The regions of amorphous material may be extensive and even be dominant in some materials that crystallise poorly. This will be the case if there are many defects such as branch points in the molecular structure. The estimation of mechanical properties of crystalline and semi-crystalline polymers has been treated in some detail by Arridge².

Some properties of polymers may depend strongly on crystalline structure or morphology³. For example the elongation to break may depend on the conformation of 'tie' molecules linking crystalline lamellae. If the ties are long they may act as soft elastic components with the possibility of withstanding large strains. Conversely to obtain polymers with a high elastic modulus it may be desirable to prepare highly crystalline materials with a large degree of orientation by extrusion or drawing of the

polymer as the modulus of the polymer in the direction of covalent bonds tends to be high³. The changes in morphology that occur under strain such as orientation of lamellae and change in long-period may be observed by small angle x-ray or neutron scattering.

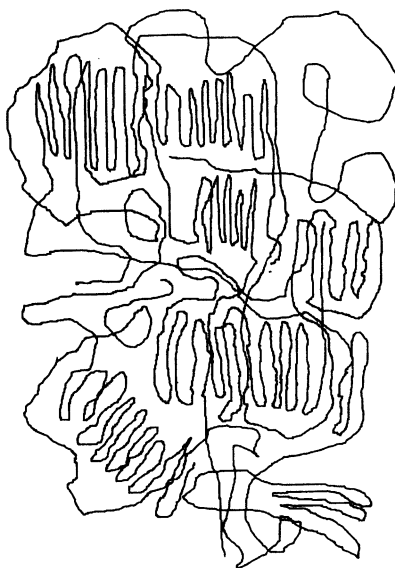


Figure 1. Schematic illustration of a semi-crystalline structure showing lamellae linked by 'tie' molecules through amorphous regions. As mentioned in the text, there may be regular arrangements of the lamellae.

REFERENCES

1. Bassett, D.C. (1981) *Principles of Polymer Morphology*. Cambridge Univ. Press, Cambridge
2. Arridge, R.G.C. (1985) *An Introduction to Polymer Mechanics* Taylor & Francis, London.
3. Ward, I.M. and Hadley, D.W. (1993) *An Introduction to the Mechanical Properties of Solid Polymers* Wiley, Chichester.

10: Crystallinity

G. M. Swallowe

Polymers, other than thermosets or some fully amorphous materials such as PMMA, may be considered to be a composite of fully crystalline material and an amorphous matrix (see **Crystalline Polymers, Amorphous Polymers**). The maximum crystallinity that can be readily achieved depends critically on the molecular structure of the polymer with symmetrical chain molecules that allow regular close packing giving the highest crystallinities. The modulus and yield stress of the crystalline material is greater than that of the amorphous component so the mechanical properties of a semi-crystalline polymer will vary depending on the ratio of crystalline to amorphous material. For example in PEEK the modulus will typically vary from 3.5 to 4.6 GPa as the crystallinity increases from 16% to 39% and the yield stress changes from 72 to 106 MPa over the same crystallinity range. Along with the increase in modulus and yield stress there is a reduction of extension to break, typically for PEEK this will reduce from 250% to 150% as the crystallinity increases over the range 15 to 35 %. The modulus of a semi-crystalline polymer may be estimated from the Tsai-Halpin equations for composites. For a mixture of crystalline and amorphous phases with crystallinity C the equations give

$$E = \frac{E_A [E_C + b(CE_C + (1-C)E_A)]}{CE_A + (1-C)E_C + bE_A} \quad (1)$$

with E , E_A and E_C the material, fully amorphous and crystalline modulus respectively and b a geometric factor. Unfortunately it is not obvious what value to choose for b (which can in principle vary from 0 to ∞) but a value of 1 is often used with reasonable results. The crystalline modulus E_C can be found using X-ray methods and E_A found from rapidly quenched amorphous samples. The expression (1) applies for any elastic property so, for example, shear modulus G could be substituted for tensile modulus E in the expression.

The yield stress can be approximately related to density (and hence crystallinity) by an expression of the form

$$\log \sigma_y = \log \sigma_A + a (\rho - \rho_A) \quad (2)$$

with σ_y the sample yield stress, σ_A the amorphous yield stress, ρ the density, ρ_A the amorphous density and a a constant. In the case of polyethylene σ_y varies from ~ 3 MPa to ~ 22 MPa as ρ varies from 0.90 to 0.95.

Crystallinity generally increases during deformation as a result of strain induced crystallisation and this leads to strain hardening. The increase can be very large for a low crystallinity sample. For example PET with initial crystallinity of 5% can increase in crystallinity to $\sim 25\%$ when strained by 300%. The increase is normally initially slow

but accelerates and eventually levels off at a value characteristic of the polymer. Figure 1 illustrates the general form of the curve. The rate of increase in crystallinity will depend on the temperature and strain rate but the maximum value reached does not vary greatly with the deformation conditions. This effect is greatly reduced in samples which are already close to their maximum crystallinity.

Since crystallinity has such profound effects on mechanical properties it is desirable to control the crystallinity of a polymer. This can be done to a certain extent by suitable heat treatments. A rapid quench will give a lower crystalline content that slow cooling and annealing will increase crystallinity. However in many products the cooling rate and imposed strain will differ greatly from place to place within the moulding and hence large variations in crystallinity may be found within the material. This problem will be greatest for thick samples. Variations as large as from 5% crystallinity at the surface to 30% in the interior have been reported in PEEK mouldings with surface variations of 5-15% crystallinity depending on location on the moulding surface. A 'holding time' of a few minutes followed by slow cooling helps to reduce these variations.

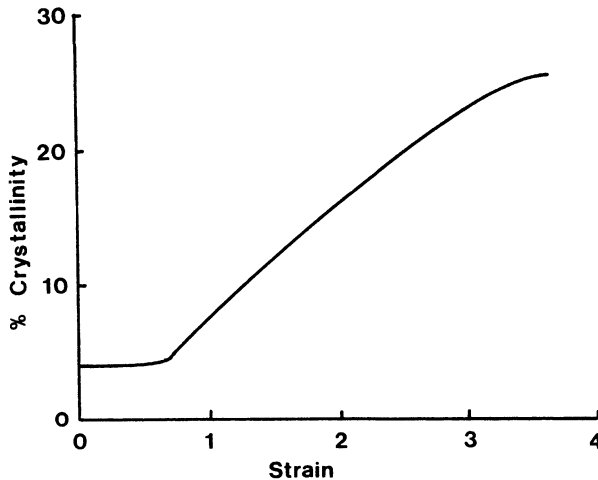


Figure 1: % crystallinity against strain showing strain induced crystallinity for a sample of PET.

CRYSTALLINITY DETERMINATION

The three most popular methods of determining crystallinity are by density measurements, thermal analysis and X-ray methods. The different techniques do not necessarily give the same value for the crystallinity since all three depend on different properties of the pure crystalline polymer and these are often difficult to determine exactly because of the difficulty in obtaining fully crystalline material.

Density Measurements

The density of a semi-crystalline polymer will be between that of a fully crystalline and fully amorphous sample. The basis of the density measurement technique is therefore to measure the density of sample of interest and compare that with the published densities of fully crystalline and fully amorphous samples. Defining ρ as the measured density ρ_a as the fully amorphous density and ρ_c as the fully crystalline density leads to an expression for W_C the weight fraction degree of crystallinity

$$W_C = \frac{1/\rho - 1/\rho_a}{1/\rho_c - 1/\rho_a} \quad (3)$$

Density may be determined by the use of density columns. This involves immersing a small sample of the polymer in a column of liquid which has been mixed to produce a variable density gradient. Calibration floats of known density within the column provide reference markers and the density of the sample is determined from the equilibrium height at which it floats within the column. Density columns usually enable the density to be determined to an accuracy of about 0.2 mg/cm^3 .

The use of a pycnometer (density bottle) provides an alternative and simple method whose accuracy is somewhat less, usually $\sim 4 \text{ mg/cm}^3$. In this method a weighed density bottle (whose volume is accurately known) is filled with a suspension of polymer particles in liquid. The increase in weight is noted and the liquid is then evaporated to dryness. The weight of the suspended polymer can then be determined and knowing the density of the pure liquid used to form the polymer particle suspension the polymer density is determined.

Flotation methods involve mixing two miscible liquids of densities greater and less than the expected polymer density and adjusting the density of the mixture until the polymer is suspended. The polymer density is then equal to the density of the mixed liquid. This density is determined by the volumes and densities of the liquids used to make the mixture.

Thermal Methods

The thermal method depends on measurements of the heat of fusion ΔH of the polymer of interest and a comparison of this value with the fully crystalline heat of fusion ΔH_C . W_C is then given by

$$W_C = \frac{\Delta H}{\Delta H_C} \quad (4)$$

The heat of fusion is usually measured from a differential scanning calorimetry (DSC) scan. This involves heating a sample at a constant heating rate in the range of 5-20

$^{\circ}\text{C}/\text{min.}$ and integrating under the heat flow rate against temperature curve to obtain the heat of fusion as illustrated in figure 2.

$$\Delta H = \frac{1}{\Phi} \int_{T_1}^{T_2} \frac{dH}{dt} dT \quad (5)$$

with Φ the heating rate in degrees/second

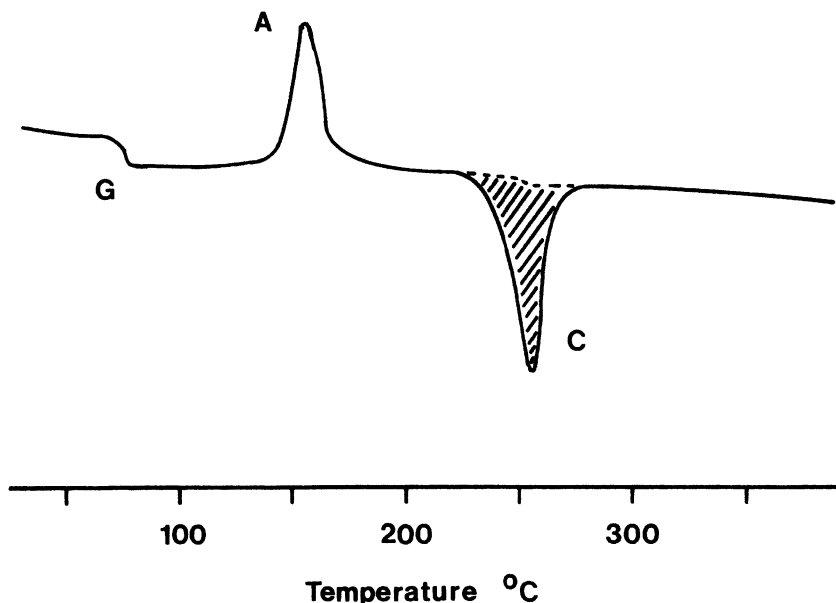


Figure 2: Heat flow rate against temperature from a DSC scan on PET. Glass Transition G, Cold Crystallisation A, Melting Peak C. Shaded area indicates area used to determine the heat of fusion.

There are a number of possible sources of error in the method. The first is that of obtaining an accurate value of ΔH_C . The other main problem is in determining the 'baseline' above which the curve is integrated to yield ΔH . Most modern DSC equipment has a range of automatic baseline determination routines which can usually reliably overcome this difficulty. However, the onset of melting is still sometimes difficult to determine and can lead to inaccuracies. Another problem is the production of erroneous values of ΔH due to cold crystallisation. This is also illustrated in figure 2. The cold crystallisation enthalpy must be subtracted from the melting enthalpy in order that the deduced crystallinity is representative of the polymer at normal temperatures. The PET DSC curve illustrated in figure 2 is a 'best case' example and frequently neither the cold crystallisation or the melting peaks will be as well defined and sharp as those in the illustrated example. Table 1 provides representative values of densities and

heats of fusion.

Table 1: Crystalline ρ_C and amorphous ρ_A densities and heats of fusion of selected polymers

	ρ_C g/cm ³	ρ_A g/cm ³	ΔH fusion J/g
polyethylene	1.004	0.853	293
polypropylene	0.946	0.853	163
nylon 6	1.190	1.090	230
nylon 6,6	1.241	1.091	301
polytetrafluoroethylene	2.301	2.000	67
poly(ethylene terephthalate)	1.514	1.336	138
polystyrene	1.126	1.054	96

X-ray methods

In this method a wide angle X-ray diffraction pattern is taken and the pattern is corrected for background scattering (see **X-Ray scattering methods**). A crystalline sample will produce a pattern with sharp well defined peaks and an amorphous sample broad diffraction ‘halos’ centered on the most probable atomic spacings. The measured pattern is decomposed into amorphous and crystalline components by comparison with a diffraction pattern taken from a fully amorphous sample. The sort of patterns involved are illustrated in figure 3. As a first approximation the fractional crystallinity may be estimated from the expression

$$C = \frac{I_A - I}{I_A - I_C} \tag{6}$$

with C the fractional crystallinity and I_A the fully amorphous intensity, I_C the crystalline intensity and I the measured sample intensity. Unfortunately factors such as the relative scattering efficiencies of amorphous and crystalline materials and corrections for absorption must be incorporated into the calculations which makes the method subject to errors and more difficult to apply than the density or DSC methods. However, it does provide a good relative method of following crystallinity changes which result from deformation or processing in a given material.

Other methods

IR and Raman spectroscopy can be adapted to determine degree of crystallinity. The observation that one or more IR bands disappear in an amorphous sample can be used to

estimate the degree of crystallinity by looking at the intensity of the band. Unfortunately exclusively crystalline bands are often not available and the spectrum must be corrected by subtraction of an appropriate background. The method therefore suffers from many of the difficulties associated with the X-ray method. NMR can in principle be used to measure crystallinity but is rarely used. Inverse gas chromatography based on the penetration of a suitable solvent into the amorphous phase but its exclusion from the crystalline phase may be used. However the density methods and the DSC thermal method are often the quickest and most reliable and will normally form the methods of first choice.

The volume by Mandelkern referenced below provides a good overview of the morphology and growth of crystals in polymers and those by Alexander and Brown excellent descriptions of the use of X-ray and Thermal methods respectively.

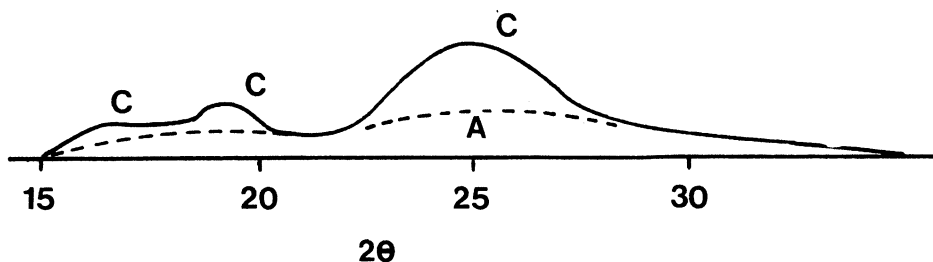


Figure 3: Intensity (corrected for background) against diffraction angle 2θ for a PVC sample. The crystalline 'peaks', continuous line, are labeled C and the amorphous contribution, dashed line, A.

REFERENCES

1. Mandelkern, L. (1964) *Crystallization of Polymers*, McGraw-Hill
2. Brown, M.E., (1988) *Introduction to thermal analysis: techniques and applications*, Chapman and Hall
3. Alexander, L.E. (1969) *X-Ray Diffraction Methods in Polymer Science*, Wiley.

11: Ductile-Brittle Transition

G M Swallowe

All thermoplastic polymers, in common with many metals, are capable of undergoing failure either in a brittle manner, like inorganic glasses, or in a ductile manner producing permanent plastic deformation. The temperature at which this transition occurs is the ductile-brittle transition temperature. This temperature is clearly of major importance to the design engineer but its value is not fixed for a given polymer but varies as a function of the strain rate and the shape and size of any notches or defects present in the polymer product (see **Fracture Mechanics, Fast Fracture in Polymers, Impact and Rapid Crack Propagation**). The Eyring theory of yield (see **Yield and Plastic Deformation**) predicts that the yield stress will vary with temperature and strain rate in a manner described by the equation

$$\sigma_y = \sigma_0 + \frac{RT}{v} \log \left(\frac{2\dot{\epsilon}}{\dot{\epsilon}_0} \right) \quad (1)$$

with σ_y the yield stress $\dot{\epsilon}$ the strain rate, T the temperature and $\dot{\epsilon}_0$, v , σ_0 and R constants. Since $\log (2\dot{\epsilon} / \dot{\epsilon}_0)$ is negative ($2\dot{\epsilon} / \dot{\epsilon}_0$ turns out to be < 1) the yield stress is predicted to increase as the temperature is lowered and also increase with strain rate in the manner depicted in Figure 1. The brittle fracture stress also increases with decrease in temperature but the rate of increase is much smaller. The relative increase in the brittle fracture stress with strain rate compared to the increase in the yield stress has, for clarity, been somewhat exaggerated in Figure 1.

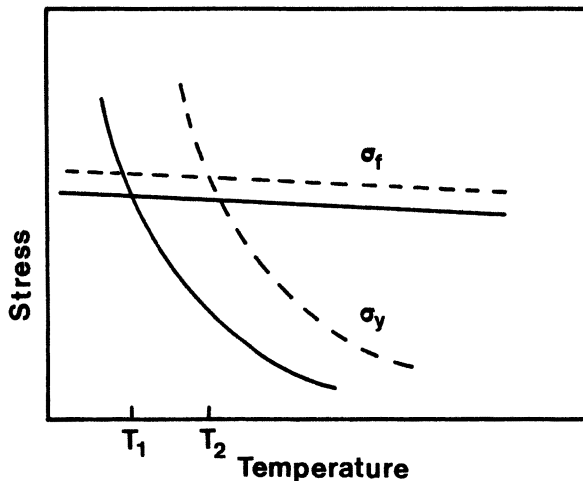


Figure 1: Schematic of the variation of Brittle fracture stress σ_f and yield stress σ_y with temperature for a polymer. At low strain rates (—) the Ductile brittle transition temperature T_1 is lower than at high strain rates (----) T_2

The Brittle fracture stress of a material on the basis of the Griffith criterion can be expressed as

$$\sigma_f > \sqrt{\frac{EG_c}{\pi a}} \quad (2)$$

with σ_f the fracture stress, E the modulus, G_c the toughness and a the length of a flaw or notch in the specimen. Although E increases with a decrease in temperature G_c falls and the overall effect is for σ_f to increase slightly with decreasing temperature. The result of the competition between the two failure processes is that as the temperature is reduced a point is reached where brittle fracture is favoured over yield. Figure 1 also indicates the effect of strain rate on the transition temperature. Both the yield and brittle fracture stress increase with strain rate but the yield stress increases at a much higher rate and the net effect is to move the transition to a higher temperature as illustrated in Figure 1. Brittle fracture is much more likely in a 'notched' specimen than an unnotched one. Introduction of a notch or slit greatly increases the factor a in equation 2 above the length of naturally occurring defects and so reduces σ_f . Equation 2 applies to plane stress conditions (thin sheets). In the case of plane strain (thick specimens) π is replaced by $\pi(1-\nu^2)$ with ν the Poisson's ratio and G_c by G_{IC} , where the I denotes that the parameter is a plane strain parameter.

Materials properties that affect the transition include molecular weight (see **Molecular Weight effects**) for which the fracture stress roughly follows the relationship

$$\sigma_f = A - \frac{B}{M_n} \quad (3)$$

with A and B constants and $\overline{M}_n$ the number average molecular weight. An increase in cross linking raises the yield stress but does not change the brittle fracture stress greatly and therefore leads to an increase in the transition temperature. On the other hand **plasticisers** reduce the yield stress to a much greater extent than the brittle fracture stress and hence decrease the transition temperature. Other factors to be taken into account include % crystallinity, orientation and presence and rigidity of side groups.

The ductile-brittle transition temperature always lies below T_g and representative values for a number of common polymers are set out in Table 1. These values are of course approximate and will vary with the grade and preparation of the polymer.

Determination of transition temperature (brittleness temperature) is carried out using standard tests such as ASTM D 746. In this test three sample geometries are defined but essentially the test consists of impacting ~25 mm long, ~ 6 mm wide and ~ 2 mm thick samples with a rounded striker travelling at ~ 2 ms⁻¹. The samples are clamped at one end and the impact occurs ~ 8mm from the clamp. 10 samples are tested at a fixed temperature and the temperature altered in temperature steps (appropriate to the polymer) to cover a range of temperatures in which all samples fail to one for which no failures are recorded. From a plot of the percentage failure against temperature the brittleness temperature is then quoted as the 50% failure temperature.

Tests such as the ASTM procedure outlined above will of course only provide a guide to the minimum temperature at which a particular polymer may be used without danger of brittle fracture, since the actual transition temperature depends critically on the presence of flaws and cracks and the strain rates experienced.

Table 1: Representative values of the ductile-brittle transition temperature

Polymer	Ductile-Brittle transition Temp. $^{\circ}\text{C}$	Glass Transition Temp. $^{\circ}\text{C}$
Polycarbonate	-200	150
PMMA	45	105
Polystyrene	90	97
PVC	-20	77
Polyethylene	-40	0

For the range of temperatures experienced in 'normal' conditions -20°C to 40°C the following table is a useful indication of the behaviour of common polymers.

Table 2: Brittle behaviour of common polymers

Polymer	Temperature			
	-20°C	0°C	20°C	40°C
Polystyrene	B	B	B	B
PMMA	B	B	B	B
Polypropylene	B	B	N	N
PET	N	N	N	N
PVC	N	C	C	C
Nylon (dry)	C	C	C	C
Polysulphone	C	C	C	C
HDPE	C	C	C	C
Polycarbonate	C	C	D	D
Nylon (wet)	C	C	D	D
PTFE	C	D	D	D
LDPE	D	D	D	D

Key: B Brittle failure, N Brittle failure when notched, C Brittle failure in presence of sharp notch or crack, D Ductile.

REFERENCES

1. Ward, I.M. (1983) *Mechanical Properties of Solid Polymers* 2nd Edition, Wiley
2. Mark, H.F., Bikales, N. M., Overberger, C.G., Menges, G. and Kroschwitz, J.I. (1987) *Encyclopedia of Polymer Science and Engineering* 2nd edition, Wiley
3. Ashby, M. and Waterman (1997) *The Materials Selector* 2nd edition, Chapman and Hall

12: Dynamic Mechanical Analysis

Techniques and Complex Modulus

J. Duncan

INTRODUCTION

In recent years dynamic mechanical analysis has moved from the research sector to be widely used throughout the polymer industry. This is due to two factors, namely the improved understanding of the dynamic mechanical technique and the availability of reasonably priced commercial instruments.

Many methods of polymer analysis are available now, so what does dynamic mechanical analysis have to offer over techniques such as Infra-red and NMR spectroscopy? Essentially it offers good value for money in that a single dynamic mechanical test taking a little over one hour yields a unique fingerprint of the relaxational processes (see **Relaxations in Polymers**) for the sample and also gives the modulus and damping factor over a wide range of temperature and frequency. These data should allow positive identification of the material and may also be used in engineering calculations and specifications. The data is obtained from a simply prepared sample of about 1-2g, often being cut directly from a component. Data also contains information about the bulk or macroscopic mechanical properties and frequently yields information on internal defects and microscopic properties, such as bonding of interfaces. In this sense dynamic mechanical analysis is a useful adjunct to IR and NMR techniques, these yielding precise chemical information on the polymer's molecular structure. These other techniques frequently take longer for sample preparation and in the case of NMR, the instrumentation is significantly more expensive. Dynamic mechanical analysis is therefore a general tool, providing a broad range of information in relatively quick tests. It is particularly useful in cure studies for thermoset materials and in testing the physical ageing of thermoplastics.

DYNAMIC MECHANICAL ANALYSIS - TERMS AND DEFINITIONS

In a dynamic mechanical test it is the sample stiffness and loss that are being measured. The sample stiffness will depend upon its Modulus of Elasticity and its geometry or shape. The modulus measured will depend upon the choice of geometry, Young's (E^*) for tension, compression and bending, Shear (G^*) for torsion. The modulus is defined as the stress per unit area divided by the strain resulting from the applied force. Therefore it is a measure of the material's resistance to deformation, the higher the modulus the more rigid the material is.

The definition given above for modulus does not take time into account. For materials that exhibit time-invariant deformation, for example metals and ceramics at room temperature, any measurement of strain will lead to a constant value of modulus. However for materials that exhibit time-dependent deformation, such as polymers, the quoted modulus must include a time to be valid (see **Viscoelasticity**). This is where dynamic mechanical testing offers a powerful advantage. Dynamic mechanical testers apply a periodic stress or strain to a sample and measure the resulting strain or stress response. Due to the time-dependent properties of polymers the resultant response is out-of-phase with the applied stimulus. The Complex Modulus M^* is defined as the instantaneous ratio of the stress/strain. To understand the deformational mechanisms occurring in the material this is resolved into an in-phase and out-of-phase response. This is equivalent to a complex number (see below), where M' is the in-phase or elastic response this being the recoverable or stored energy.

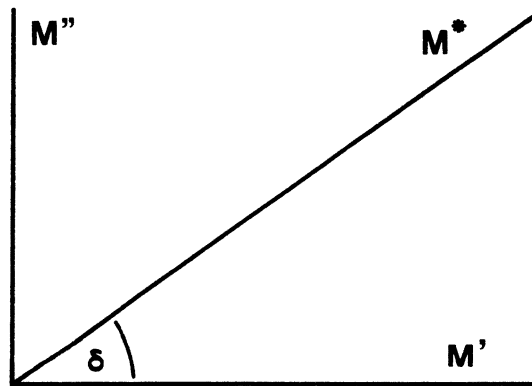


Figure 1: Illustration of relationship between M' M'' M^* and δ

M'' is the imaginary or viscous response, this being proportional to the irrecoverable or dissipated energy. Thus for a completely elastic material $M^*=M'$, whilst for a totally viscous material $M^*=M''$. δ is the measured phase lag between the applied stimulus and the response. $\tan \delta$ is given by the ratio M''/M' and is proportional to the ratio of energy dissipated / energy stored. This is called the loss tangent or damping factor. This is one of the key parameters in dynamic mechanical testing, since it is seen to increase during transitions between different deformational mechanisms.

Modern dynamic mechanical testers allow for most geometries: simple shear, compression, tension, clamped and simply-supported bending and torsional shear. These are listed in approximate order of stiffness. Consider a steel rule. The relative force to twist the rule (torsion) will be the least, followed by that for flexing the rule (bending), the force then required to stretch the rule is significantly greater (tension) and finally the force to shear the top and bottom surface is by far the greatest (simple shear). Choice of geometry will be discussed later in this article.

A typical dynamic mechanical test result may be seen in Figure 2. The left hand axis

displays the modulus data (E'), whilst the right hand axis shows $\tan \delta$. The material under test was poly(carbonate), a totally amorphous polymer. It is seen that the modulus is greatest at the lowest temperature and suffers a decrease during the β relaxation (peaks in $\tan \delta$ curve indicate relaxations) and continues falling gradually up until the glass transition temperature, where it is observed to decrease dramatically (3 orders of magnitude). This is accompanied by a much larger relaxation peak, typical of the glass transition, T_g .

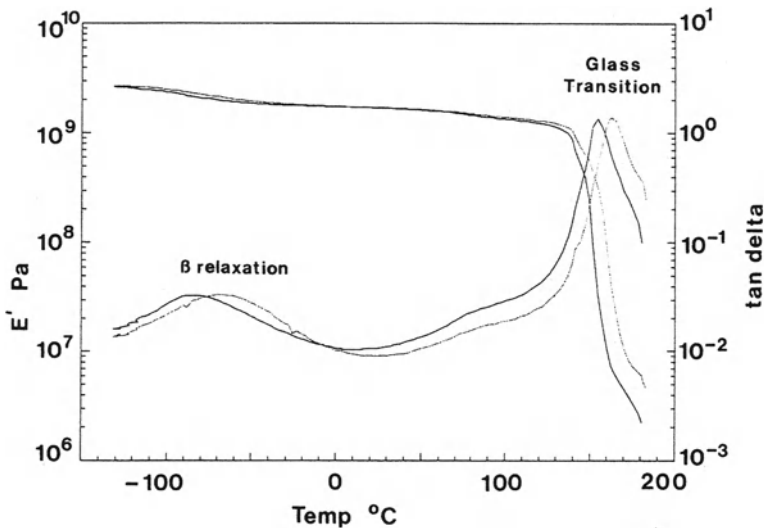


Figure 2: Modulus and $\tan \delta$ vs temperature for polycarbonate. The data (.....) was recorded at a higher frequency than the data (——).

Whilst the results are from a specific polymer, they are typical of features commonly observed. The slight decrease in modulus through the β relaxation is due to the extra mobility that arises from the molecular motion that now occurs freely above the transition temperature. Since such molecular motions are usually concerned with side groups on the main chain, their freedom to move does not have a great effect on the modulus, which is largely determined by the polymer backbone. However such sub- T_g relaxations are vitally important indicators of a material's mechanical properties. Large relaxations, as evidenced by large $\tan \delta$ peaks, mean that a molecular energy dispersion mechanism operates. Such mechanisms are responsible for toughness in materials. The addition of a poly(butadiene) rubber to poly(styrene) as in High Impact Polystyrene (HIPS) is done for exactly the same reason. The rubbery phase acts as an energy dispersive mechanism over a range of temperatures down to its T_g (see **Toughening**).

Since poly(carbonate) is amorphous it will transform from a glassy material to a rubbery one at the glass transition, with no further loss processes occurring until the material decomposes. Generally the modulus (E') of a glassy, amorphous material at room temperature is around 5GPa. It only increases for high levels of orientation or if

the material is crystalline. The rubbery modulus will be set by the effective cross-link density of the polymer. For cross-linked systems, this will be the physical cross-links that exist between the backbone molecules, whilst in linear materials it will be an entanglement density. An estimate of this molecular weight between cross-links can be given from the shear modulus measurement (G') (see **Structure Property Relationships: Rubbery Polymers** and **Structure Property Relationships: Glassy Polymers**).

Another feature readily apparent in figure 2 is the separation of the relaxation peaks in $\tan \delta$. This is due to the frequency dependence of relaxational processes. Essentially the faster the applied stimulus, the less time the molecules have to respond to it. Therefore as the temperature increases and with stimuli applied over a range of frequency, the glass transition is seen first for the lower frequencies. At low frequencies the molecules have a longer time to respond to the applied stress or strain, whilst at high frequencies the time is too short and the response is a glassy one, i.e. the molecules cannot move rapidly. From the frequency dependence of any relaxation it is possible to evaluate the activation energy for the process. This can be compared against theoretical calculations for likely molecular groups rotating from one state to the next. If a match is made, it is likely that this is indeed the molecular motion that is occurring.

In semi-crystalline materials, behaviour below T_g will be very similar to that for amorphous materials, however more relaxations are frequently seen above T_g . The magnitude of the glass transition $\tan \delta$ peak is frequently much smaller, as is the observed change in modulus. This can be explained by the crystalline regions (whose modulus has not fallen with increasing temperature) acting as effective cross-linking points for the rubbery material. This will enhance the sample rubbery modulus. If an amorphous sample is heated in such a test, it may crystallise above T_g , showing a large $\tan \delta$ peak and an accompanying rise in modulus. This is one of the few effects that can cause modulus to increase with increasing temperature. Relaxations may be observed at higher temperatures, often due to annealing and perfection of the crystallite structure. The final relaxation is very sharp and independent of frequency. This is the melting point.

CHOICE OF SAMPLE GEOMETRY

Most dynamic mechanical testers offer a full range of sample geometry (see fig 3). Often the choice of geometry will be dictated by the sample being investigated. For example thin films can only be measured accurately in tension. Fortunately all good dynamic mechanical testers perform well in tension and should deal with the necessary pretension forces fully and automatically. They should also cope with large modulus changes that occur as the temperature is varied, for example through the glass transition. Pretension is necessary in order to maintain the sample under a net tension to prevent buckling that would otherwise occur. Tension should be the first choice for any sample, but if it is too stiff for the instrument in the chosen geometry, another mode must be selected.

Materials that creep excessively, such as polyethylene, may be difficult to test in tension, due to creep under the pretension.

Bending mode is probably the most accommodating geometry, in that common-sized bars (50x10x2mm) of material are readily tested. Such sizes are within the ranges of most commercial dynamic mechanical testers. Clamped modes will yield better results over the whole temperature range, but suffer from clamping effects (see below), whilst simply supported modes (3-point bending) yield the most accurate moduli.

Torsion is a good choice of geometry, but since this has a low inherent stiffness it necessitates reasonably large samples. Also few dynamic mechanical testers have a torsional capability.

Simple shear is an excellent means of measuring low modulus materials, such as rubbers, gels and pastes. Glassy materials will be too stiff for most dynamic mechanical testers in this mode.

Compression is the worst choice for any sample. It is the mode with the most geometrical errors (see **Tensile and Compressive Testing**), but is often the only resort for irregular shaped samples. Under these circumstances an accurate modulus cannot be obtained, but transition information should not be compromised. Again due to instrument range it is only suitable for rubbers, gels and pastes.

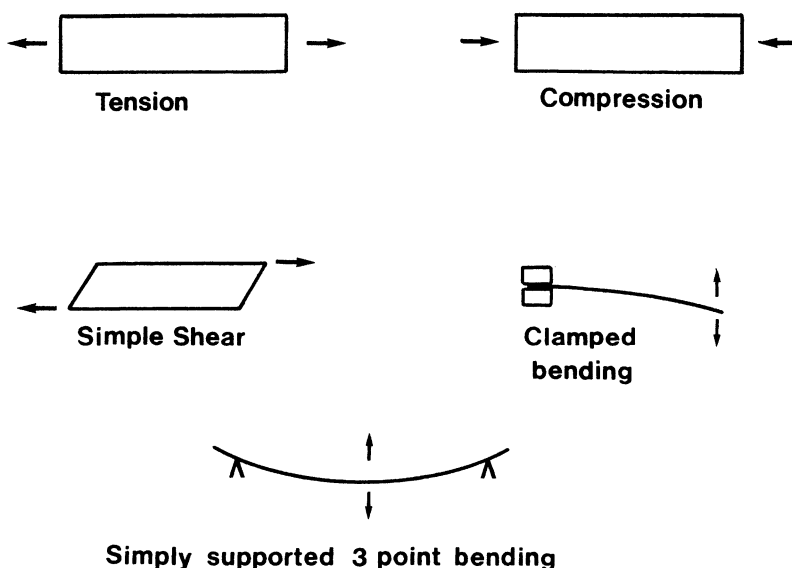


Figure 3: Test geometries available on DMA equipment

ERRORS

Many comments are often made about the ability of dynamic mechanical testers to deliver an accurate modulus. In fact their ability to measure *stiffness* is usually very good

(typically better than 1% accuracy). Most errors occur when the measured stiffness is converted into a modulus. Usually the chief culprit turns out to be an inappropriate choice of sample geometry, where the sample stiffness is close to or outside of the limits of the machine being used. Also the importance of accurate sample dimensions is often overlooked. An accuracy of 1% is only attainable if sample dimensions are measured to this level or better (see **Accuracy and Errors**). In fact for a bending geometry the length and thickness must be determined considerably more accurately due to the cubic relationship between length and thickness in bending mode.

Another source of error is clamp compliance. Many dynamic mechanical testers choose to cater for small samples, since this permits faster heating rates and consumes small amounts of material, which is an advantage if supply is scarce. The small sizes are harder to measure accurately and more importantly the machine clamps are often small as well. If the material's modulus is close to that of the clamp, as for metals and heavily filled materials, a considerable amount of sample moves within the constraint of the clamp. This leads to a longer effective length than the measured one, causing a lower modulus. Empirical routines will often allow correction of these effects.

SUMMARY

It can be seen that dynamic mechanical analysis offers considerable information on all types of polymers and similar materials having time-dependent properties. Dynamic mechanical analysis is a fast and easy test that produces a wealth of physical and chemical data which is useful for design and quality control purposes. It compliments the IR and NMR spectroscopic methods that yield chemical information particularly well. Further Information of the technique is available from the references.

REFERENCES

1. Nielsen, L.E. (1962) *Mechanical Properties of Polymers*, Reinhold
2. Murayama, T. (1979) *Dynamic Mechanical Analysis of Polymeric Material*, Materials Science monograph series, Elsevier
3. Gradin, P., Howgate, P.G., Selden, R. and Brown, R. (1979) in *Comprehensive polymer Science* V.2, ed. G. Allen, Pergamon

13: Electron Microscopy applied to the Study of Polymer Deformation

Athene M Donald

INTRODUCTION

Both scanning and electron microscopy have been extensively applied to the study of the nature of polymer deformation and fracture (for a general review of the techniques see reference 1, see also **Fast Fracture in Polymers** and **Slow Crack Growth and Fracture**). Their uses and obtainable resolution are rather different, and the two techniques should be regarded as complementary but both are of wide applicability for studying deformation, as a quick look through textbooks on the subject will show (e.g. ref. 2).

SCANNING ELECTRON MICROSCOPY

Scanning Electron Microscopy (SEM) works by scanning an electron beam, typically with energy in the range 5-25keV, across the surface of a sample. Either secondary (low energy) or backscattered (rather higher energy) electrons are then detected and an image formed with them. Secondary electrons principally provide topographic information, whereas backscattered can give atomic number contrast. For the study of fracture surfaces of polymers, secondary electrons are therefore the more useful and SEM has been extensively used for this purpose. Usually samples are fractured outside the microscope and then coated with some conducting material (e.g. carbon or gold) to prevent charge build up on the otherwise insulating polymer surface. Spatial resolution of up to 5 nm may in principle be obtained, although this is often neither necessary nor achievable, due to problems of damage caused by the high energy electron beam (possible damage mechanisms include mass loss and crosslinking).

SEM for the study of fracture mechanisms, and the nature of the deformation that precedes fracture, has proved very fertile. It is comparatively straightforward, for instance, to determine when fracture has proceeded via brittle failure mechanisms without substantial prior deformation since the fracture surface will then appear flat and featureless. The more deformation has occurred the more likely the surface is to appear rough, with (for instance) drawn out material standing locally proud of the surface. However, it is not always possible to distinguish unambiguously the nature of the deformation mechanism from such a fracture surface analysis, particularly when the sample is initially inhomogeneous (due to crystallinity or the presence of second phase particles, as in rubber toughened materials). The use of etching, particularly

permanganate etching as pioneered by Bassett's group³, has also helped in such analysis, by differentiating between crystalline and amorphous material.

There have been some limited attempts to study the deformation process *in situ*, but these are complicated by the fact that as new surfaces open up, which have not been coated with a conducting layer, charging will frequently occur obstructing the image. Additionally, the behaviour of the free surface under observation may be atypical for two reasons: firstly the stress state at a free surface will in general be different from the bulk sample due to loss of constraint there; secondly, the imaging process itself may change the surface via the beam damage mechanisms mentioned above, and therefore the images may contain artifacts.

TRANSMISSION ELECTRON MICROSCOPY

The principles of image formation in transmission electron microscopy (TEM) are rather different from SEM. As its name indicates, TEM works by forming an image with those electrons that have been transmitted through a sample. It is a technique, therefore, which can only be used for thin samples, typically 100 nm or less in thickness, even when working with quite high energy electrons (usually upwards of 100 keV). Although a few polymer films may naturally be manufactured this thin, this is the exception not the rule. Therefore mechanisms must be found for creating such thin samples. A frequently used strategy is microtoming ultrathin sections from bulk samples which have been previously been deformed. The drawback of this approach is that additional damage may occur during the sectioning, not representative of the initial deformation, and that relaxation of stresses may occur. One approach which is frequently successful in overcoming this problem is to use a stain such as OsO_4 which has a twofold advantage. Firstly the stain 'fixes' the material by (in the case of OsO_4) crosslinking preferentially unsaturated bonds, which pushes up the modulus of the material rendering it less susceptible to knife damage during sectioning. Secondly, the stain can differentiate between different regions aiding in the interpretation of the image. OsO_4 has been extensively used in the study of rubber toughened thermoplastics, since it stains the rubber particles and not the matrix. Other stains are used for other materials.

An alternative solution to the problem is to use films prepared by solvent casting. These thin films can then be directly strained, and the nature of their deformation studied in the TEM. Since TEM is inherently a higher resolution technique than SEM (sub-nm resolution being readily obtainable, subject to the constraints of beam damage), this approach can provide direct information on the deformation of small scale structures including lamellae in semi-crystalline polymers (see **Crystalline Polymers**). Staining is also sometimes used to differentiate between crystalline and amorphous material. Additionally, since electron diffraction patterns can be obtained from the same area as an image is formed, it is possible to correlate molecular packing information derived from the diffraction pattern with structures observed. In this way information can be obtained on which crystal orientations are most favourable for permitting deformation to

proceed, and the type of orientation that accompanies the deformation. This approach has also been extensively used to characterise the fibril structure in crazes in glassy polymers (see **crazing** and ref. 4).

The drawback of using thin films (as with studying deformation at free surfaces) is that their stress state will differ from bulk samples (the film will be in a state approximating plane stress), and the nature of the deformation may accordingly be altered. However, in some instances at least, it is possible to retain the samples under stress even during observation so that relaxation does not occur. This can be done by placing the sample on a copper grid to which it is bonded, and then deforming the grid. Since the metal deforms plastically the stress state can be retained even when individual grid squares are observed in the TEM.

HIGH VOLTAGE TRANSMISSION ELECTRON MICROSCOPY

Recent developments have led to the possibility of carrying out *in situ* deformation in a high (1000 keV) voltage transmission electron microscope. This approach has been pioneered by Michler's group⁵. Because of the high voltage, thicker samples can be examined than in conventional TEM, but they are still far from true bulk samples. However the problems associated with beam damage occurring simultaneously with deformation may still be present.

REFERENCES

1. Sawyer, L.C. and Grubb, D.T. (1987) *Polymer Microscopy*; Chapman and Hall: London
2. Kinloch, A.J. and Young, R.J. (1983) *Fracture behaviour of polymers*; Applied Science, London
3. Bassett, D.C. (1988) In *Developments in Crystalline Polymers-2*; (ed. Bassett, D. C.) Elsevier Applied Science, London
4. Kramer, E.J. and Berger, L.L. (1990) In *Adv Poly Sci* 91/2; (ed. H.H. Kausch) Springer, Berlin
5. Michler, G. T. (1986) *Coll.Poly.Sci.*, **265**, 522.

14: Environmental Effects

G. M. Swallowe

CHEMICAL EFFECTS

Although polymers have a very desirable resistance to chemical attack they may be susceptible to slow degradation even when exposed to what appear to be rather benign conditions. Degradation leads to deterioration in mechanical properties and is caused by a breakdown in the polymer structure due to one or more factors. The most common factors causing degradation are thermal effects, oxidation, photo-degradation, chemical attack, hydrolysis and radiation. Defects caused by one form of degradation will frequently act as sites for further attack e.g. traces of oxygen introduced during processing may lead to the formation of carbonyl groups in polyolefins which act as sites for UV absorption and lead to photo-degradation. Degradation can be due to oxidation by agents as apparently benign as atmospheric oxygen and hence antioxidants are frequently incorporated into polymer products both to protect the polymer during molding where the high temperatures employed makes it very susceptible to oxidation and to provide long term protection against oxygen attack.

Molecular degradation almost always occurs at a defect in the polymer structure and is frequently due to photo-oxidation. Dissociation energies of polymer bonds are in the range 60 to 100 kcal mol⁻¹ and the UV component of sunlight has an energy equivalent to about 90 kcal mol⁻¹ and can therefore degrade most polymer bonds. Polymer degradation begins with the scission of weak bonds and the radical formed by the scission easily reacts with oxygen to yield oxidised polymer and another radical. The process continues until terminated through the reaction of a pair of radicals. The chemical reactions involved are fully discussed in reference 1. Trace metal impurities in the polymer from the original polymerising catalyst or the degradation of pigments can act as initiators of the photo-oxidation reactions and the amount of oxidation occurring during processing also has a major influence. Tertiary bonds are usually weaker than primary or secondary ones and so act as the sites of initial degradation. As well as degradation of colour (yellowing) the chief effect of oxygen attack is embrittlement which causes a reduction in strength and elongation to failure.

Hydrolysis can also lead to chain scission and the resulting reduction in molecular weight will change mechanical properties. Polycarbonate is particularly susceptible to this process. Water absorption causes a plasticising (see **Plasticisers**) effect in some polymers (e.g. Nylon) with a resultant reduction of modulus and strength. The difference observed between stressed polyesters and polyethers in a high humidity environment where polyether suffers very little strength reduction while a polyester can suffer a reduction of strength of a factor of 5 or more during a years exposure is a good example of how hydrolysis must be considered in the choice of polymer. The actual reduction in strength of the component will depend on its size since the controlling step will be the

rate of water diffusion into the polymer.

MECHANICAL EFFECTS

Stress corrosion cracking, also known as environmental stress cracking, is a problem caused when polymers are exposed to certain substances either while under external stress or stresses formed as a result of internal residual stresses caused by processing. The hallmark of this effect is that the crack formation and growth does not take place in the absence of the corrosive substance or environment. An example is the cracks formed on the inside of polyethylene pipes carrying chlorinated water supplies. Organic solvents such as acetone, toluene, ethyl acetate etc. are very liable to cause corrosion cracking but only by testing can it be established which products will be affected since a 'good' moulding with very little residual stress may not suffer while a 'bad' moulding may be readily attacked. The most highly stressed bonds, those at the tips of cracks, are the most likely to react and hence further crack growth occurs with a consequent increase in stress at the crack tip (see **Fracture Mechanics**). This may result in the failure of a component if the crack grows large enough to grow spontaneously under the applied stress conditions. The reaction rate of bonds may be related to stress by an equation of the form

$$\alpha = A \exp((\Delta G - B\sigma)/RT) \quad (1)$$

with α the reaction rate, A a rate constant, B an activation volume ΔG the Gibbs free energy, σ the applied stress and T the temperature. This is the same form of equation as used in the Eyring expression for plastic flow (see **Yield and Plastic Deformation**). It can be seen that positive (tensile) stresses will reduce the overall activation energy for the reaction ($\Delta G - B\sigma$) whereas a negative (compressive) stress will raise it and so inhibit the reaction. This has been confirmed by DeVires and Hornberger² who found that residual compressive surface stresses inhibited attack by corrosive gases.

GENERALISATIONS

The only generalisation that can be readily made about environmental effects are that they are very environment and system specific! Both chain scission and cross linking can occur. Cross linking causes a stiffening in the polymer, a reduction in ductility and hence a disposition to crack. Chain scission causes a reduction in material strength but an increase in ductility. The ingress of water, or other solvents, causes swelling of the polymer and is particularly likely to occur in amorphous polymers. It also causes an increase in resistance to shear flow and results in easier craze formation and growth. In general the more highly crystalline the polymer the more resistant it is to degradation. The morphology of a polymer moulding will vary from point to point because of the

different cooling rates experienced in different parts of the moulding. In a semi-crystalline polymer regions in which there is a large fraction of amorphous material will be more susceptible to degradation than more highly crystalline regions. This will be compounded by variations in residual stresses caused by differential cooling and so even within the same moulding variations in resistance to the environment can occur.

In general the corrosion resistance of thermoplastics follows a trend in which the higher the percentage of C-H and C-Cl bonds the more susceptible a polymer will be to corrosion. At the other end of the scale a high proportion of C-F bonds offers protection from corrosion. Thus polymers such as PTFE, fluorinated ethylene propylene or ethylene chlorotrifluoroethylene provide excellent corrosion resistance in comparison to materials such as polypropylene, PVC or polyethylene. Further details on the corrosion resistance of particular polymers may be found in such publications as the Handbook of Materials Selection for Engineering Applications³.

TEST METHODS

The traditional method of studying environmental degradation is by 'weathering' where samples of the polymer are exposed outdoors to the action of the weather and samples are taken every few months. Conditions vary considerably between sites but the most important influences are sunshine and moisture so tests may be carried out in Arizona to assess performance in sunny, hot and dry conditions and also in Florida for sunny, hot and humid conditions. However other variables such as frost, dust levels in the wind etc. are also important and ideally a large number of test sites should be used to obtain a comprehensive picture of the polymer performance. These tests are, by their very nature, long term often lasting 5 years or longer. They may be speeded up by placing the samples on steerable racks which use mirrors to increase the intensity of the solar radiation exposure and track the sun in the same manner as astronomical telescopes track stars.

Laboratory methods attempt to speed up the process by using thermal techniques such as differential scanning calorimetry DSC, thermogravimetry TG and thermal volatilisation analysis TVA. These can be used to obtain such information as the activation energy for decomposition, induction time for onset of degradation (as measured by weight loss or DSC peak), temperature for 50% decomposition etc. All these tests can be carried out in controlled atmospheres. The disadvantages are that, although the results are produced rapidly, it is not always the case that the degradation mechanisms will be the same at ambient temperatures as at the elevated ones used in the tests and that the polymer reaction mechanisms may even be different in the different temperature ranges. Other laboratory methods include the use of UV lamps and high oxygen pressures to speed up the degradation process while maintaining the temperature in the ambient range and the use of higher concentrations of corrosive chemicals in the medium in contact with the polymer than is met in practice. It is however generally accepted that accelerated tests can only give a rough indication of the relationship

between natural and artificial degradation and cannot be used for accurate lifetime predictions.

ASSESSMENT OF DEGRADATION

The amount of degradation in a sample may be assessed by a variety of means. The simplest is by visual inspection. Yellowing, a cracked, blistered or friable surface are clear signs of degradation. More quantitative methods of measuring oxygen uptake include measuring the carbonyl absorption band at $1710\text{--}1740\text{ cm}^{-1}$. By sectioning and measuring carbonyl absorption at points through the thickness of a sample a depth profile of the extent of degradation can be carried out. Chain scission is frequently accompanied by an increase in **crystallinity** and because of the very small quantities of sample required DSC can be used as a tool to study crystallinity changes with depth in a sample. Chromatography will provide information on the molecular weight of the polymer and again in conjunction with samples from different positions and depths in the polymer product will enable the extent of degradation to be mapped. To assess mechanical performance tensile and impact test samples can be machined from the product and mechanical degradation directly evaluated (see **Tensile and Compressive Testing** and **Impact Strength**). This latter course, together with microscopic examination for cracks, is perhaps the best method since it is the only way of obtaining direct evidence of the loss of strength, ductility etc. The main drawback is the requirement of specimens large enough to machine test pieces from and the danger that the averaging involved over the thickness of a test piece will mask any loss in strength which may only extend a small distance into the specimen. To be valid tests all the above methods will ideally require comparative measurements to be made on a pristine specimen.

Environmental factors such as degradation have been widely researched in the past twenty years and are a major concern of manufacturers and users of polymer products. As a result of degradation problems manufacturers add UV absorbers and metal deactivators as well as antioxidants to polymer resins. These are normally present in parts ranging from hundredths to several tenths of a percent. The types of additives that can be added depend on the intended end use of the polymer (e.g. manufacture of pipes for water for human consumption) and are regulated by national and international standards such as BS EN 852: Migration assessment for plastic piping systems for the transport of water intended for human consumption. Other standards cover resistance to corrosive fluids (e.g. ISO 4433: Polyolefin pipes - Resistance to chemical fluids by immersion test method) and the comprehensive standard BS 2782: Methods of testing plastics, covers a huge range of recommended test methods for polymers including natural weathering tests, laboratory UV light source tests, artificial ageing among many others. The problems caused by environmental degradation of polymers cover a very wide field, reference 4 and 6 provide a good introduction to all aspects of polymer degradation and reference 5 is a good survey of the field.

REFERENCES

1. Grassie, N. and Scott, G. (1985) *Polymer Degradation and Stabilisation*, Cambridge University Press
2. DeVries, K.L. and Hornberger, L.E. (1989) *Polym. Degrad. and Stab.*, **24**, 213.
3. Murray, G.T. (ed.) (1997) *Handbook of Materials Selection for Engineering Applications*, Dekker
4. Kellen, T. (1983) *Polymer Degradation*, Van Nostrand Reinhold
5. White, J.R. and Turnbull, A. (1994) Review - Weathering of Polymers, *J. Mat. Sci.*, 584
6. *Polymer Durability: Degradation, Stabilisation and Lifetime Prediction*, ed. R. L. Clough, N. C. Billingham and K.T. Gillen, (1996) Advances in Chemistry Series No. 249, American Chemical Society

15: Falling Weight Impact Tests

P. E. Reed

INTRODUCTION

Several variants of the falling weight impact test have been used to assess the impact behaviour of polymers and polymer products. Table 1 gives a list of current test methods included in the ASTM Standards for testing¹. Equivalent or similar tests exist in Standards from other parts of the world.

Table 1 Selected ASTM falling weight impact test Standards

	Title
ASTM-D1709	Test methods for impact resistance of polyethylene film by free falling dart method
ASTM-D3029	Test methods for impact resistance of flat, rigid plastic specimens by means of a tup
ASTM-D4272	Test method for total energy impact of plastics film by Dart drop
ASTM-D3763	Test method for high speed puncture properties of plastics using load and displacement sensors
ASTM-D2463	Test method for drop impact resistance of blow moulded thermoplastic containers

Test methods D1709 and D3029 form the basis for non-instrumented dart drop testing. Both adopt the 'staircase' method of assessment to determine the energy required for failure of 50% of the specimens. Only the incident energy of the dart is used in the assessment with these tests.

In test method D4272 the velocity of the dart is measured before and after penetration of the clamped film specimen. Hence, with additional knowledge of the mass of the freely falling dart, the energy absorbed in breaking through the specimen is determined for every test piece.

Test method D3763 is the ASTM Standard for instrumented falling weight impact (IFWIM) testing, in which the force and displacement are measured throughout the test. The displacement can either be calculated from the force measurement alone, or measured directly using a second measuring device. This method can give much more information about the initiation and propagation of damage in each test than the previous non-instrumented falling weight tests.

The inclusion of D2463 in Table 1 (drop impact resistance of blow moulded thermoplastic containers) is of interest, because it is a test on a component made from thermoplastic and is clearly not a 'material' test. All the previous test methods have appeared to measure a material property, namely the energy required to break a

particular specimen (see **Impact Strength**). However the inclusion of a component test in the list is not surprising when it is recognised that ASTM stands for American Society for Testing *and* Materials (and not *of* Materials). Thus testing of components as well as tests for material properties are both within the remit for ASTM.

The drop test for blow moulded containers requires a series of vessels to be filled with water, then dropped from different drop heights to determine the minimum drop height for failure (usually splitting or tearing) of the container. The test reproduces an actual impact situation for the component, but set in a Standard procedure. In this test it is the test piece that is dropped onto a hard surface (which can be instrumented with force transducers) rather than having a dart or mass dropped onto the test piece, as in the other falling weight tests reviewed.

FALLING WEIGHT COMPONENT TESTS.

The IFWIM system described in the article **Falling Weight Impact Testing Equipment** can be used to impact test a range of components. The instrumented dart, with its force transducer, can be viewed as an instrumented hammer. A force-time or force-displacement curve is obtained from the impact event whatever test piece is used. Thus the IFWIM system can be used for a diverse range of component tests, including footwear, pipes, protective helmets, car components through to polystyrene meat trays. The possibilities are endless, but in many cases it becomes an instrumented impact test which reproduces an in-service impact event for the component in a standardised form.

The results of such component tests can be presented in a similar manner to those of the Standard tests, giving the maximum force or energy to break through the component with the selected dart. However much is now done in seeking to model the observed force/displacement data of the impact event using finite element analysis (FEA) (see **The Finite Element Method**). Such FEA modelling of the impact events requires material property data, especially true stress/true strain data for the material concerned, over a range of strain rates.

Instrumented impact tests on components do not produce fundamental impact property data for the materials used in their construction. They examine and measure the performance of the complete structure, which depends on many factors, including the geometry of the piece, the manner in which it is supported in the test, the processing of the material used as well as the material used for the component. Where FEA modelling is applied, the fundamental material property required is the stress/strain data to model the force/deflection curve of the impact event accurately and hence calculate the energy absorbed from that force/deflection curve. Hence the energy to break the component can be seen as deriving from the test piece and test method selected, rather than being a fundamental material property.

The foregoing argument for component impact tests applies equally to Standard falling weight impact tests and other forms of impact testing, which measure the energy to break the test piece. The energy measured to break the specimen is not a fundamental

material property, but rather a measure of the energy required to break the particular test specimen used in the test set-up adopted. Changes to the test method (such as specimen size, method of specimen support, dimensions of the dart used) can change the energy required to break the specimen. All the Standard falling weight impact tests can be considered as component tests, although the component is normally standardised. In a Standard test the properties of the different materials are being compared under standard component conditions. Such conditions may relate directly to different products in the same material, but this cannot always be assumed.

IMPACT FRACTURE MECHANICS TESTING

Notched bar Charpy tests, usually conducted on swinging pendulum impact test equipment, can also be performed on IFWIM drop towers. It requires the normal flat plate specimen support to be replaced by a Charpy bar support system and the falling dart to have a Charpy form hammer tip instead of the usual hemispherical tip.

Instrumented Charpy impact testing on the centrally notched test specimen (Fig. 1) records the force/displacement curve to the point of fracture. A typical curve is shown in Fig.2. This curve contains data from which **fracture mechanics** parameters can be determined for the material under impact loading conditions. The critical stress intensity factor (K_{IC}) can be calculated from the force at fracture (F_M) and the critical strain energy release rate (G_{IC}) can be determined from the energy under the force/displacement curve to the point of fracture. These fracture mechanics parameters may be considered as fundamental properties of the material under test². The development of a protocol/Standard for the determination of K_{IC} and G_{IC} of polymers under impact loading at impact speeds up to 1m/s is currently being undertaken by ESIS Technical Committee 4. This protocol extends existing Standards for the determination of fracture mechanics parameters for plastics under quasi-static loading³.

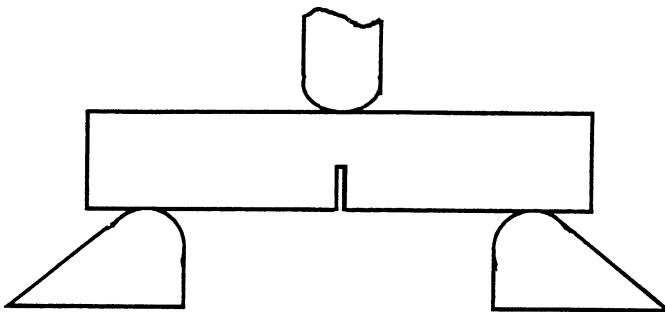


Figure 1: Charpy test specimen

Oscillations on the force/displacement curve (see Fig.2) are a problem in impact fracture mechanics testing. These oscillations arise from dynamic effects, particularly the initial inertia loading on the specimen, as the specimen is accelerated to the speed of the striker on initial contact, plus various vibrations occurring within the specimen and test system. These oscillations lead to difficulty in determining the precise fracture point on the force/displacement curve and hence the accurate determination of the force and energy at fracture. The oscillations become more severe as the impact speed is increased and with stiffer or more brittle materials. Some form of damping can be applied to maintain the oscillations within reasonable limits, thus helping to define the underlying force/displacement curve (see also **The Hopkinson Bar**).

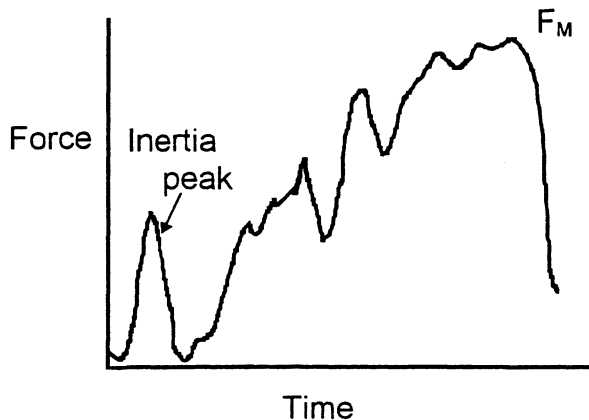


Figure 2: Typical load time record

Electronic filtering of the signal is not recommended in the ESIS TC4 protocol, preferring a minimal mechanical damping at the contact point of striker with specimen to keep the oscillation amplitude within a $\pm 5\%$ envelope of the mean current load value over the final half of the force/time curve. Suitable mechanical damping materials are a uniform layer of a viscous grease or viscoelastic rubber material applied to the specimen in the contact zone. In all cases the thickness of the damper should be kept to the minimum required to limit the oscillations to the $\pm 5\%$ limit. Excessive damping, although producing smooth curves, distorts the basic curve and produces incorrect failure loads and energy values.

REFERENCES

1. Annual Book of ASTM Standards. American Technical Publishers Ltd. UK
2. Williams, J.G. and Pavan, A. (eds) (1995) *Impact and Dynamic Fracture of Polymers and Composites*. ESIS Publication 19. Mechanical Engineering Publications
3. ISO/TC 61/SC2. ISO Draft Standard Plastics-Determination of fracture toughness G_C and K_{IC} - Linear elastic fracture mechanics (LEFM) approach.

16: Falling Weight Impact Testing Equipment

L. Warnet and P. E. Reed

INTRODUCTION

Fig. 1 shows the elements of an instrumented falling weight impact (IFWIM) testing system (see **Falling Weight Impact Testing Principles**). The equipment usually includes

- (a) a tower, consisting of a rigid base and top plate, connected by two polished columns on which the striker carriage and release platform slide
- (b) an instrumented striker or tup (fitted with a force transducer)
- (c) a striker velocity measuring system
- (d) a striker carriage arrest system
- (e) the data acquisition system
- (f) specimen support and clamping attachments.
- (g) Optional extras can include (i) an energy 'assist' system to increase the impact velocity (ii) environmental chambers for testing at different temperatures and (iii) alternative base stands for testing large components.

In the basic test, the release platform with striker carriage and striker is raised to a pre-determined height, h , to obtain a particular incident impact speed, v_0 , where $v_0 = \sqrt{2gh}$. The striker carriage is then released to fall freely under gravity so that the striker hits the specimen at the required speed. Practical limitations on the height of the tower limit the 'free fall' impact velocity to about 4.5 m/s. The impact velocity can be increased by using an energy 'assist' system, which stores energy in a compressed spring or equivalent as the striker carriage is raised to the top of the tower. The striker carriage is then 'fired' on release, to achieve impact speeds between 4 - 20 m/s, depending on the initial 'assist' energy stored.

The incident energy available for the test is determined by the total mass of the striker carriage and striker, m , and the incident impact speed, v_0 .

$$(E_0 = \frac{1}{2} m v_0^2)$$

INSTRUMENTED STRIKER

The striker (tup or dart) comprises a cylindrical tube or rod, commonly fitted with a hemispherical tip, and incorporates a force transducer (see **Transducers**) to measure the force during the test. The cylindrical section must be smooth and of sufficient length to punch through the specimen, without damage to the transducer, before the striker

carriage hits the stops.

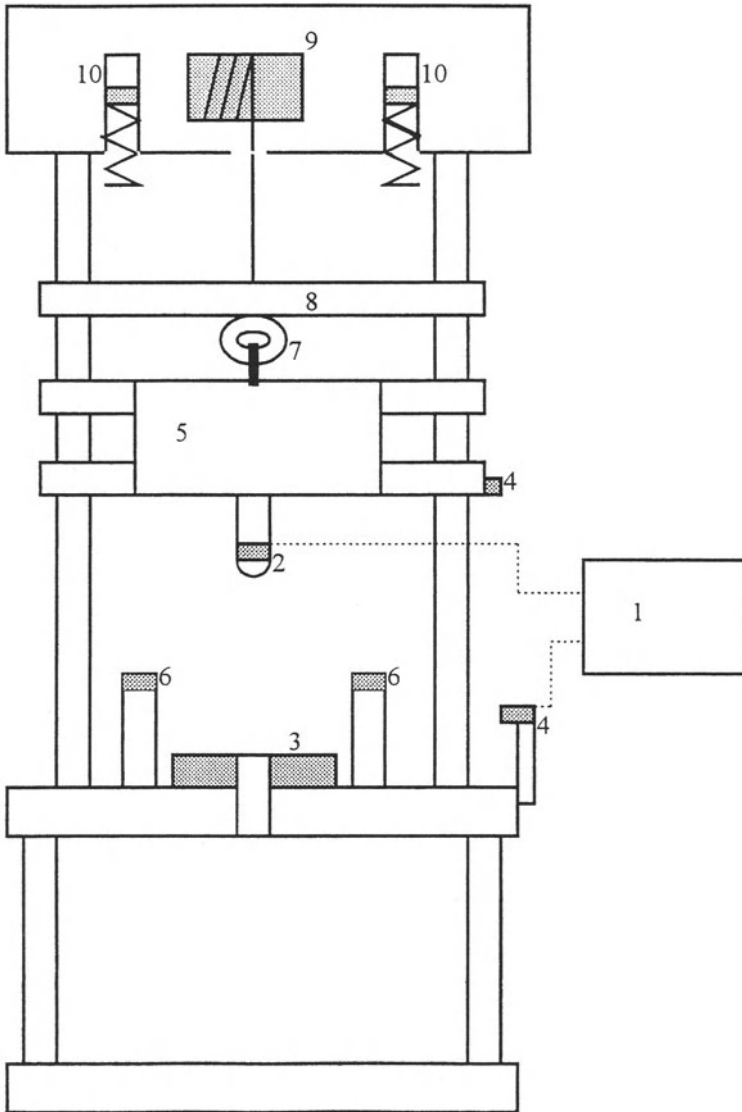


Figure 1: Schematic of the IFWIM system. 1 Data acquisition system, 2 Striker with force cell, 3 Specimen support system, 4 Velocity measuring system, 5 Striker carriage, 6 Striker carriage arrest system, 7 Carriage release link, 8 Release platform, 9 Striker winch system, 10 Energy 'assist' system.

Two types of transducer are used, based on either strain gauge or piezoelectric transducers. The essential requirement is a high natural frequency for the system, since

impact tests are of short duration (typically 1-10 ms). The natural frequency of the striker is determined by a combination of the stiffness of the transducer and the striker mass used in front of the transducer. While piezoelectric transducers have a high natural frequency in isolation, this advantage can be lost when these have to be located well away from the striker tip.

VELOCITY MEASURING SYSTEM

Analysis of the IFWIM data requires measurement of the impact speed of the striker, v_0 . While this can be calculated from the drop height, h , assuming free fall under gravity, it is usually measured just before the moment of impact. One possible system is to use a velocity 'flag' attached to the carriage, which passes through a photo-optic sensor just before the moment of impact. The speed is determined by the time of flight of the 'flag' of known width through the sensor. The same system can also be used to trigger the data acquisition system to record the force/time data for the test.

STRIKER CARRIAGE ARREST SYSTEM

With 'excess energy' testing, the incident energy contained in the falling striker carriage and striker greatly exceeds that required to break the specimen. Consequently the change in striker speed during the test is small, which is one reason for excess energy testing. However the striker carriage has to be caught or stopped after the test is completed and before it causes damage to the rest of the equipment. This is usually achieved using two adjustable stop blocks to catch the carriage squarely, without tilting. The height of these stop blocks is adjustable to permit different size or shaped test pieces and different specimen support systems. The stop blocks can be simple energy absorbing pads or more sophisticated pneumatic or hydraulic devices and must be capable of absorbing the large energies involved.

In 'low energy' testing, the arrest system fulfills a second function. The striker carriage is stopped by the specimen in 'low energy' testing and then rebounds, before the specimen is completely broken. The specimen may then be submitted to several rebound impacts, causing possible further damage and making it difficult to distinguish the damage from each impact. Also only the first impact data are recorded. The stop blocks can be fitted with an anti-rebound device, causing the tops of the stop blocks to 'pop-up' after the first impact, so preventing the striker from hitting the specimen a second time. Various systems exist for the timing of the 'pop-up', based on signals received from the velocity measuring system or the data acquisition system.

DATA ACQUISITION SYSTEM

Data acquisition involves a computer system with the following features

- (a) software/processor to control the test
- (b) data logging facilities to record the basic data from the force transducer and velocity sensor
- (c) performs the necessary calculations
- (d) displays the results.
- (e) Commercial software receives and files the fundamental force-time data and converts this to data of force-velocity-displacement-energy for each data point in the file. Generally 2000 - 4000 data points are recorded during the test over a time period selected by the operator. The data can then be displayed in any combination of the five quantities (force, velocity, displacement, energy, time). Common outputs are force-time (or force-displacement) in combination with energy-time (or energy-displacement). Specific features, such as maximum (peak) force and associated quantities, can be automatically displayed, or the data files and displayed curves can be variously interrogated.

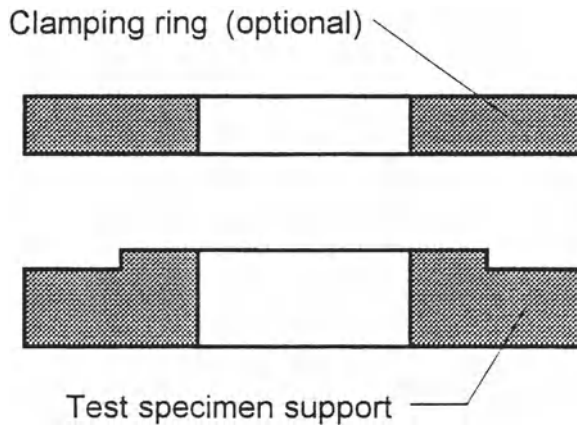


Figure 2: Specimen support system with optional clamping

SPECIMENS AND SPECIMEN SUPPORT.

Specimens for the IFWIM test are plates which have been specially moulded or cut from larger components. The geometry of the test piece and specimen support system are defined in various Standards. Dimensions for two Standards are given in Table 1.

The specimen may be clamped or simply supported (Fig.2). Clamping is never perfect and does not prevent total radial slippage or rotation at the clamp. Clamping prevents buckling of the outer region of the specimen and is necessary with highly ductile specimens to prevent total collapse of the specimen into the hole under the striker.

Results for clamped and unclamped specimens are likely to be different, since any changes to the test piece geometry or boundary conditions can affect the test results.

Table 1 Specimen and striker specifications for two Standards

Test method ISO 6603

Specimen size mm	Specimen thickness mm	Support diameter mm	Striker
60 square	2	40	20 mm hemispherical
60 round	2	40	-
140 square	5	100	20 mm hemispherical
140 round	5	100	-

Test method ASM D 3029

Specimen size mm	Specimen thickness mm	Support diameter mm	Striker
not specified	not specified	38	12.7 mm conical
not specified	not specified	76	15.86 mm hemispherical
not specified	not specified	127	38.1 mm hemispherical

17: Falling Weight Impact Testing Principles

L. Warnet and P. E. Reed

INTRODUCTION

The falling weight impact test (or dart drop test) is one of the methods used to assess the impact properties of polymers (see **Fast Fracture in Polymers** and **Impact and Rapid Crack Propagation Measurement Techniques**). The specimen used for the test is commonly a flat plate, either specially moulded or cut from a larger component. It is supported at its edges and impacted centrally by a vertically falling dart. Impact performance of polymeric components is concerned with absorbing energy in the system when the component is struck, either through deformation or damage development. Hence initially it was only the energy required to break the specimen in a falling weight impact test that was recorded to characterise the impact behaviour of the material.

Early falling weight tests¹ were not instrumented and the 'staircase' method was used to determine the minimum energy required to break the specimen. The incident energy of the dropped dart could be changed incrementally, either by varying the mass of the dart while keeping the drop height constant or keeping the mass constant and changing the drop height. A series of 100 specimens had to be tested to obtain the fracture energy, using incident impact energies near the fracture point. Each specimen was tested only once. If fracture did not occur, the incident energy was increased one increment for the following specimen and vice-versa if fracture did occur. By testing 100 specimens, an average energy that just caused fracture could be obtained. While this method gave some information on the statistical variation of the impact strength of a series of specimens, it was tedious to perform. Also it gave only the average energy required to break the test piece.

In the instrumented falling weight impact (IFWIM) test, the falling dart is fitted with a force transducer to measure the force throughout the impact test. This basic force-time data is then processed to provide a wealth of information from each specimen tested, giving force, displacement and energy data throughout the test².

IFWIM ANALYSIS

The basis of the method is shown in Fig.1. The dart (alternatively called striker or tup) attached to a carriage of total mass, m , falls under gravity to hit the specimen. Newtonian mechanics is then applied to the striker and carriage using the following equation.

$$mg - F = m \frac{dv}{dt} \quad (1)$$

$$\text{or} \quad \frac{dv}{dt} = g - \frac{F}{m}$$

where F is the force applied to the striker, measured by the force transducer.

Integrating equation (1) gives first the velocity at any time, t .

$$v = v_0 + gt - \frac{1}{m} \int_0^t F dt \quad (2)$$

A second stage of integration gives the displacement, x

$$x = v_0 t + \frac{gt^2}{2} - \frac{1}{m} \int_0^t \left(\int_0^t F dt \right) dt. \quad (3)$$

Hence the velocity and displacement during the impact test can be calculated from the force/time record alone, provided the mass, m , of the striker and the velocity, v_0 , at the moment of initial contact with the specimen are known. The energy, U , is found by further calculation $U = \int F dx$ or

$$U = v_0 \int_0^t F dt + g \int_0^t t F dt - \frac{1}{2m} \left(\int_0^t F dt \right)^2 \quad (4)$$

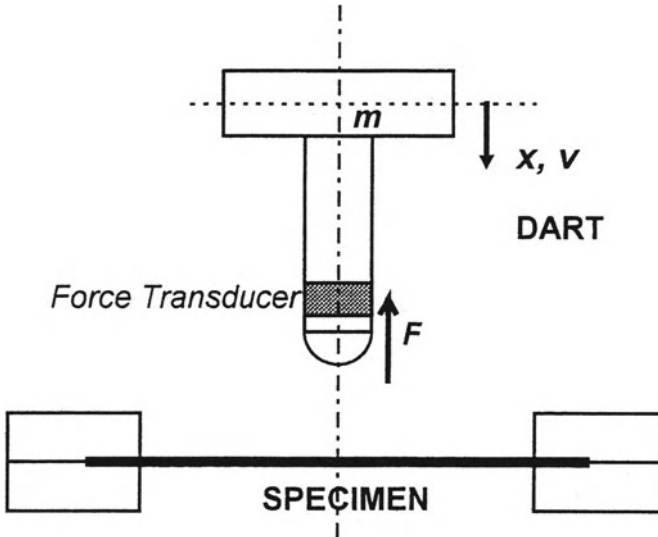


Figure 1: The instrumented falling weight impact test method.

All calculations are performed on a dedicated microcomputer with associated software. Hence the IFWIM test provides simultaneous information on the force, displacement, energy and velocity at any time throughout the impact test.

The computations are based on the forces acting on the striker and calculate the velocity and displacement of the striker. It is assumed that the specimen remains in contact with the striker throughout impact and that the velocity and displacement of the specimen at the point of contact with the striker are the same.

LOW ENERGY TESTING

The IFWIM system and analytical method above were developed for 'excess energy' testing, where the incident energy in the striker is much greater than that required to puncture the specimen. In such cases the velocity change of the striker during the test is very small.

The same equipment can be used for low energy (or low blow) impact testing, seeking to provide just enough energy to initiate damage in the specimen. However errors can occur in the computed velocity and displacement values based only on the force measurement and the Newtonian mechanics analysis of the dart. In low blow testing the striker comes to rest ($v = 0$) and then rebounds, when v becomes negative. In some cases it may be found that the computed velocity values disagree with that which is observed visually, in that the computed value does not reach zero. The source of such errors comes from inadequacies in the basic assumption of a totally freely falling body (equation 1) and/or inaccurate measurement of the force, F , and the incident velocity used in equation 2 and subsequently. Equation 2 shows that for the striker to come to rest ($v = 0$)

$$v_0 + gt = \frac{1}{m} \int_0^t F dt \quad (5)$$

In a very sensitive test, small errors in measuring F can result in this equality not being achieved in the calculation. Precise measurement of the incident velocity, v_0 , used in the calculations can also be difficult when the striker is dropped from a very low height. Furthermore equation 1 does not include any terms for possible friction in the guides which, although usually negligible, may become significant in low blow testing.

Use of the simple Newtonian mechanics analysis for a freely falling body can therefore lead to errors in the calculated values of displacement and energy in sensitive, low energy testing. Consequently recent developments have been to measure not only the force acting on the striker, but also measure simultaneously the displacement of the striker directly during the impact test.

INTERPRETATION OF IFWIM TEST RESULTS

Force-deflection curves obtained from IFWIM tests take many different forms, depending on the type of polymer, the test temperature, the type of any reinforcement included and the processing conditions. Any curve contains details of a complete impact event on the specimen, including the type of deformation (brittle or ductile), fracture initiation and propagation. Fig.2a shows a typical force-deflection curve for a tough polymer, which exhibits yielding with cup formation (zero slope at maximum force), followed by diametrical splitting of the cup (sudden drop in force) and stable tearing. The International Standard (ISO 6603)³ recommends the routine characterisation of the test results as

- (a) deflection at maximum force s_M
- (b) energy to maximum force W_M
- (c) maximum force F_M
- (d) puncture deflection s_P
- (e) puncture energy W_P

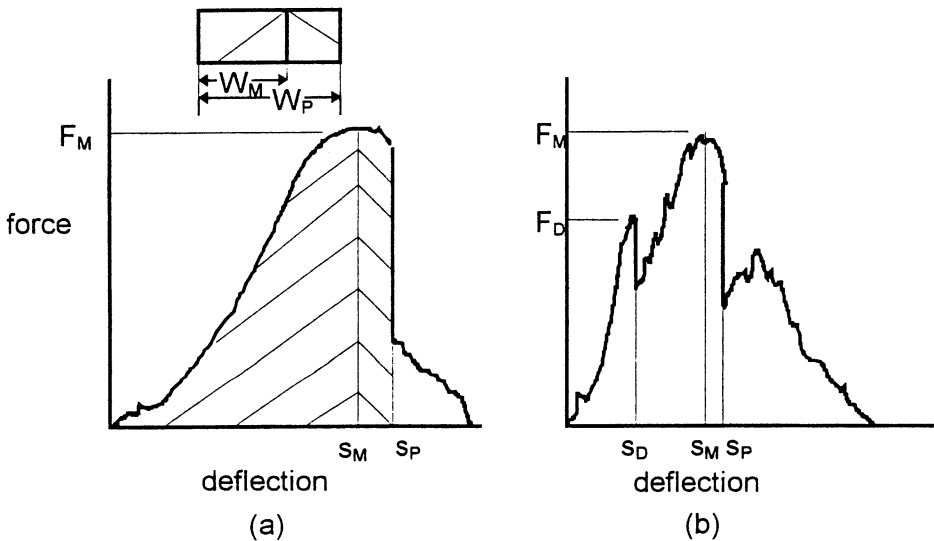


Figure 2: Force deflection curves, a) Typical curve for a tough polymer, b) Curve for a fibre reinforced material.

Force-deflection curves can show many more features than the 'idealised' behaviour shown in Fig.2a. Fig.2b shows a curve from a test on a fibre reinforced material. A 'first damage' peak (at F_D , s_D) occurs before the maximum force is reached. Such peaks are often associated with localised splitting, resulting in the load drop and change in specimen compliance. The local damage then stops growing, requiring increased force

and energy for the damage to progress further at F_M . Fig. 2b also shows that considerable energy is required to progress the damage beyond s_P to produce total penetration of the specimen by the striker.

Force-deflection curves thus can contain much information about the initiation and propagation of damage during the test. The interpretation of the data obtained can be complex, but very informative on the effects of material or processing variations. Some force-deflection curves can contain many minor peaks besides the maximum force peak. The full interpretation of the physical events associated with each peak normally requires the use of auxiliary equipment in addition to the basic IFWIM system, such as short pulse photography, acoustic emission or high speed photography.

The IFWIM system can be used in two very different modes:

- 1) as a routine impact test according to the appropriate Standard test method, such as comparing values of energy, force and deflection at the peak force point.
- 2) as a research tool, with much greater attention given to the detailed interpretation and characterisation of the various features on the force-time curves and their relation to the damage mechanisms operating under impact of the specimen.

REFERENCES

1. Reed, P.E. (1979) *Impact performance of Polymers*, in *Developments in Polymer Fracture* (ed. E. H. Andrews) Applied Science, London, pp. 121 - 153
2. Kessler, S.L. Adams, G.C. Driscoll, S.B. and Ireland, D.R. (eds) (1987) *Instrumented Impact Testing of Plastics and Composite Materials*. ASTM STP936 . American Society for Testing and Materials. Philadelphia.
3. ISO 6603. *Plastics - Determination of multi axial impact behaviour of rigid plastics*. Part 2: Instrumented puncture test.

18: Fast fracture in polymers

P S Leever

INTRODUCTION

Many polymers used in load-bearing applications show a range of fracture behaviour from 'brittle' to 'ductile' (see **Ductile-Brittle Transition**). All thermoplastics can show both kinds of behaviour, and unexpected tough-to-brittle transitions led to many service failures in the first few decades of their use. It is useful to distinguish three main regimes of brittle behaviour under relatively low stresses. **Fatigue** crack propagation is seen as a result of cyclic loading, slow crack growth is usually seen after long times under load at higher temperatures, and *rapid crack propagation* is usually seen as a result of rapid loading at lower temperatures.

FAST FRACTURE IN IMPACT

Some plastics which show extremely high toughness under slowly applied loads will fail in a brittle manner, under the same environmental conditions, if subjected to impact. This is particularly significant for unreinforced crystalline thermoplastics such as polyethylene which can otherwise be drawn slowly to 600% strain or more, even if slightly notched. In such materials impact is often the simplest way, and sometimes the only way, to precipitate brittle fracture from a notch, in order to test fracture resistance. Charpy and Izod pendulum impact test methods (see **Impact and Rapid Crack Propagation: Measurement techniques**) have therefore gained wide currency as 'material tests' for plastics. Unfortunately, the results cannot be used in any meaningful way for design; they confuse at least two distinct phenomena, and to isolate geometry-independent material data from them is very difficult.

A Charpy test is little more than a fracture test done quickly, using a notched three point bend specimen (see **Torsion and Bend Tests**). The absorbed energy is measured, rather than the failure load, merely because - until instrumented high-rate test machines became available - there was no alternative (see **Falling Weight Impact Tests**). With better instrumentation, the effect of impact speed on (say) a tough polyethylene at 23°C, can be clarified by testing successive specimens at increasing displacement rates.

At low rates, the notch blunts and the specimen yields or tears, absorbing considerable energy, by the propagation of a narrow voided zone (a craze, see **Crazing**) from notch tip to free surface. At higher displacement rates, a new phenomenon emerges: the crack begins to jump at high speed, leaving a glassy surface and almost instantaneously unloading, or partially unloading, the specimen. This *rapid crack propagation* event absorbs so little energy that no further external work is needed to drive it. In other

materials, stick-slip crack propagation - repeated cycles of arrest and re-initiation - may occur, but these intermediate crack arrests usually disappear as the test rate increases.

The two phenomena to distinguish here are crack initiation and crack propagation¹. A crack initiation resistance G_C or toughness K_C determines the peak load, and therefore (along with the specimen stiffness) determines the energy absorbed up to peak load. For thermoplastics, G_C usually falls with impact speed, whilst glasses such as PMMA show simpler constant G_C behaviour (although the notch sharpness may be important).

Once initiated, a crack often jumps rapidly, suggesting that resistance to propagation is lower. In a material with a higher resistance to rapid crack propagation, however, the crack will need to be driven externally. A classical impact test measures total absorbed energy and, expressing it as an impact strength fails to separate these energy sinks, whilst an impact fracture test isolates the initiation resistance but discards the evidence concerning propagation.

RAPID CRACK PROPAGATION

Rapid crack propagation is studied in its own right partly in order to understand impact fracture tests. However, a more immediate concern is to avoid catastrophic failure of the largest load-bearing engineering structures constructed from plastics: pressurised fuel gas and water-distribution pipelines².

Fracture tests on plastic pipe are carried out at both laboratory scale and full scale. In either case, pressurisation (usually with nitrogen or air) is followed by the initiation of a fast crack under impact of a sharp dart. The crack jumps straight along the pipe, separating the plane of maximum stress. At low pressures, this crack arrests after extending by one pipe-diameter or so under wedge-opening from the dart. At higher pressures, however, the crack may continue to extend indefinitely, driven by the strain energy in the pipe walls and the wedge-opening action of the expanding fluid. A crack which has propagated so far from its initiation point is no longer an 'impact' crack. The important question is whether or not its steady propagation can be stopped. Rapid fracture surfaces are usually quite smooth, like faintly misted glass. It is common (though not, as yet, fully explained) to see quite regular sinusoidal weaving of the path. Measured crack speeds seldom fall below 100 m/s and may exceed 400 m/s. Any deviation of the crack speed below about 100 m/s is usually followed promptly by a transition through ductile tearing to crack arrest. The pressure needed to sustain a low speed is much higher than that needed to sustain a high speed.

MECHANISMS OF RAPID CRACK PROPAGATION

The collapse in fracture resistance with increasing crack speed was, until recently, attributed to a more rapid increase in yield stress than in fracture toughness with strain rate. For crystalline polymers, in which the drop in fracture resistance is particularly

pronounced, it has more recently been explained by a mechanism of thermal decohesion³. The propagating crack is assumed to carry, at its tip, a craze like that seen at a static or slowly-extending one. At high speeds, the surfaces of this craze are the site of an intense drawing process which leads to a high adiabatic temperature rise. The craze fibril at the crack mouth fails when its roots are engulfed by a melt layer. This theory provides quantitative predictions for crack resistance, which are well borne out by experimental results. At low speeds resistance to this fracture mode is very high. As crack speed increases, it falls to a plateau. At very high speeds, a further rapid increase is predicted. This pattern of behaviour also seems to be followed qualitatively (though not quantitatively) by amorphous polymers. The same mechanism explains why, at least for crystalline polymers, G_C falls with increasing impact speed - and suggests that G_C falls to a minimum which is identical to the minimum resistance to rapid crack propagation.

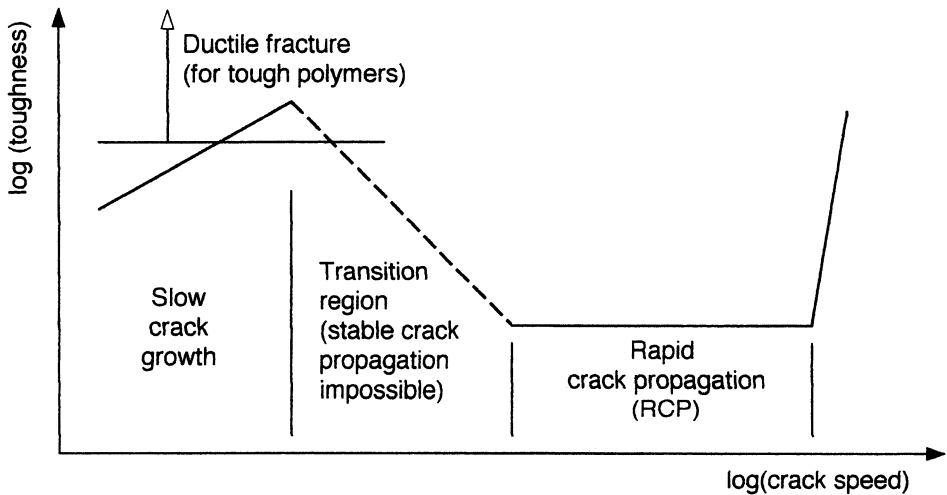


Figure 1: Dependence of toughness on crack speed in a thermoplastic (schematic), showing a cusp separating slow crack growth from rapid crack propagation regimes.

DEPENDENCE OF TOUGHNESS ON CRACK SPEED

Fig. 1 extends this picture to a general schematic view of both high and low speed crack propagation behaviour in polymers. Low and high speed regimes are clearly separated by the cusp which represents a basic change in fracture mode. Under a low, constant

crack extension force, most polymers suffer slow crack growth. Increasing the crack extension force in a brittle polymer like PMMA (which will happen as the crack extends under constant load) will accelerate the crack until, at a speed of 1 m/s or so, the cusp is reached and there is a sudden jump to a much higher speed. This is due to an isothermal/adiabatic transition, at which the resistance to fracture by thermal decohesion falls below that to slow crack growth, and continues with crack speed to fall further. Propagation on a falling force/rate characteristic is usually dynamically unstable: an increase in speed causes self sustained acceleration whereas a deceleration precipitates arrest. The dotted region on the characteristic cannot therefore, easily be measured directly. Rapid crack propagation, however, will generally settle into the floor of the plateau region at higher speeds (greater than about 100 m/s). The sharp climb at very high crack speeds is predictable for long-chain polymers as a result of the limiting time scale, and appears in much of the limited data for glassy polymers.

In a tough polymer such as PE, increasing the extension force during slow crack growth activates near-tip processes which blunt, shield and arrest it. The only way to jump the cusp in tough polymers is by artificial re-initiation of a sharp crack; this can occur, for example, during re-loading after temporary arrest during impact.

REFERENCES

1. Clutton, E.Q. and Channell, A.D. (1995) Energy Partitioning in Impact Fracture Toughness Measurements, in *Impact and Dynamic Fracture of Polymers and Composites,ESIS 19* (Eds. Williams, J.G. and Pavan, A.), Mechanical Engineering Publications, London, 137-146
2. Greig, J.M., Leever, P.S. & Yayla, P. (1992) Rapid Crack Propagation in Pressurised Plastic Pipe. I: Full Scale and Small Scale RCP Testing. *Engineering Fracture Mechanics* **42**, 663-673.
3. Leever, P.S. (1995) Impact and dynamic fracture of tough polymers by thermal decohesion in a Dugdale zone. *International Journal of Fracture* **73**, 109-127.

19: Fatigue

E J MOSKALA

INTRODUCTION

Fatigue failure in polymers has received considerable attention in recent years as polymers have become more prevalent in load bearing applications¹⁻³. Fatigue is defined as the loss of strength or other measure of performance as a result of the application of a prolonged stress. The stress can be monotonic, as in static **creep** rupture, or, more commonly, oscillatory in nature. The latter condition is referred to as dynamic fatigue and will be the topic of discussion. Dynamic fatigue can pose as an insidious problem for the design engineer. While one load excursion may not cause failure, repeated stressing to the same load level, perhaps well below the yield strength of the polymer (see **Yield and Plastic Deformation**), may result in the accumulation of damage that may render it incapable of performing its intended function.

Evaluating the fatigue resistance of a polymer is complicated by the numerous variables introduced by the oscillatory nature of the applied stress. Testing is often performed either under stress-controlled conditions of periodic loading between fixed stress limits or under strain-controlled conditions of periodic loading between fixed strain limits. The response of a polymer to dynamic fatigue under stress-controlled conditions will depend on the waveform, the frequency of the applied stress, and the stress variables shown in Figure 1 and defined by

$\sigma_{\max}$ = maximum stress

$\sigma_{\min}$ = minimum stress

σ_m = mean stress = $(\sigma_{\min} + \sigma_{\max})/2$

σ_a = average stress = $(\sigma_{\max} - \sigma_{\min})/2$

$\Delta\sigma$ = stress range = $\sigma_{\max} - \sigma_{\min}$

R = stress ratio = $\sigma_{\min}/\sigma_{\max}$

When evaluating the fatigue resistance of a polymer for a potential application testing should be performed under conditions that most closely simulate end-use conditions.

THE S-N CURVE

The fatigue resistance of a polymer is often represented by a plot of stress (S) versus number of cycles to failure (N), also known as the S-N curve or Whöler diagram. Typically a material will fail at progressively longer times as the magnitude of applied stress is decreased. Many polymers exhibit a limiting stress, called the fatigue endurance limit (σ_{FEL}) below which failure will not occur over any reasonable number of cycles, usually of the order of 10^7 to 10^8 cycles. An illustrative S-N curve is shown in Figure 2. The S-N curve has obvious utility for the design engineer but gives no insight into the mechanisms by which failure occurs. Guidelines for constructing an S-N curve are found in ASTM D671-93 Standard Test Method for Flexural Fatigue of Plastics by Constant-Amplitude-of-Force⁴. In this test method, a specimen with a constant bending stress across the gauge section is subjected to a constant flexural stress by a fixed-cantilever type testing machine operating at a cyclic frequency of 30 Hz and a stress ratio of -1. The Standard is careful to state that the resulting S-N curve can be used in design applications only when all design factors such as cyclic frequency, waveform, stress variables, ambient temperature, and environmental conditions, are analogous to the test conditions. The Standard is also careful to recognize two possible failure modes. In one case, failure may occur by the initiation and propagation of a crack across the gauge of the specimen resulting in catastrophic failure. In the other case, thermal failure may occur from hysteretic heating within the polymer. Thermal failure may be a particularly acute problem when testing is performed at high frequencies or stress amplitudes.

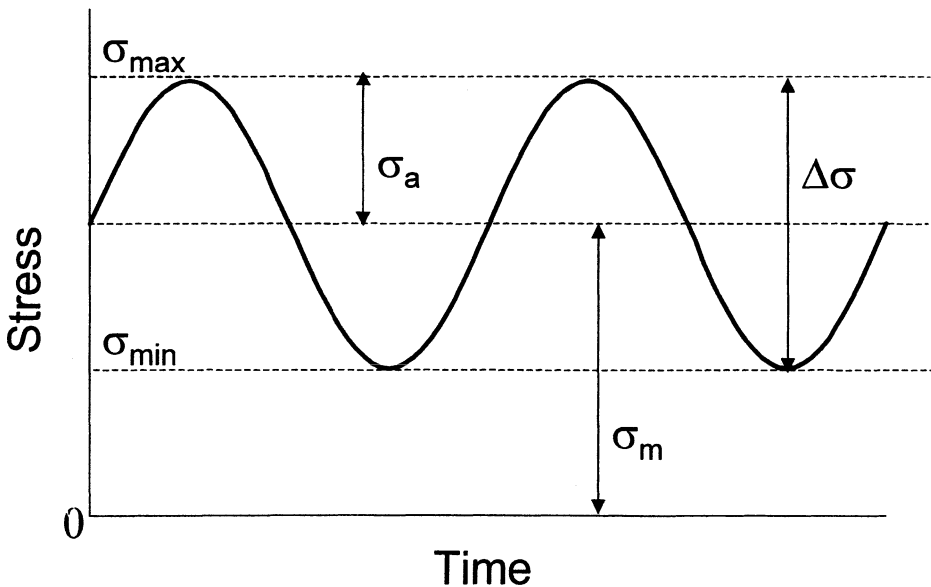


Figure 1: Stress variables associated with stress-controlled dynamic fatigue.

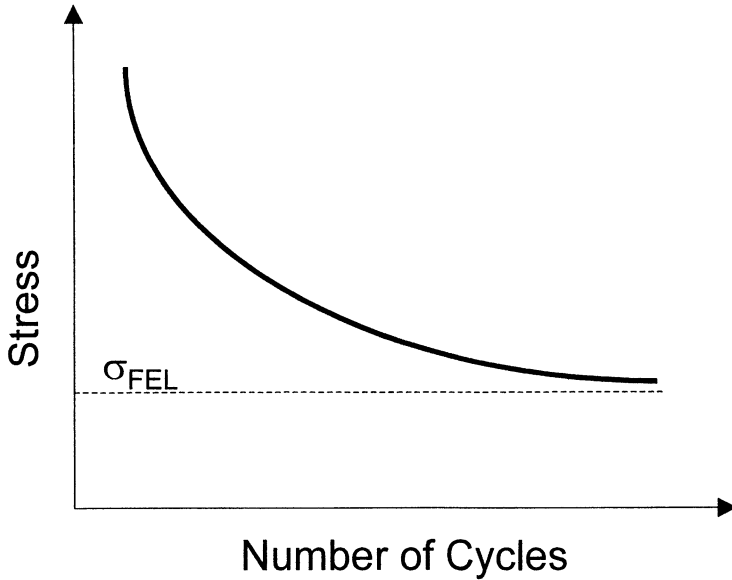


Figure 2: Typical S-N curve for a polymer with fatigue endurance limit

It is important to emphasize that an S-N curve represents the number of cycles required to initiate a crack plus the number of cycles required to propagate the crack to failure. Crack initiation is normally a random process and can consequently lead to significant scatter in the S-N curve. However, an actual plastic part in service may very well contain adventitious defects such as voids, weld lines, and foreign particles that may act as flaws capable of readily initiating crack growth. Under these conditions, the S-N approach may seriously overestimate fatigue lifetime. A conservative approach to design would be to assume that some type of defect is present and that the fatigue lifetime is consumed entirely by the process of fatigue crack propagation (FCP).

FATIGUE CRACK PROPAGATION

FCP testing usually involves measuring the change in crack length of a precracked specimen as a function of the total number of loading cycles. Several techniques have been used to measure crack length including compliance measurements, a traveling microscope, and electropotential measurements¹. Commonly used specimen geometries include compact tension and single edge notch specimens. A plot of typical crack length data is shown in Figure 3. The fatigue crack growth rate per cycle (da/dN) is determined from the slope of a line tangent to the curve and for most specimen geometries will increase with increasing length.

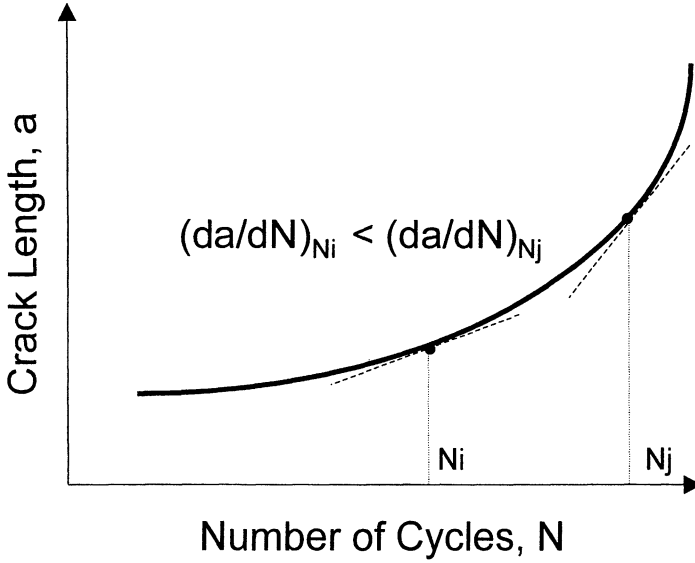


Figure 3: Crack length data showing that crack growth rate increases with increasing crack length

It has been found that for a wide range of materials da/dN is related to the cyclic stress according to the Paris equation⁵

$$da/dN = A\Delta K^m \quad (1)$$

where ΔK is the stress intensity factor range and A and m are functions of the test environment, frequency, and material properties. The stress intensity factor (K) expresses the stress field associated with a sharp crack in an elastic continuum and is a function of the remote stress, crack length, and specimen geometry. The Paris equation suggests that FCP rate is a logarithmically linear function of ΔK . However, the typical response of a polymer contains three distinct regions as illustrated in Figure 4. Region I begins at the threshold value of the stress intensity factor (ΔK_{th}) below which crack propagation does not occur. Hence ΔK_{th} is somewhat analogous to σ_{FEL} from the S-N test. The slope of the FCP curve in region I is initially very steep but decreases rapidly as the crack grows. In region II the slope of the FCP curve is constant and obeys the Paris equation. In region III the slope of the FCP curve increases rapidly and reaches an asymptote at the critical stress intensity factor (K_C) where crack propagation becomes unstable. The relative fatigue resistance of materials to FCP can be determined by examining the FCP rate at a particular value of ΔK ; the higher the value of da/dN the lower the fatigue resistance. Obviously if the FCP curves for two materials intersect, the relative ranking of fatigue resistance will depend on the choice of the value of ΔK . It has been observed that crystalline polymers tend to be more resistant to FCP than amorphous polymers. Crosslinking often leads to lower resistance to FCP. Increasing

polymer molecular weight generally improves resistance to FCP (see **Molecular Weight Distribution and Mechanical Properties**). For a complete discussion of the effects of materials and experimental variables on FCP behavior, the reader is referred to the notable work of Hertzberg and Manson¹.

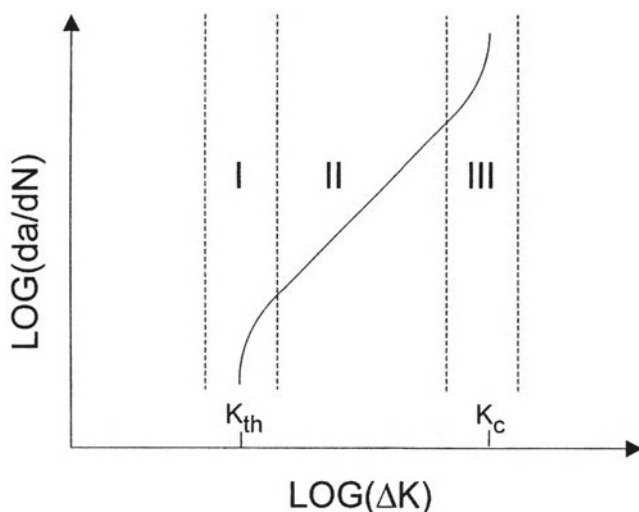


Figure 4: FCP curves showing three distinctive regions of response.

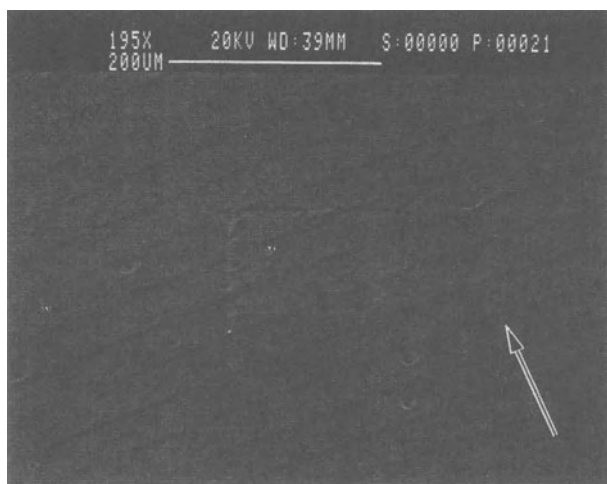


Figure 5: Scanning electron micrograph of fatigue striations in plasticised cellulose ester showing electron beam damage in the centre of the micrograph. The arrow indicates the direction of crack growth.

Microscopic examination of the fracture surface of a polymer that has been subject to repeated loading often reveals a series of concentric curved bands that radiate from the

fracture origin (the starter crack in an FCP test). Bands that are created by the advancing crack front during an individual load excursion are called striations. A scanning electron micrograph (see **Applications of Electron Microscopy to the study of Polymer Deformation**) of fatigue striations in a plasticized cellulose ester is shown in Figure 5. The center of the micrograph shows damage to the fracture surface caused by the electron beam, a problem often encountered in scanning electron microscopy of polymeric materials. It is also possible to observe bands that arise from crack growth that is associated with multiple load excursions. These so-called discontinuous growth bands may be distinguished from striations by comparing the macroscopically observed crack growth rate with the band width.

REFERENCES

1. Hertzberg, R.W. and Manson, J.A. (1980) *Fatigue of Engineering Plastics*, Academic Press, London.
2. Kinloch, A.J. and Young, R.J. (1983) *Fracture Behavior of Polymers*, Elsevier, London.
3. Döll, W. and Könczöl, L. (1990) *Advances in Polymer Science*, 91/92, 137-214.
4. ASTM D671 in Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, published annually.
5. Paris, P.C. and Erdogan, F. (1963) A critical analysis of crack propagation laws. *Journal of Basic Engineering*, **85** (4), 528-34.

20: The Finite Element Method

M. Ashton

INTRODUCTION

The Finite Element Method (FEM) has been used for over 40 years by scientists and engineers to determine the stresses and strains in structures too complex to analyse by purely analytical methods. The structure is subdivided into a mesh of small elements interconnected at their edges at node points. Each element is simple enough to be analysed in turn, and if equilibrium conditions are considered between each element and its neighbours at the node points, then the stress distribution in the whole structure can be determined. A simple meshed structure is shown in Figure 1.

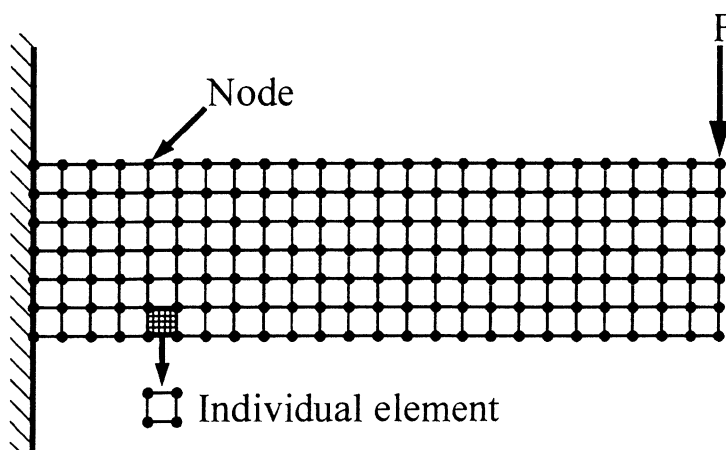


Fig. 1: A simple meshed structure.

The numerical analysis of a single element is straightforward, however the analysis of a structure with hundreds or thousands of elements would be impractical without the aid of a computer. The more elements in a FEM simulation the greater the accuracy due to the improved resolution of the stress distribution across the structure. It should be emphasised that the FEM produces a numerical solution that approximates to the true solution. The FEM can therefore only be as accurate as the latest constitutive models of real material behaviour. Constitutive models are only valid over the range of parameters (stress, strain, strain rate and temperature) that were used to create the model. If a FEM simulation is run outside the range of parameters used to create the constitutive model then its results will be inaccurate.

A SIMPLE EXAMPLE

Consider a one dimensional finite element - the spring, as shown in Figure 2a. This problem is purely one dimensional.

The forces applied to the spring, F_i , are related to the resultant displacements, u_i , by:

$$F_A = k_A(u_A - u_B) = k_A u_A - k_A u_B \quad (1)$$

$$F_B = k_A(u_B - u_A) = -k_A u_A + k_A u_B \quad (2)$$

where k_A is the spring stiffness.

Expressing equations (1) and (2) in matrix form gives:

$$\begin{Bmatrix} F_A \\ F_B \end{Bmatrix} = \begin{bmatrix} k_A & -k_A \\ -k_A & k_A \end{bmatrix} \begin{Bmatrix} u_A \\ u_B \end{Bmatrix} \quad (3)$$

or

$$\{F\} = [k]\{u\} \quad (4)$$

where $[k]$ is the “stiffness matrix” for the single element.

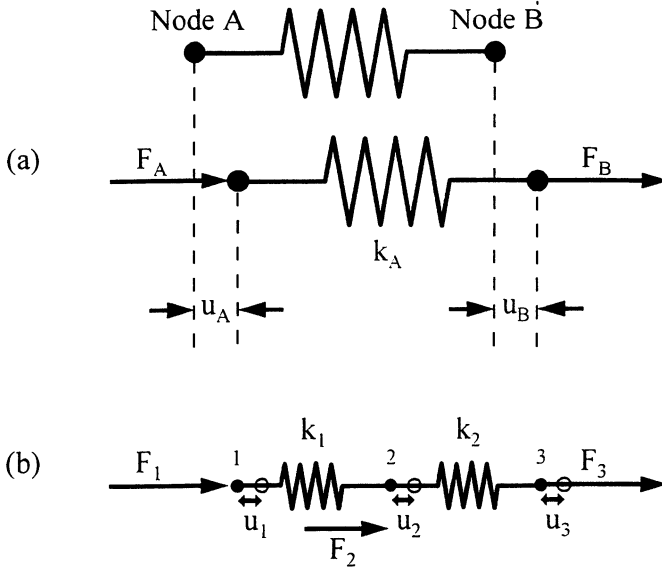


Fig. 2: (a) A spring element, (b) A two element 'structure'.

Analysis of the two spring element “structure” in Figure 2b gives:

$$F_1 = k_1(u_1 - u_2) = k_1u_1 - k_1u_2 \quad (5)$$

$$\begin{aligned} F_2 &= k_1(u_2 - u_1) + k_2(u_2 - u_3) \\ &= -k_1u_1 + (k_1 + k_2)u_2 - k_2u_3 \end{aligned} \quad (6)$$

$$F_3 = k_2(u_3 - u_2) = -k_2u_2 + k_2u_3 \quad (7)$$

Expressing equations (5), (6) and (7) in matrix form gives:

$$\begin{Bmatrix} F_1 \\ F_2 \\ F_3 \end{Bmatrix} = \begin{bmatrix} k_1 & -k_1 & 0 \\ -k_1 & k_1 + k_2 & -k_2 \\ 0 & -k_2 & k_2 \end{bmatrix} \begin{Bmatrix} u_1 \\ u_2 \\ u_3 \end{Bmatrix} \quad (8)$$

or

$$\{F\} = [K]\{u\} \quad (9)$$

where $[K]$ is the “global stiffness matrix” for the structure.

The force matrix $\{F\}$ is known as it consists of the initial loading constraints. $[K]$ is known for a given element (in this case the spring). Therefore equation (9) can be solved to give the displacements at nodes 1, 2 and 3 in Figure 2b. Once the displacement matrix is known, the strains, ϵ_i , at the element nodes can be calculated using:

$$\begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \end{Bmatrix} = \begin{bmatrix} \frac{1}{L} & 0 & 0 \\ 0 & \frac{1}{L} & 0 \\ 0 & 0 & \frac{1}{L} \end{bmatrix} \begin{Bmatrix} u_1 \\ u_2 \\ u_3 \end{Bmatrix} \quad (10)$$

$$\{\epsilon\} = [B]\{u\} \quad (11)$$

where L is the initial length of the spring. $[B]$ is a matrix dependent on the shape and size of the element. Finally the stress distribution, σ_i , across the structure can be calculated using:

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{Bmatrix} = \begin{bmatrix} E & 0 & 0 \\ 0 & E & 0 \\ 0 & 0 & E \end{bmatrix} \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \end{Bmatrix} \quad (12)$$

or

$$\{\sigma\} = [D]\{\varepsilon\} \quad (13)$$

where $[D]$ is a matrix expressing the stiffness properties of the element. E is the spring element's modulus of elasticity given by:

$$E = \frac{k_i L_i}{A_i} \quad (14)$$

where A_i is the cross-sectional area.

Combining equations (11) and (13) gives a fundamental FEM relationship describing stress in the element to nodal displacements:

$$\{\sigma\} = [D][B]\{u\} \quad (15)$$

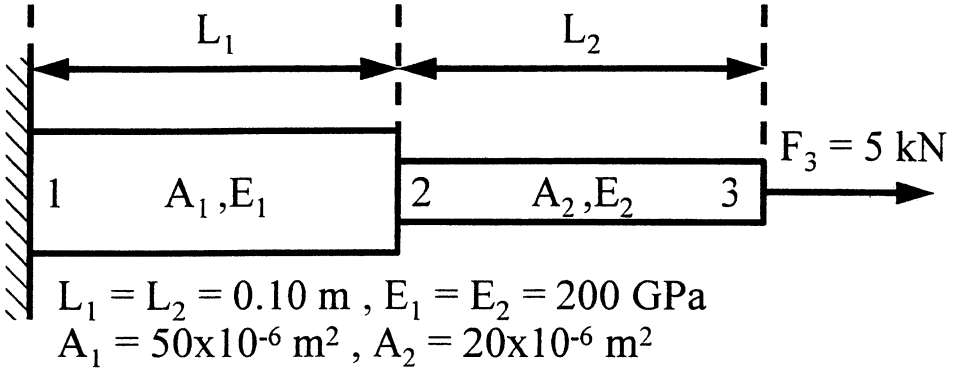


Fig. 3: A simple structure.

If we apply the above equations to the structure in Figure 3, and knowing the boundary conditions $u_1 = 0$ and $F_2 = 0$, and the loading condition $F_3 = 5 \text{ kN}$ then:

$$k_1 = \frac{E_1 A_1}{L_1} = \frac{(200 \times 10^9)(50 \times 10^{-6})}{0.1} = 100 \text{ MN m}^{-1} \quad (16)$$

similarly: $k_2 = 40 \text{ MN m}^{-1}$

Equation (5) becomes: $F_1 = -(100 \times 10^6)u_2$

Equation (6) becomes: $0 = (140 \times 10^6)u_2 - (40 \times 10^6)u_3$

Equation (7) becomes: $5000 = (40 \times 10^6)(u_3 - u_2)$

Solving the above set of simultaneous equations gives $u_2 = 0.05 \text{ mm}$, $u_3 = 0.175 \text{ mm}$

and $F_1 = 5 \text{ kN}$ (as expected). The stresses and strains in the structure can be determined by solving equations (10) and (12).

A GENERAL FEM.

The above example illustrates many of the fundamental steps that are taken in solving a finite element problem. A general FEM implemented using a computer package may be composed of the following steps:

Preprocessing

The preprocessing stage is basically the preparation of data into a format that clearly defines the problem. Before this data can be “preprocessed” by a computer, the user has to consider if the simulation will be static or dynamic, linear or nonlinear. Also can the simulation be simplified by considering symmetry or making reasonable assumptions. Once these points have been considered then the relevant information can be fed into a computer preprocessor package. This package usually takes the form of a graphical interface simplifying and automating data entry. This data includes a description of the mesh in terms of choice of element type(s), element and node numbering, nodal coordinates, different materials and corresponding constitutive equations, and loading and boundary conditions.

Analysis

The mathematics involved in the analysis stage can become quite involved and the reader is referred to the references given. Fortunately, the user who knows the fundamental principles of the FEM, together with a good physical understanding for the problem under analysis, will probably achieve reliable results. It should be understood that the FEM produces a numerical solution that approximates to the true solution; therefore the FEM can only be as accurate as the latest mathematical models of real behaviour. The analysis stage can be summarised as:

- a) generating a stiffness matrix for an element and then generating a global stiffness matrix for the whole structure,
- b) applying boundary conditions, and
- c) solving a system of equations for nodal displacements.

Postprocessing

Stresses and strains are calculated and the results viewed by the user via a graphical

interface. Results can be presented in various formats including line and contour plots and deformed mesh plots. The most important part of postprocessing is the estimation of error in the results compared to the true values. An experienced user might be able to cast an opinion as to whether the results seem reasonable or not, but cannot establish their accuracy without actual prototype testing.

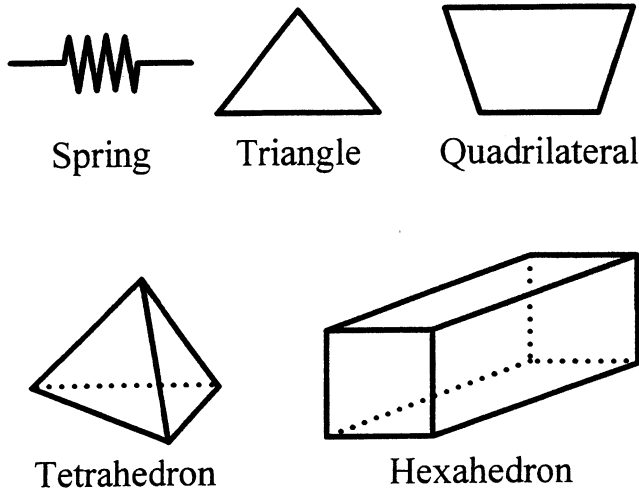


Fig. 4: Some common elements.

FURTHER APPLICATIONS

If real world two and three dimensional nonlinear applications are to be simulated using the FEM, then the FEM has to be very flexible. The theory presented for the one dimensional example can be extended to two and three dimensions. The “building blocks” for any simulation are the finite elements, a selection of which are shown in Figure 4. The main parameters in the selection of a particular element are the stress / strain state, symmetry in the structure, computing power available and number of dimensions.

Most FEM simulations are nonlinear because the material is viscoelastic/viscoplastic or loaded beyond a linear elastic limit. Therefore a yield criterion defining when the material is no longer elastic might have to be incorporated into the FEM. A constitutive equation describing the viscoelastic/viscoplastic material response as a function of strain, strain-rate and temperature must be defined. Also the stiffness matrix for each element will have to be modified for each small increment of plastic strain. A “flow rule” enables the next increment of plastic strain to be calculated for a given stress state when the loads are increased incrementally. Finally, the growth of the yield surface through the structure can be described using a “hardening rule”.

The FEM has been modified from its foundations in solid mechanics and has been applied to many other branches of science including acoustics, electromagnetism, fluid mechanics, heat transfer, and thermal analysis.

A FINAL WORD

Unfortunately, the flexibility of the FEM has led to a bewildering number of highly mathematical books which usually dismay many potential FEM users. Also the growth in computer processing power, hand-in-hand with the vast array of PC based finite element packages, means that most scientists and engineers will one day meet the FEM. Fortunately, there are many excellent introductory books on the FEM (some of which are listed below), and with user friendly FEM packages emerging, the FEM will rapidly become another everyday tool in polymer engineering.

REFERENCES

1. Chandrupatla, T.R. and Belegundu, A.D., (1997) *Introduction to Finite Elements in Engineering*, 2nd Edition, Prentice Hall.
2. Lewis, P.E. and Ward, J.P., (1991), *The Finite Element Method - Principles and Applications*, Addison-Wesley.
3. Logan, D.L., (1993) *A First Course in the Finite Element Method*, 2nd Edition, PWS Publishing Company.

21: Flow Properties of Molten Polymers

P C Dawson

INTRODUCTION

Flow properties of molten polymers are important since processing of thermoplastics involves flow of the polymer melt. Rheology is the study of the flow and deformation of materials, and is concerned with the relationships between stress, strain and time. An extrusion process is any manufacturing operation in which a fluid is forced through an orifice to give an extrudate of constant cross-section. In the processing of plastics, the material is usually molten and pumped through the orifice or die using a screw pump. The process is used for mixing operations as well as making finished objects using techniques such as injection moulding and film production. Molten plastic is shaped under an applied stress, and shear viscosity data is required to model processing behaviour and determine suitable processing conditions.

A temperature range exists in which processing is possible, and this range depends on the molecular structure of the polymer. It is bounded by a lower crystalline melting point and an upper temperature which is associated with the onset of thermal degradation. These properties can be measured by techniques such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The rate of heat exchange during processing is also important and this is determined by thermal diffusion:

$$\text{Thermal diffusivity} = \text{Thermal conductivity}/(\text{density} \times \text{specific heat}).$$

In practical processing the concept of a Fourier number is used where the Fourier number is defined as

$$\text{Fourier number} = (\text{thermal diffusivity} \times \text{time})/(\text{section thickness})^2$$

Polymer melts are **viscoelastic** in their response to an applied stress. This means that under certain conditions they will behave like a liquid and will continue to deform while the stress is applied. Under other conditions the material behaves like an elastic solid and there will be some recovery of the deformation when the applied stress is removed. Alternatively, if strain is held constant at the end of an experiment, stress will not immediately return to zero but will relax with time. Hence both viscous and elastic responses to applied stress must be measured in order to characterise the flow behaviour of polymer melts.

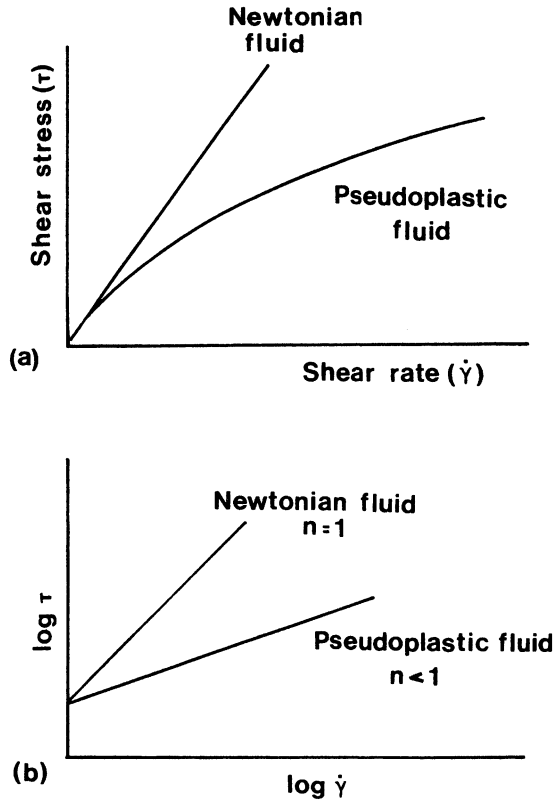


Figure 1: a) Shear stress-strain relationships of Newtonian and pseudoplastic fluids b) Log τ -log $\dot{\gamma}$ plots for Newtonian fluid and pseudoplastic fluid obeying the power law.

VISCOSITY

At a given temperature some materials flow more easily than others. Plots of pressure against flow rate for material flowing in a tube will produce a graph which may be either a straight line or a curve. The slope of the plot gives a measure of the viscosity of a liquid where the viscosity η is defined by the relationship

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (1)$$

with τ the shear stress and $\dot{\gamma}$ the shear strain rate, the SI units of viscosity are Nsm^{-2} . Newtonian fluids show a linear relationship between shear stress and shear rate, while

polymer melts are said to be pseudoplastic and do not show such a simple relationship, see figure 1a. Although there is no simple equation to represent the viscosity of polymer melts, the power law equation gives an approximate empirical model:

$$\tau = k(\dot{\gamma})^n \quad (2)$$

where k and n are material parameters.

Figure 1b shows a plot of $\log \tau$ versus $\log \dot{\gamma}$ for Newtonian and pseudoplastic fluids, although in practice a flow curve is only linear over a limited range of shear rates for polymer melts. Figure 2 shows typical polymer flow curves (in this case for low density polyethylene).

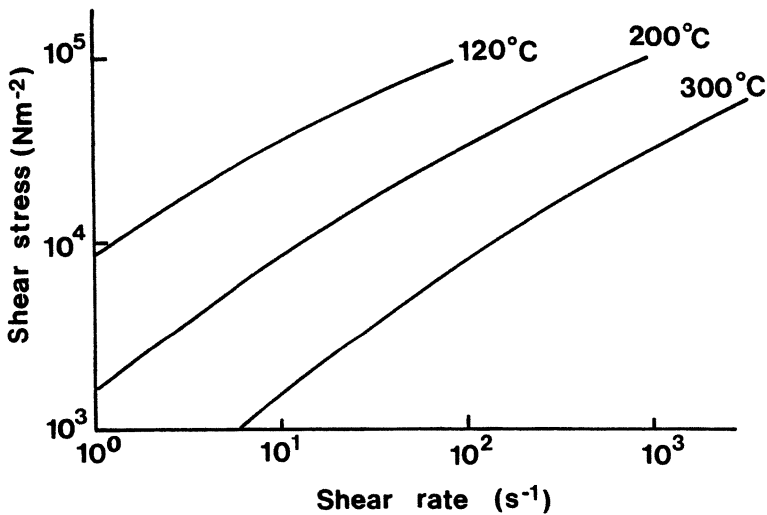


Figure 2. Typical flow curves for LDPE at various temperatures (after Birley et. al. ⁴)

MELT ELASTICITY

Polymers are made up of long chain molecules which become entangled during flow in the melt instead of sliding past each other as in simple liquids. When shearing stresses are released the molecules tend to return to their original randomly coiled position and there will be some elastic recovery. Recovery will not be complete because some chain slippage occurs during flow. There are several manifestations of elasticity superimposed on the viscous flow. Polymer molecules are sheared on passing through the die of an

extruder. When the melt emerges from the die the extrudate cross section is greater than the die cross section. This is because the molecules, in the absence of continuing shear forces, tend to coil up, shrinking in the direction of flow but expanding at right angles to the flow, resulting in *die swell*.

Above a critical point in the flow curve (i.e. above a critical shear stress and shear rate) *melt fracture* occurs. The extrudate appears irregular and distorted, showing some form of helical distortion. This occurs mostly with products having a small cross section and is avoided by keeping below the critical point. This may be achieved by lowering the temperature, lowering the molecular weight of the polymer or altering the die. Another form of surface defect, known as *sharkskin*, shows distortions in the form of ridges perpendicular to the flow. This occurs above a critical linear extrusion rate rather than shear rate, but can be avoided by use of a broad molecular weight polymer. Changing the temperature may also help.

Many textbooks have been written on the subject including books by Brydson^{1,2} which deal with the basic principles of rheology of plastic melts and give practical information for plastic processors. Cogswell³ investigates the ways in which melt flow behaviour can be exploited for better efficiency, control of properties and selection of materials. Birley⁴ gives a more general approach to the physics of plastics and the measurement of properties, and discusses the properties which determine the processing characteristics and performance. For detailed analysis of polymer processing, reference can be made to McKelvey⁵.

METHODS FOR MEASURING SHEAR FLOW PROPERTIES

There are many methods available for the measurement of shear flow properties of a polymer melt. The method chosen will depend on factors such as whether precise measurement, design data, comparison of a series of materials, or development of new materials is the objective. Cogswell³ has reviewed the different techniques available and Table 1 shows classes of rheometers in common use. Two methods are described below:

Melt Flow Indexer

This consists of a heated barrel with a die fitted at the bottom. The barrel is filled with polymer, a piston is inserted above the polymer and a weight (2.16kg for polyethylene) is placed on the piston. The rate of extrusion varies with time, and the weight of material extruded in a given time is recorded between specified limits of the piston position. The result is known as the *melt flow index* (MFI). This method was originally developed for polyolefins and is the basis of national and international standards such as ASTM D1238 and BS2782. The equipment is relatively crude but is suitable for quality control purposes and many raw material manufacturers quote the MFI of their polymers. The technique is not suitable for fundamental rheological studies as it is subject to sources of

error such as end effects and slip at the barrel wall, and is carried out at much lower shear rates than those usually found in processes such as extrusion and injection moulding. However, it is a useful test to check batch to batch consistency or the effect of processing by taking measurements at intervals. Manufacturers produce different MFI polymers and copolymers to match different processing requirements, e.g. low MFI polyethylene (MFI 0.5 at 90°C/2.16kg) is used for film grades while high MFI (MFI 20 at 90°C/2.16kg) is used for injection moulding grades

Brabender Viscometer

This machine is a torque recording rheometer which imitates internal mixers, such as the Banbury, on a small scale (30-50 gm chamber capacity) and provides information on resistance to flow, heat generation and time-scale to fusion (and sometimes degradation) under approximate processing conditions. It consists of a chamber with a pair of contra-rotating rotors fitted side by side. The chamber temperature and rotor speeds are variable and the torque required to turn the rotors can be measured. Production processes such as extrusion and calendering can therefore be simulated in the laboratory. The measuring principle is based on the resistance which the testing material puts up against the rotating blades, screws, rotors etc. in the measuring head. Fundamental flow curves are obtained which are said to compare well with those obtained from capillary measurements, although the maximum shear rates obtained are somewhat lower than those from capillary machines and assumptions are made in carrying out the flow analysis to account for this.

FACTORS AFFECTING VISCOUS FLOW

Flow occurs when polymer molecules slide past each other, and the ease of flow depends on chain mobility and entanglement forces holding the molecules together. Viscosity is influenced by temperature and pressure as well as material characteristics and shearing history of the polymer melt. For liquids which show Newtonian behaviour, viscosity and temperature have an Arrhenius relationship:

$$\eta = A \exp(-E/RT) \quad (3)$$

Where A is a constant, E is the activation energy and R is the universal gas constant. A plot of $\log \eta$ versus $1/T$ is linear for Newtonian fluids but polymers only show restricted linear relationships over a temperature range of about 50 - 60°C. The variation of viscosity with temperature depends on polymer type and varies widely. As a polymer is heated the molecules vibrate more rapidly and increase in mobility and so viscosity decreases.

Polymers are also sensitive to changes in pressure. As pressure is increased the free

volume and mobility of the chains is reduced and the viscosity of the melt increases.

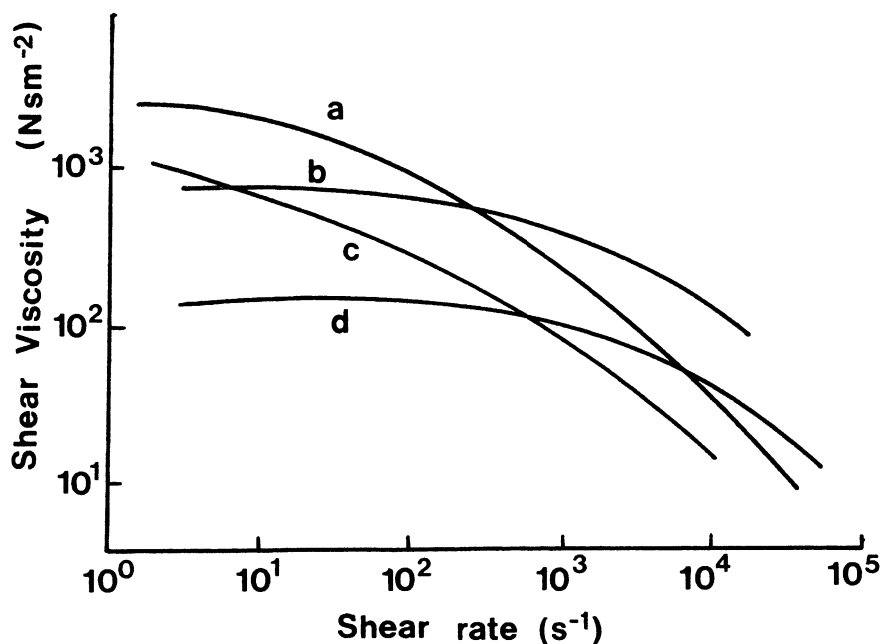


Figure 3. Flow curves of some typical thermoplastic melts (after Birley et. al.⁴)

Thermal and mechanical treatment which occur during processing influence viscosity, and highly sheared polymer has a reduced melt viscosity. When a stress is applied the chains tend to become aligned and disentangled and there is some slippage of the chains over each other. This previous shearing history creates less resistance to flow and hence viscosity decreases. Figure 3 shows the effect of increasing shear rate on viscosity for some typical thermoplastic melts. Molecular weight (see **Molecular Weight Distribution and Mechanical Properties**) is one of the most important parameters in determining the viscosity of a polymer. The longer the molecular chains the greater the number of entanglements which can occur, and hence viscosity will be increased. A factor of two increase in molecular weight produces a tenfold change in viscosity at a given shear stress. The molecular weight distribution, represented by the ratio of weight to number average molecular weight, also affects viscosity. As molecular weight distribution increases, the viscosity becomes more sensitive to shear, temperature and pressure. Chain branching also affects viscosity in a similar manner to an increase in molecular weight distribution. In manufacture, polymers are generally blended with additives such as fillers, plasticisers, stabilisers, lubricants etc. which significantly alter processing characteristics. Thus any measurement of rheological properties must include all constituents to determine the performance of the material.

Table 1 Classes of Rheometer for Melts in Common Use (after Cogswell ref. 3)

	Method	Variables	Output	Limitations
ROTATIONAL METHODS	Eccentric rotating disc and 'balance' rheometer Oscillatory cone and plate	Strain amplitude and frequency	Dynamic shear viscosity and elasticity PRECISE DATA	Near to linear response Strain <1.0
	Steady flow cone and plate Concentric cylinders	Strain Strain rate Strain recovery Stress Stress growth Stress relaxation Time	Viscosity and elasticity Normal stress PRECISE DATA	Low stress level $<10^4 \text{ N/m}^2$
	Torsion	As above	Apparent shear viscosity	High viscosity $>10^8 \text{ Ns/m}^2$
SQUEEZING	Penetrometer Parallel plate	Complex history	Apparently shear viscosity	Usually only used for viscosity $>10^5 \text{ Ns/m}^2$
EXTRUSION	Melt flow rate		Comparative fluidity (kinematic)	Single point determination
	Capillary flow Converging flow	Flow rate Pressure Swell ration Extrudate appearance	Apparent viscosity and elasticity in shear Apparent extensional rheology COMPARATIVE ENGINEERING DATA	Stress level $10^4\text{-}10^6 \text{ N/m}^2$ Viscosity $<10^6 \text{ Ns/m}^2$ Interpretation APPARENT PROPERTIES
TORQUE	Instrument extruder 'Brabender' type	Speed Packing force Charge volume	Comparative Resistance to flow gelation	Scaling Interpretation
FREE SURFACE FLOWS	Simple elongation	Stress Strain Strain rate Time	Extensional viscosity and elasticity PRECISE DATA	Handling difficulties Viscosity $>10^4 \text{ Ns/m}^2$ Strain rate $<1 \text{ s}^{-1}$
	Extrudate drawing	Speed Tension	Drawing force Drawing stability Rupture COMPARATIVE	Interpretation
	Sheet inflation Bubble inflation		PRECISE DATA Biaxial extension COMPARATIVE	Handling difficulties

REFERENCES

1. Brydson, J.A. (1981), *Flow properties of polymer melts*, George Godwin Ltd.
2. Brydson, J.A. (1990), *Handbook for plastic processors*, Heinemann Newnes.
3. Cogswell, F.N. (1994), *Polymer melt rheology*, Woodhead Publishing Ltd.
4. Birley, A.W., Haworth, B., Batchelor, J. (1991), *Physics of plastics*, Hanser Publishers.
5. McKelvey, J. M. (1962), *Polymer processing*, John Wiley & Sons, Inc.

22: Fracture Mechanics

P S Leever

The *toughness* of a material is its capacity to retain strength following damage. The most severe form of damage being a sharp crack, the most severe measure of toughness is the maximum stress which can be applied before such a crack extends. Unlike tensile strength, for example, this stress will depend on the geometry of the cracked body, as well as on inherent properties of the material.

Fracture Mechanics is the theory of stress and strength parameters for toughness. The principles outlined here are general, though polymers demand some special considerations which will be referred to as they arise.

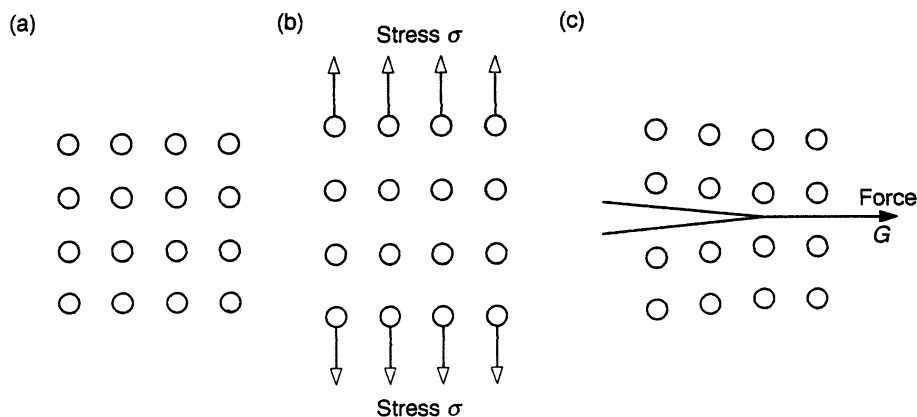


Figure 1: (a) A quasi-crystalline solid, and its separation by (b) tensile failure at the theoretical strength, or (c) progressive advance of a crack extension force.

STRENGTH AND TOUGHNESS

By visualising a solid as a quasi-crystalline array of atoms (Fig. 1(a)), its theoretical strength can be estimated as the peak stress needed to separate a plane of bonds connecting them (Fig. 1(b)). In most cases, this is much *higher* than the measured strength. However, at the tip of any sharp crack (which, in practice, will always be present), local stresses exceed the theoretical strength even under an infinitesimally *low* applied stress. This paradox can be resolved using either of two approaches¹ which loosely correspond to the two main questions which Fracture Mechanics is asked to

answer:

1. How can a material's toughness be measured, and used quantitatively in design?
2. Why does toughness differ between materials and, in a given material, why does it vary with testing conditions?

THE STRESS ANALYSIS APPROACH:

Fig. 2 illustrates some common fracture test specimens, in each of which the 'crack front' line is perpendicular to the paper. These specimens vary widely in size, shape and loading geometry (as, of course, do stressed components), but linear-elastic stress analysis reveals an underlying unity. The stress-concentrating effect of a sharp crack is so dominant that, *near its tip*, the stress distribution is almost identical in every case. The tensile stress σ_y across the crack line at a small distance r ahead of the tip increases with $r^{-1/2}$ to infinity as the tip is approached but the product $\sigma_y r^{1/2}$ remains constant. It can be concluded that K , the *stress intensity factor*, which is proportional to $\sigma_y r^{1/2}$, completely describes the magnitude of stresses. which act to open the crack.

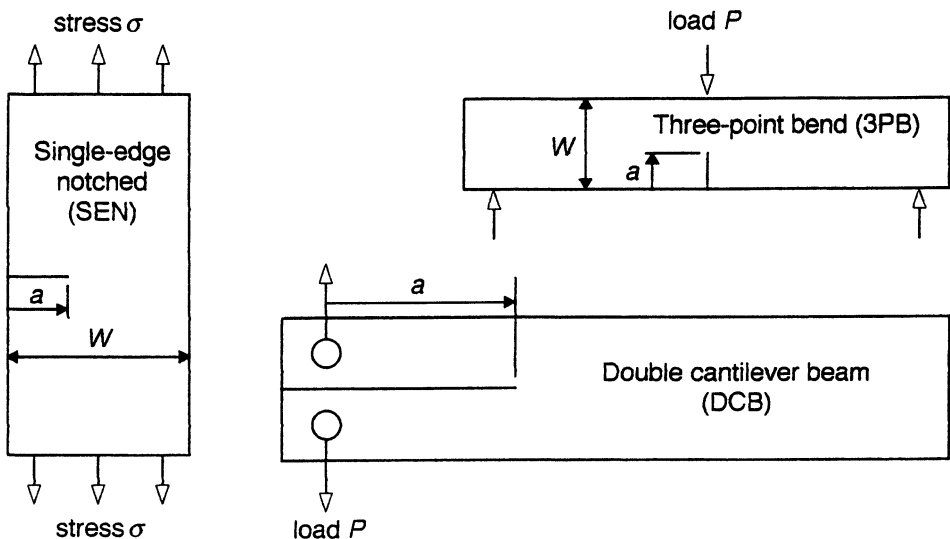


Figure 2: Various fracture specimen geometries.

Linear elastic fracture mechanics (LEFM) rests on the assumption that, for a given material in a given environment, crack behaviour is determined by K . For simple, brittle materials such as glass, 'fracture' will ensue when $K=K_C$ where K_C , the *fracture toughness*, is a material constant. In the specimen geometries shown in Fig. 2, as in many practical situations, a single independent applied stress σ (or a single load P which

can be represented as such) opens the crack. K is then given by

$$K = Y\sigma \sqrt{a} \quad (1)$$

where Y is a numerical factor which depends on geometry and crack length only. For example, for a short, through-thickness crack in the centre of a large, uniaxially-stressed plate, $Y = \sqrt{\pi}$. Many standard Y solutions have been tabulated³ and well-proven computational methods exist to evaluate those which have not. Thus K_C can be measured from the fracture stress in one geometry and used to predict the fracture stress in another. Polymers may raise special problems corresponding to the assumptions made in the stress analysis: i.e. small strains, linear behaviour and a time-independent modulus² (see **Viscoelasticity**). The fact that polymers show a wide range of crack *behaviour* across a wide spectrum of K values and histories, is a separate issue (see **Slow Crack Growth and Fracture**).

THE SURFACE-ENERGY APPROACH

Fig. 1(c) visualises a more realistic alternative to the 'all-at-once' separation model of Fig. 1(b). An external *crack extension force*, G per unit length, is applied to a frictionless wedge, like an ideal 'cheesewire'. A modest critical force G_C per unit width, *the fracture resistance*, can drag the wedge through the material. It is easy to show that G_C (also known as the *critical energy release rate* or *strain energy release rate*) is simply the work done per unit area of material cut through. In reality, of course, the crack extension force G originates from the external force P and is transmitted to the crack tip by the surrounding body itself. It can be shown (if inertial forces are neglected) that G is proportional to P^2 and to the rate at which the compliance of the body increases as the crack extends. The latter depends only on the geometry of the body (including where the load is applied and how long the crack is) and the modulus of its material; it is easily computed using stress analysis.

Again, solving a fracture problem involves two steps. Firstly, G must be expressed in terms of P (or an equivalent stress σ or displacement. This is really the same problem as that of finding K in terms of σ , and it can be shown that for a linearly elastic material

$$G = K_I^2/E' = \pi Y^2 \sigma^2 / E' \quad (2)$$

where E is the tensile modulus of the surrounding material and $E' \equiv E/(1-\nu)^2$ for plane strain and E for plane stress (see below). Thus G solutions need not be tabulated separately from K solutions.

Secondly, G_C must be evaluated. It follows that the fracture criterion

$$G = G_C \quad (3)$$

corresponds to $K = K_C$.

SOURCES OF TOUGHNESS: THE PROCESS ZONE

The surface-energy approach helps to explain the *source* of a material's toughness. The fracture process involves much more than just material separation. It is the region surrounding the separation point (rather than the imaginary cheesewire of Fig 1(c)) which transmits the necessary stress and displacement to it. In doing so, the material in this *process zone* suffers irreversible flow and damage which protects the crack tip. As it is dragged forwards with the crack front through each unit area, the process zone absorbs work G_C , and the toughness K_C is determined partly by G_C and partly by the rigidity of the loaded body as a whole.

For a von-Mises material of uniaxial yield stress σ_0 , the process zone size can be estimated as the radius r_p at which the crack-tip stress field, determined by K , initiates yield

$$r_p = K_C^2 / 2\pi\sigma_0^2 \quad (4)$$

The bigger the process zone, the tougher the material. However, LEFM only remains valid if r_p is smaller than any of the body dimensions, otherwise the process zone will be affected by the stress field beyond the crack's own K field, and K_C will become geometry dependent.

THICKNESS EFFECTS

The thickness of a fracture specimen - i.e. the length of the crack front - may affect fracture in two distinct ways. Firstly, increasing thickness increases the proportion of crack front under plane-strain conditions. As the crack is forced open, tensile stresses develop along its front, and tend to shorten it. At the surfaces, i.e. the ends of the crack front, plane stress conditions prevail: contraction occurs freely and a surface 'dimple' forms (from which, in fact, K can be measured experimentally). Internally, plane strain conditions prevail and the high tensile stresses which develop along the front increase the crack extension force.

Secondly, the response of the material may itself be affected by this elevation of stress triaxiality (negative pressure). Damage mechanisms such as void growth may be favoured at the expense of mechanisms driven by shear stress (e.g. shear yielding) which can blunt and protect the crack tip.

In practice, plane strain conditions can be assumed to dominate if expression (5) holds where B is the thickness

$$B > 2.5 (K_C/\sigma_0)^2 \quad (5)$$

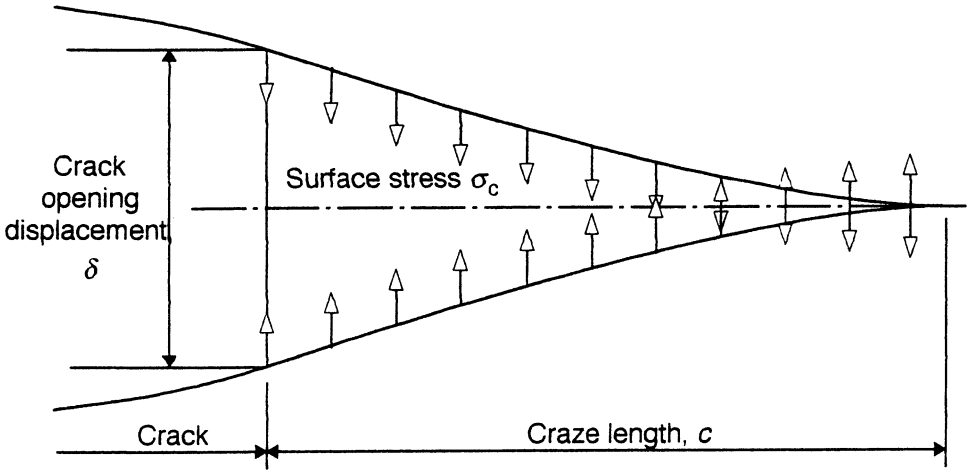


Figure 3: A crack tip with a craze-like 'Dugdale zone'.

THE DUGDALE MODEL

The surface-energy approach emphasises that fracture can be understood without having to imagine infinitely sharp cracks or infinitely high stresses. The Dugdale model visualises the process zone, which grows while the crack is loaded, as an extension of the crack, opening against a restraining stress σ_c (Fig. 3). The model is very suitable for polymers because it closely matches a craze (see **Crazing**).

The Dugdale analysis determines the size of this process zone on the basis that stresses around a real crack tip cannot be infinite. A zone of the right length c under tensile stress σ_c can cancel out K and eliminate the infinite stress field which it represents. For a central crack in a very large, flat, uniaxially stressed plate this length is

$$c = \pi K^2 / 8 \sigma_c^2 \quad (6)$$

where K is calculated as if it still existed. At the end of the physical crack the *crack opening displacement*, δ , is given by

$$\delta = K_I^2 / E \sigma_c \quad (7)$$

Eqns. (6) and (7) emphasise that if any two of δ , σ_c , and c could be predicted (for example, the stress needed to extend craze material and the length to which this material could be drawn), then so could the fracture resistance. Strictly speaking, the Dugdale

analysis applies only to a centre-cracked plate under plane stress. In practice, it is commonly applied to other geometries unless the craze is long compared to the crack, and some other computed solutions are available².

REFERENCES

1. Williams, J.G. (1987) *Fracture Mechanics of Polymers*, Ellis Horwood (London)
2. Broek, D. (1991) *Elementary Engineering Fracture Mechanics*, Kluwer Academic Publishers.
3. Rooke, D.P., and Cartwright, D.J. (1976) *Compendium of Stress Intensity Factors*, HMSO (London)

23: Friction

B. J. Briscoe and S. K. Sinha

INTRODUCTION

Polymers and their composites are important tribological materials for applications in aerospace, automotive components, micro machines and bio-systems. In the past, a considerable amount of research has been carried out to understand the mechanisms of friction and wear when a polymer surface interacts with another (hard or soft) surface¹⁻⁵. This understanding has led to the greater use of polymeric materials and their composites in tribological applications. This article provides a brief review of the frictional properties of engineering polymers.

FRICTION

There are generally two types of friction processes; sliding and rolling. Sliding process involves both subsurface deformation and the interface adhesive functions while the rolling process incorporates mainly the subsurface visco-elastic work loss which depends upon the nature of the interacting materials and the imposed strain path.

The classical Coulombic friction coefficient is defined as $\mu = F/N$, where μ is the friction coefficient, F is the friction force and N is the applied normal load. By definition the friction coefficient is a property of two interacting solid surfaces and independent of the applied normal load. However, in practice friction coefficient depends upon a number of factors and important amongst them are the normal load, the relative sliding velocity, the ambient environment and the temperature. The friction between two surfaces arises due to interactions both at micro and macroscopic levels. An important result of friction is the generation of heat and an increase in the interfacial temperature. For organic polymers this often has major consequences and limits their applications. The current wisdom is that there are two main surface interactions which are of major importance in the friction of solids in general and of polymers in particular. These interactions are the ploughing and adhesion components. Ploughing is a process which involves significant subsurface deformation and perhaps the removal of material from the softer surface by the action of asperities on the surface of a harder body. The process takes place by the visco-elastic and plastic deformation of the soft surface. The ploughing mechanism deals with relatively large volume deformation and involves relatively small strains. The adhesion component, on the other hand, is due to the bonding between two interacting bodies at the regions of contact and the subsequent repeated shear of these junctions. The adhesion mechanism generally operates when the two surfaces are rather smooth and free from foreign 'dirt' to facilitate contact between

molecules or atoms of the two surfaces. Figure 1 (a) and (b) shows, diagrammatically, the two interaction processes between a hard and a soft surface.

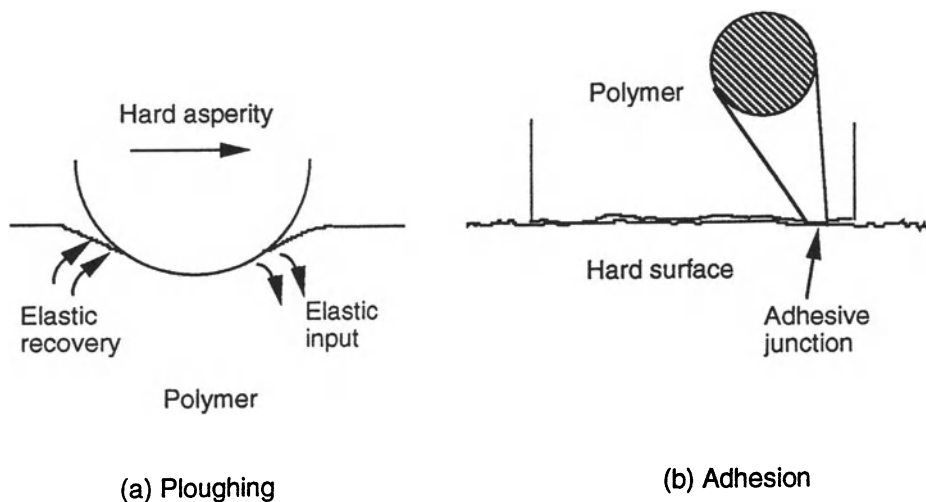


Figure 1: Surface interaction between polymer and hard surface. (a) The figure shows ploughing of the polymer surface by a hard asperity in the absence of interfacial adhesion. (b) When the surfaces are smooth interfacial bonding takes place between the two contacting surfaces.

The relative amount of these two types of deformations that takes place in a surface interaction depends upon the respective surface roughnesses of the materials and the interfacial temperature generated during the process as well as the contact geometry. The friction force measured during a two body interactive process is often supposed to be the sum of the ploughing and the adhesion components. This is the proposition of the two term model of friction.

THE PLOUGHING TERM IN FRICTION

When a hard slider or an asperity moves over a polymer surface in the absence of any adhesion (for example with efficient lubrication), the work is carried out at the front edge and some part of the energy is retrieved at the rear end as the slider passes through a point. This is analogous to simple tension or simple shear at a comparable deformation rate involving a loading-unloading cycle. In such a situation the viscoelastic work done is the energy lost due to hysteresis or internal friction. If α is the fraction of energy lost due to hysteresis and ϕ is the elastic work done by the slider per unit sliding distance then the deformation force may be given as

$$F = \alpha\phi \quad (1)$$

The value of ϕ depends upon the geometry of the indenter and the loading. For a spherical indenter of radius R traversing a surface under a load W ,

$$\phi = 0.17W^{4/3}R^{-2/3}(1-\nu^2)^{1/3}E^{-1/3} \quad (2)$$

where E is the real part of Young's modulus (see **Viscoelasticity**) of the solid and ν is **Poisson's ratio**⁶. The expression for a conical indenter of semi-apical angle ψ is given as

$$\phi = (W/\pi)\cot\psi \quad (3)$$

Equation (3) is applicable provided no tearing or cutting of the softer surface takes place. These deformations provide an additional work component and the friction is increased as a result. Combining equations (2) and (3) with equation (1), it is possible to accurately calculate the friction force due to ploughing deformation.

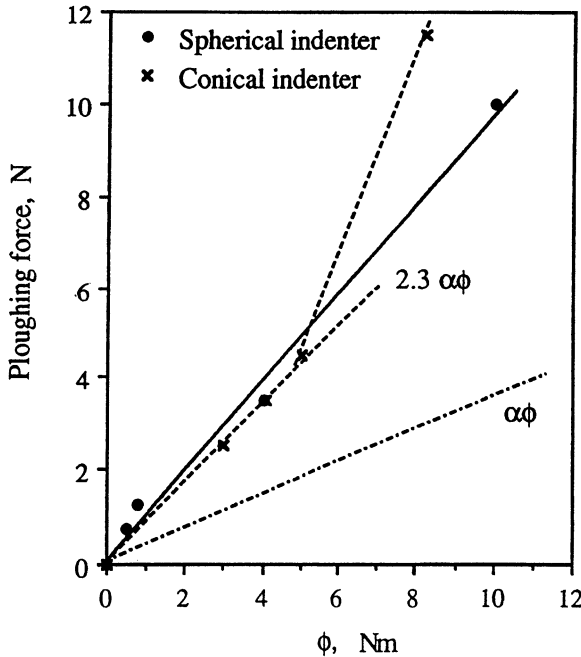


Figure 2: The observed ploughing force F_d as a function of the input energy ϕ per unit distance of sliding for a hard slider traversing a well-lubricated rubber surface of high loss factor $\alpha = 0.35$. The input energy ϕ was varied for the spherical indenter by changing the normal load W and for the conical slider by changing the included cone angle.

It is often observed that for rubbers or where the elastic work done is relatively high, the ploughing force is about 2 to 3 times higher than $\alpha\phi$. Indeed, both theory and experiment show that the effective loss is about $3\alpha\phi$ instead of $\alpha\phi$ per unit distance of traverse. The energy loss also depends upon the imposed strain cycle in any ploughing process. Also if tearing occurs the tearing work will contribute to the friction; Figure 2 shows the measured ploughing force for spherical and conical indenters sliding on a rubber surface. For the conical indenter result it is seen that the ploughing force deviates from linearity when the included semi angle of the cone is reduced below 45° . This is due to the initiation of tearing and fracture of the rubber surface in a characteristic stick-slip way for sharp indenters.

THE ADHESION TERM IN FRICTION

The adoption "adhesion term in friction" between two solid bodies was first popularised by Bowden and Tabor¹. The adhesive force in polymers and elastomers arises from the electrostatic and intermolecular forces between the molecules of the two interacting bodies (see **Adhesion of Elastomers**). The shearing force required to overcome this adhesion between solids is the adhesion term in friction. The adhesive interaction during sliding can occur in two modes. If the attachment of the polymer to the counterface is weaker than the polymer, sliding occurs truly at the interface: if it is stronger than the polymer, shear will occur a short distance from the interface within the polymer itself. This distance may range from a few nanometers to a few micrometers. There is still a great debate about the actual mechanism of adhesion between solids. Some of the theories have been discussed critically by Tabor⁷. In contrast to the general acceptance of adhesion as one of the friction mechanism, Bikerman⁷ believes that 'in true friction no adhesion takes place'. According to him adhesion between two solids is always prevented due to the presence of a very thin layer of air on the surface of materials. In general, it is accepted that the intermolecular and electrostatic forces are the main causes of adhesion between solids. For rubbers, Schallamach⁸ observed 'waves of detachment' passing through the adhered surface during sliding of rubber against smooth glass surface. Such waves of detachment have not been observed for thermoplastic polymers; it appears that a strain of ca. unity is required in order that the process occurs.

The adhesive frictional force, F_a , acting on a surface in contact with another surface in relative motion may be given by

$$F_a = A\tau \quad (4)$$

where A is the area of contact and τ is the interface shear strength of the polymer. For a wide range of polymers the interface shear strength at constant velocity (v) and temperature (T) is related to the contact pressure p by an expression of the form

$$\tau = \tau_0 + \alpha p \quad (5)$$

where τ_0 is the shear yield strength of the polymer and α is a coefficient (see **Yield and Plastic Deformation**). The adhesive friction coefficient can be given as

$$\mu_a = \tau/p = (\alpha + \tau_0/p) \quad (6)$$

For very high normal loads ($\tau_0/p \ll \alpha$)

$$\mu_a \cong \alpha \quad (7)$$

where μ_a is the adhesive component of the coefficient of friction. For a wide range of thermoplastics, the relationship (6) is reasonably well obeyed.

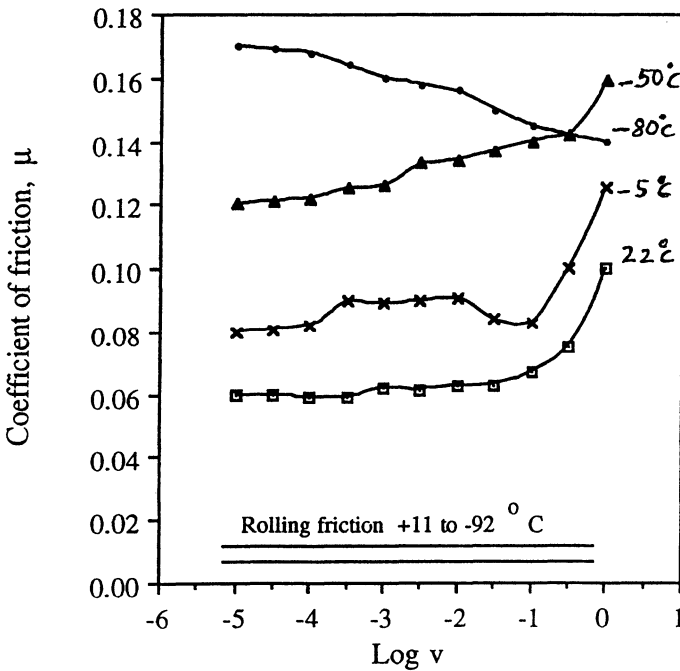


Figure 3: Friction coefficient between a hard slider and a PTFE surface of low crystallinity as a function of logarithm of sliding velocity v for different temperatures (after ref. 10). The figure also shows the friction coefficient for rolling contact in the temperature range $+11$ to -92°C .

In a friction measurement test it is possible, in principle, to separate the ploughing and adhesive components, as previously defined, from the total measured friction

coefficient. These techniques are described in the section on frictional testing. Generally, in a rolling test, where a roller of a hard material is passed over a softer polymer surface in rolling contact, the adhesive force between the two surfaces may be neglected. Figure 3, for example, shows the friction coefficient between a hard slider and PTFE surface as a function of speed and temperature¹⁰. The rolling friction (ploughing component) has been compared with the total friction coefficient.

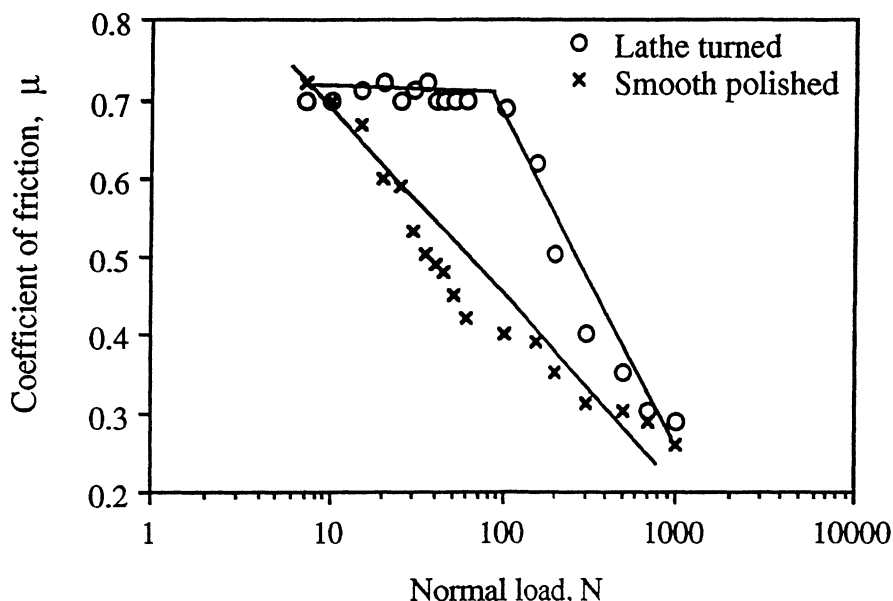


Figure 4: Variation of coefficient of friction with normal load for sliding of crossed cylinders of polymethylmethacrylate (PMMA) with different surface roughnesses (after ref. 11).

The friction of polymers against themselves or a hard surface (metal or ceramic) greatly depends upon the factors which will influence the adhesive and ploughing forces. Important factors affecting friction are the surface roughness, interfacial temperature, normal load and the relative velocity between the surfaces. Figure 4 shows the effects of normal load and surface roughness for PMMA on the measured friction coefficient¹¹. The interfacial temperature which is the result of frictional heat generation influences mechanical properties of materials. Softening and melting of polymers may occur near the interface leading to an initial reduction in the friction coefficient. This is because a smaller amount of energy is required to shear a softer layer of polymer than overcoming the adhesion and ploughing forces when the surfaces are harder. Surface melting is a major factor in sliding polymers against hard surfaces at higher sliding speed and normal load conditions⁷. Under such situations friction is entirely controlled by the viscous properties of the thin molten layer of the polymer formed at the interface.

A considerable amount of research has been carried out in polymer tribology to understand the low friction mechanism of polymers such as PTFE and High and Ultra

High Density Polyethylene. These polymers give very low friction (as low as 0.05 for PTFE) when slid against hard and smooth surfaces and have found many application (e.g. PTFE coating for sliding components in machines, gears and non-stick cooking pans, UHMWPE for femoral bone replacement etc.). It has been speculated that the low friction for these polymers arises due to their molecular structure. The molecular structures of these polymers are characterised by 'molecularly 'smooth' linear, unbranched chains without bulky or polar side groups¹⁰. During sliding these polymers deposit a transfer layer on the counterface and subsequent interaction takes place between the bulk polymer and the transfer film. The transfer films are very thin (perhaps few hundred nanometers) and contains molecular chains strongly oriented parallel to the sliding direction.

REFERENCES

1. Bowden F.P. and Tabor D., (1964) in *The Friction and Lubrication of Solids*, Part I & II, Claredon Press.
2. Briscoe, B.J., (1982) *Tribology of polymers: State of an art*, in *Physicochemical Aspects of Polymer Surfaces*, (ed. Mittal K.) Plenum Press.
3. Briscoe, B.J., (1980) *The sliding wear of polymers: A brief review*, in *Fundamentals of Tribology*, (eds. N. P. Suh and K. Saka) MIT Press, 733-758.
4. Briscoe, B.J., (1990) *Materials aspects of polymer wear*, *Scripta Metallurgica*, **24** (5), 839-844.
5. Briscoe, B.J., (1992) *Friction of organic polymers*, in *Fundamentals of friction: Macroscopic Origins*, (eds I. Singer and H. Pollock), Kluwer Academic Publisliers, The Netherlands.
6. Greenwood J.A. and Tabor D., (1958) *Proc. Phys. Soc.*, **71**, 989-1001.
7. Tabor, D. (1974) *Advances in Polymer Friction and Wear*, Vol 5A, Plenum Press, New York and London, 5-30
8. Schallamach, A. (1952) *J. Polymer Sci.*, **9**, 385-396 (1952).
9. Briscoe B.J. and Tabor D. (1978) in *Surface properties of polymers* (eds. D. Clark and J. Feast), John Wiley.
10. Ludema K.C. and Tabor D. (1966) *Wear*, **9**, 329.
11. Archard J.F.(1957), *Proc. Roy. Soc. Lond.*, **A 243**, 190

24: Glass Transition

D. J. HOURSTON

INTRODUCTION

The glass transition, T_g , is the most important thermal transition shown by amorphous polymers. As the glass transition is a phenomenon of the non-crystalline state, it follows that it is a less dramatic event in semi-crystalline polymers. Fig. 1 shows how the modulus of an amorphous polymer changes with temperature and also indicates the influences of crystallinity and crosslinking on modulus.

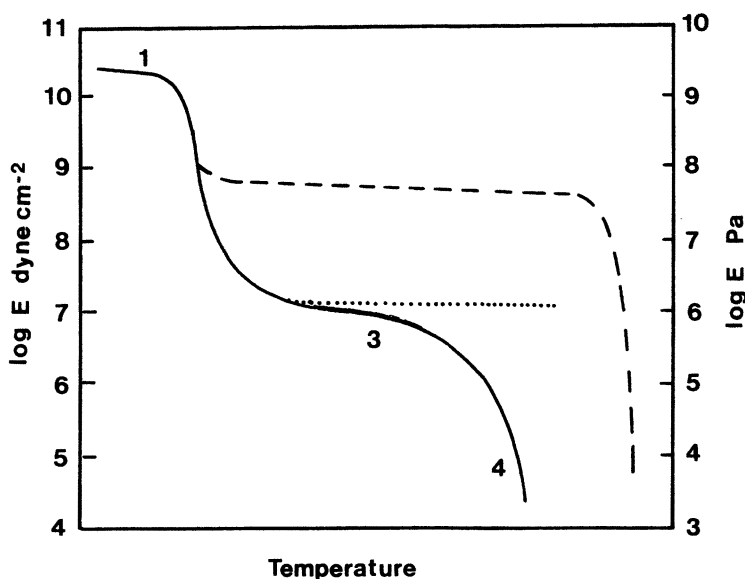


Figure 1: A typical log modulus (E) versus temperature plot for an amorphous polymer (solid line), a semi-crystalline polymer (dashed line) and a crosslinked sample of the amorphous polymer (dotted line). Region 1 is the glassy state, region 2 is the glass transition region, region 3 is the rubbery plateau and region 4 is the melt region.

Before an amorphous, or even a semi-crystalline, polymer can be selected for a particular task, it is essential to know the glass transition temperature as the modulus change in the T_g region is commonly about three orders of magnitude. At temperatures below the T_g , the polymer is in its glassy state. Here the chains are in essentially frozen conformations. There may be some localised motions¹, but there is no long-scale concerted segmental motion because rotation about backbone bonds is highly restricted.

This glassy region is followed by the glass transition region which occurs over a range of temperature, often about 20°C to 30°C, but can be as much as 50°C or more. However, T_g is always quoted as a single value of temperature. It is conventional to take T_g at the mid-point of the modulus drop. The glass transition region is followed by the rubbery plateau region and then by the viscous melt region.

The glass transition can be thought of as the onset of long-range, co-ordinated molecular motions² (see **Relaxations**). As polymer molecules commonly consist of thousands of backbone atoms, these are motions of chain segments and not entire chains. It is believed that for the molecular motions occurring below T_g the number of atoms involved may be as few as 1 to 4, while in the glass transition region this number is believed to be in the 30 to 100 backbone atom range. The value of T_g varies very widely depending on molecular structure and a range of other molecular and experimental parameters. There are several theories of the glass transition⁶ which are beyond the scope of this short article.

DETERMINATION OF THE GLASS TRANSITION

As the properties of polymers, especially amorphous polymers, change dramatically in the transition region, there are many ways of determining T_g experimentally based on a thermodynamic, physical, mechanical or electrical property changes as a function of temperature.

- a) Dilatometry: In this method a plot of specific volume versus temperature is constructed. There is a change of slope at the glass transition.
- b) Thermal methods: The principal method here is differential scanning calorimetry, DSC³. The technique is sensitive to exothermic and endothermic transitions and to changes in heat capacity such as occur at the glass transition. A recent modification of DSC, modulated-temperature differential scanning calorimetry, M-TDSC, has been shown⁴ to be much more sensitive to the glass transition than conventional DSC.
- c) Mechanical Techniques: In addition to modulus (Fig.1), other related properties such as hardness and the coefficient of restitution may form the basis of T_g detection techniques. However, **dynamic mechanical thermal analysis**, DMTA, is by far the most important technique in this category. A periodic displacement is applied to the test piece. The resulting periodic stress and strain waves can be analysed to yield the dynamic storage modulus (a measure of the energy stored per cycle), the dynamic loss modulus (a measure of the energy dissipated as heat per cycle) and the tangent of the out-of-phase angle, $\tan \delta$. The first shows a plot versus temperature as seen in Fig.1, but the dynamic loss modulus and $\tan \delta$ reach maxima in the T_g region (see **Viscoelasticity**). This is a convenient, widely applicable and sensitive technique for T_g detection.

Because of the viscoelastic nature of polymers in the glass transition region, changes in the frequency of the experiment will result in a change of the position of T_g.

INFLUENCE OF MOLECULAR STRUCTURE ON THE GLASS TRANSITION

In considering how a molecular or experimental parameter might change the value of T_g , it is useful to think in terms of the flexibility of the chain concerned, about the intermolecular forces involved and of the likely changes in free volume. Increasing chain flexibility leads to a decrease in T_g . An increase in intermolecular forces causes T_g to rise and any factor increasing the free volume occasions a decrease in T_g .

a) Molar mass: The equation proposed by Fox and Flory is presented below

$$T_g = T_{g\alpha} - K/(\alpha_r - \alpha_g)M \quad (1)$$

where $T_{g\alpha}$ is the T_g for a sample of infinite molar mass, K is a constant, α and α_g are the coefficients of volume expansion above and below the glass transition, respectively, and M is the molar mass. The term $K/(\alpha_r - \alpha_g)$ is about 2×10^5 for polystyrene.

b) Crosslinking: As crosslinking increases, the stage is eventually reached where the T_g is undetectable because of segmental motion restriction occasioned by the crosslinks. At low and intermediate levels of crosslinking, T_g shifts to higher temperatures and the rubbery plateau occurs at higher modulus values.

c) Copolymers and polymer blends: Copolymers generally exhibit a single T_g value which lies in a position intermediate with respect to the T_g s of the constituent homopolymers. Several relations, including the following, have been developed to predict copolymer T_g values.

$$1/T_{g_{cop}} = m_1/T_{g_1} + m_2/T_{g_2} \quad (2)$$

m_1 , m_2 , T_{g_1} and T_{g_2} are the masses and T_g s of the two constituents.

In block copolymers, where the blocks are large enough to phase separate, two glass transitions are in evidence. If phase separation is complete, the T_g s lie at the temperatures of the corresponding homopolymers. If in the relatively unlikely case that the blocks of such a copolymer are miscible, then a single T_g results. Again, it will lie in an intermediate position governed by the relative amounts of the constituent blocks.

For immiscible polymer blends, two T_g s result and are located at the T_g s of the constituent polymers. If, on the other hand, the pair of constituent polymers are miscible, as for the block copolymer case, there will be only a single T_g . If there is some degree of mixing of the constituent polymers, then the T_g s are shifted inwards towards each other relative to the constituent polymer values.

d) Crystallinity: The amorphous regions of semi-crystalline polymers also exhibit a glass transition which may be influenced if the crystallites restrict to some extent the freedom of segmental motion. Many semi-crystalline polymers appear to have two T_g s². The lower one is associated with completely unrestricted amorphous chain segments and the other with segments whose motions are to some extent restricted by crystalline elements.

e) Polarity: Polar interactions such as hydrogen bonding and dipole-dipole interactions raise the T_g because they have to be overcome before the segments are free to rotate to new conformations.

f) Side groups: The effects of side groups attached to the chain backbones differ depending on whether the side groups are flexible or stiff. Flexibility refers to the ease of rotation which is possible about the skeletal bonds of the side groups. This controls the conformations available to these side groups. As side chain flexibility increases, the T_g decreases. It is thought that the side groups act as internal diluents, thus reducing the frictional interactions between chains. For stiff side groups, there are very limited possibilities for conformational change through skeletal bond rotation. These side groups may also be regarded as being bulky. Their influence is to increase the value of T_g .

g) Tacticity: The effect of tacticity on T_g can in some cases be substantial. Karasz and MacKnight⁵ have illustrated this point for polymethacrylates. For example, they report the T_g of isotactic polymethyl methacrylate to be 43°C, while a value for dominantly syndiotactic polymethyl methacrylate was 105°C.

INFLUENCE OF PRESSURE ON THE GLASS TRANSITION

As the free volume content of a polymer strongly influences T_g , a pressure increase causes an increase in T_g . In going from atmospheric pressure to say 3000 bars may easily result in a T_g increase of 20 to 30°C.

REFERENCES

1. Shen, M., Eisenberg, A. (1970) *Rubber Chem. Technol.*, **43**, 95.
2. Boyer, R. (1977) *Encyclopedia of Polymer Science and Technology, Suppl.* Vol. 2 Bikales N. M., Ed., Interscience, New York, 822-823.
3. Kow, C., Morton, M., Fetters, L. (1982) *Rubber Chem. Technol.*, **55**, 245.
4. Hourston, D.J., Song, M., Hammiche, A., Pollock, H.M., Reading, M. (1997) *Polymer*, **38**, 1.
5. Karasz, F.E., MacKnight, W.T., (1968) *Macromolecules*, **1**, 537.
6. Sperling, L.H. (1986) *Introduction to Physical Polymer Science*, Wiley-Interscience, New York.

25: Hardness and Normal Indentation of Polymers

B. J. Briscoe and S. K. Sinha

The hardness measurement has wide applications in the characterisation of the mechanical and physical properties of materials. This method is frequently used for metals, polymers, ceramics and coatings¹. It has been used to relate hardness with certain physical and mechanical properties of materials. It has also been used to monitor and predict the service lifetime of prosthetic thermoplastics against a simulated human body environment². Hardness is generally defined as the resistance of a material against local surface deformation. In an indentation test, a softer material is indented upon by a rigid indenter of specified tip geometry (conical, spherical, pyramid etc.) and hardness is usually computed as the ratio of indentation load to the projected area of contact between the indenter and the material in the plane of deforming surface. The area of contact may be measured actually, or indirectly, from the image of the residual indent on the softer surface after the indenter is removed. In this case the hardness value is controlled by a plastic property of the material. As an alternative the contact compliance curve (load-displacement curve) can be used to extract both plastic and elasto-plastic properties of the material. The actual choice of the technique used for hardness measurement depends to a great extent upon the type of the material tested and the kind of information desired from the test. For elastomeric materials such as rubbers, the rebound hardness is commonly used. In a rebound hardness test a rigid indenter is made to fall onto the sample surface from a specified height and the height of the rebound is measured. The energy absorbed by the sample material on impact is then related to the product of a "dynamic yield pressure" and the volume of the indent.

This article introduces some common methods for obtaining normal hardness of materials as applied to polymers. Results on the hardness of polymers are presented along with correlations between hardness and some other mechanical and physical properties of these materials. Common practical problems encountered in normal hardness measurements are also briefly discussed.

STANDARD HARDNESS TESTS

Hardness is defined as the resistance of a material against local deformation by an indenter and it is measured as the reaction force per unit area of some contact area between the indenter and the test material. Figure 1 shows a common procedure used in the hardness measurement. Different standards have been formulated for the measurement of normal indentation hardness. They are based on different geometrical shapes of the indenter. The most commonly used are (a) Brinell (sphere), (b) Vickers

(pyramid) and (c) Rockwell (cone and sphere). Table 1 lists important features of the major standard test methods. It may be noted that different hardness numbers (as they are called) are obtained, for a given material, by the different procedures and some of them do not directly correspond to the definition of hardness given above.

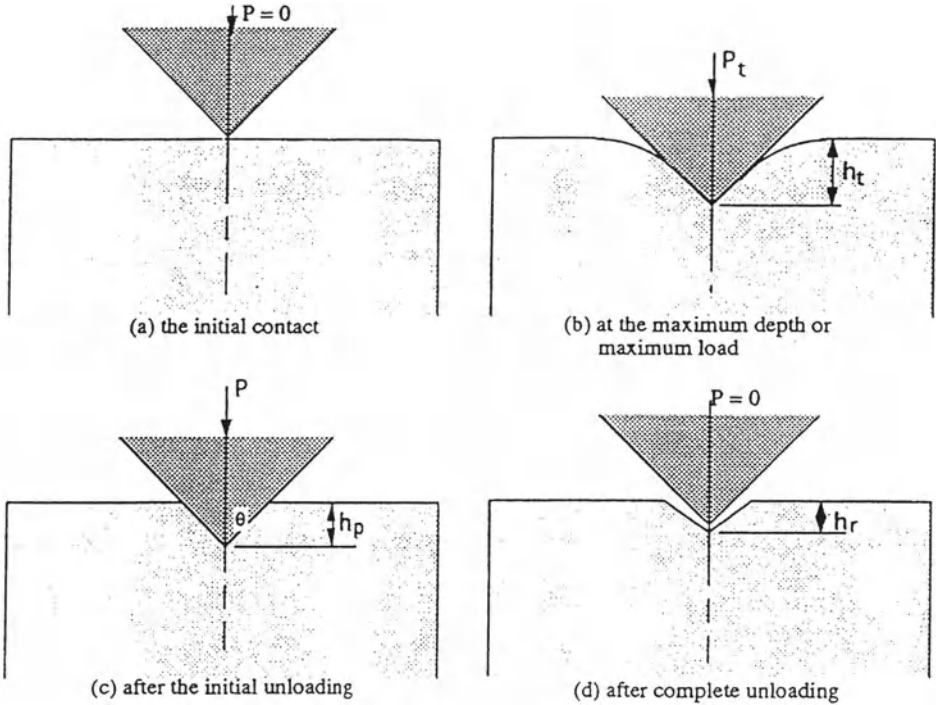


Figure 1: Schematic representation of the procedure of normal hardness testing.

Considering the fact that different hardnesses sense different properties of materials viz. elastic, plastic and visco-elastic, the hardness values obtained in these tests are generally not interrelated. Based on this notion we may separate hardnesses into three different classes, elastic, plastic and elastovisco-plastic. For elastomers and natural rubbers it is common to obtain hardness as the elastic response (International Rubber Hardness Degree)³. Here, hardness represents the depth of penetration of an indenter of specified geometry into the rubber specimen for a fixed load (BS903). For metals, hardness invariably indicates the plastic component as the hardness (e.g. BHN is computed from the permanent impression of the indenter on the sample material). Such definitions are difficult to apply to polymers as they show a range of deformation behaviour viz. elastic, plastic and visco-elastic for a small change in the intrinsic (material) or extrinsic (ambient environment) parameters. The recent approach for the hardness measurement of polymers utilises elastic-plastic time dependent effects.

Table 1 Standards of Indentation Hardness Measurement

Name	Standard	Hardness function	Indenter
Brinell hardness	BS 240: 1986	$H_B = \frac{2L(Kgf.)}{\pi D \left\{ D - \sqrt{D^2 - d^2} \right\}}$	Sphere: dia in mm 10, 5, 2.5, 2, and 1
Vickers hardness	BS 427: 1990 ≡ ISO 6507	$H_V = 1.8544 \frac{L}{d^2}$	Square based pyramid, 136° across faces
Rockwell hardness	BS 891: 1989 ≡ ISO 6508	A function of the difference in the depth of penetration corresponding to a test load and a minor load	A, C and D scales: 120° cone with 0.2 mm <i>R</i> spherical tip. B, F and G scales: sphere, dia 1.587 mm E, H and K scales: sphere, dia 3.175 mm
Knoop hardness	BS 5411(6): 1981 ≡ ISO 4516	$H_K = 14.229 \frac{L}{d^2}$	Rhomboid base pyramid, angles between opposite edges: 172.5° and 130°
International Rubber Hardness Degree (IRHD)	BS 903: Pt.A26: 1969 ≡ ISO 48	Given as a function of the difference in the depth of penetration corresponding to the full load and the initial load	Spheres, standard: 2.38 or 2.50 mm dia micro: 0.395 mm dia
Shore hardness	BS 903: Pt.A57: 1989 ≡ ISO 1719	Inversely proportional to the depth of penetration	Scale A: truncated 35° cone with 0.79 mm dia flat tip Scale D: 30° cone with 0.1 mm <i>R</i> spherical tip
Berkovich	nil	same $A(h)$ relationship as that of the Vickers indenter; preferred in micro indentation	Triangle based pyramid: 65.3° between the axis and face, 77.05° between the axis and edge

INDENTATION OF ELASTO PLASTIC MATERIALS

The theoretical basis for elasto-plastic indentation has been studied quite extensively for various indenter geometries. When an indenter, particularly a 'sharp' indenter, is pressed into an elastic surface the contact stresses are generally not Hertzian but

normally involve a stress singularity. As the pressure is increased beyond a limiting value a central plastic region is formed at the tip of the indenter. The plastic region, which is surrounded by an elastic hinterland, gradually expands as the indentation pressure is increased. For such a situation, Johnson⁴ showed that for a wedge indenter (two dimensional) the indentation pressure, P_m is given as

$$P_m = \frac{\sigma_0}{\sqrt{3}} \left[1 + \ln \frac{4E}{3\pi\sigma_0} \cot\theta \right] \quad (1)$$

where σ_0 is the yield stress, E is the elastic modulus and θ is the included semi wedge angle. Equation (1) indicates that in both fully elastic and elastic-plastic cases, the indentation pressure depends upon the group $(E/\sigma_0)\cot\theta$, time dependent effects are not considered at this stage. The ratio σ_0/E can be regarded as the maximum strain a material can sustain before yielding while $(E/\sigma_0)\cot\theta$ is the ratio of the strain imposed by the indenter (strain for cone and wedge indentation is approximated as proportional to $\cot\theta$) to the maximum elastic strain for the material before yielding. Johnson⁴ plotted P_m/σ_0 as a function of $(E/\sigma_0)\cot\theta$ for different materials and found that if the value of $(E/\sigma_0)\cot\theta$ is greater than 100, the deformation is fully plastic. Under this condition the ratio P_m/σ_0 is about 3.

COMPLIANCE METHOD AND MICROHARDNESS

The traditional methods of hardness characterisation for metals use the imaging technique for the computation of the residual area of contact and the hardness values. Hence, this method provides only the plastic property of the material. The imaging technique is not suitable for obtaining the elastic and elasto-plastic properties of the material. The other limitation is that this method is not very suitable for micro and nano scale hardness measurements as the errors involved in the contact area measurements can be quite large. For these applications, the compliance method (generally applied for rubbers) which utilises the force-displacement curve during loading and unloading, is often useful. This method and the errors involved, in the context of thermoplastics have been investigated by Briscoe & Sebastian⁵ in the context of organic polymers. The test records the force-displacement curve as the indenter is pressed into the softer material. Both the loading and unloading curves are recorded for data analysis.

Figure 2 shows a loading-unloading force-displacement curve for a cone indentation of a PMMA sample at 20 °C. The unloading curve provides the elastic and plastic strains and, the elastic modulus can be obtained from the slope of the tangent at the point of unloading.

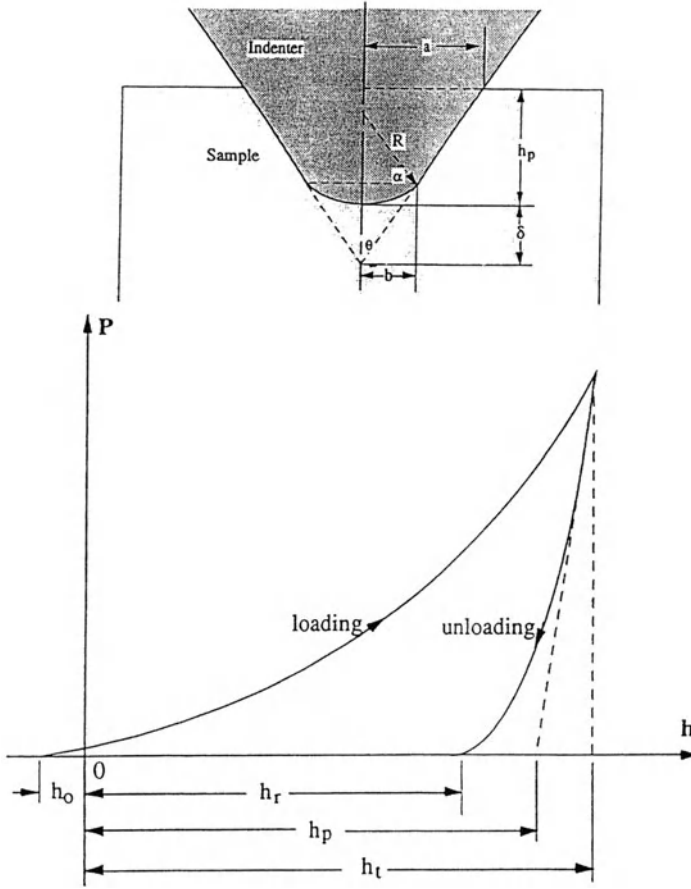


Figure 2: Force-displacement curve during the loading and unloading of a PMMA surface by a conical indenter.

The extraction of hardness and elastic modulus from the loading/unloading, curve, however, requires the application of a suitable curve fitting procedure to the experimental data which is capable of reducing errors caused due to the problem in setting the zero displacement of the indenter (zero error). A statistical curve fitting procedure known as the Box-Cox transformation was used by Briscoe & Sebastian⁵ to fit to the loading-unloading data a curve of the type;

$$P = m(h - h_0)^n \quad (2)$$

where, P is the indentation load, $m = gE^*$ (for the elastic response in loading), h_0 is the zero error in the measured value of h , n is the index of deformation g is a geometric factor and E^* is the reduced elastic modulus which is given as

$$(1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2 \quad (3)$$

E and ν are the Poisson's ratio and moduli of the polymer (subscript 1) and the indenter material (subscript 2) respectively. If the elastic modulus of the indenter is considered to be very high compared to that of polymer, which will generally be the case in hardness studies then E^* may simply be given as $E^* = (1 - \nu_1^2)/E_1$. The reduced elastic modulus is related to the contact stiffness, S , upon unloading near h_t as

$$\frac{\partial P}{\partial h} = S = 2E^*a \quad (4)$$

From the consideration of the geometry of cones and spheres the contact area (in the plane of the surface) may be computed. The contact radius, a , for cones is

$$a = (h_p + \delta) \tan \theta \quad (5)$$

δ and θ are defined in figure 2. Hence, hardness may be calculated as

$$H = P/\pi a^2 \quad (6)$$

SOURCES OF ERRORS IN HARDNESS MEASUREMENT

Though the contact compliance hardness measurement is a very convenient method for material characterisation, there are several sources of significant error which may influence the accuracy of the hardness values. Hence, it is necessary that appropriate precautions are taken while measuring the hardness or during the subsequent data analysis. Such error corrections are more important for micro and nano scale hardness measurements. The common errors are caused due to:

- (1) The zero error for the start of the indentation process.
- (2) The machine compliance originating from the elastic deformation of the force transducer.
- (3) Deviation of the indenter geometry from the nominal form.
- (4) Change in the contact mechanics due to the indenter tip defects such as rounded or broken tip.

These errors and correction procedures have been described by Sebastian⁶.

Without the implementation of an appropriate correction procedure to the hardness data, obtained from the load-displacement curve, there can be large errors in the computed values of hardness or elastic modulus.

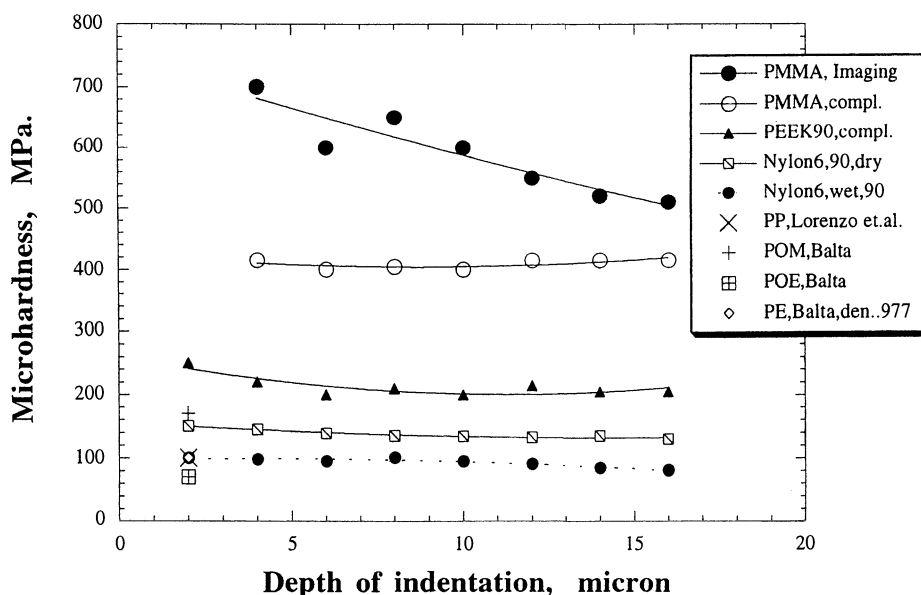


Figure 3: Microhardness of polymers as a function of the depth of indentation. Data obtained from compliance and imaging techniques are reported. ● and ○ are the data for PMMA indentation by a 90° cone using imaging and compliance techniques respectively (see ref. 9). Δ PEEK indented by a 90° cone; and ●-●- Nylon 6 indented by a 90° cone angle under dry and wet (water) conditions respectively. X polypropylene indented at 25°C under a normal load of 0.147 N with contact time of 10 sec using Vickers indenter (see ref. 7). +, ⊕ and ◇ are data for POM, POE and PE (density = 0.977 g. cm^3) respectively using Vickers indenter (see ref. 8).

MICRO HARDNESS OF POLYMERS

Figure 3 shows microhardness data for some polymers as a function of the depth of indentation using the compliance and imaging techniques^{7,8,9}. In this Figure it is observed that the data for PMMA (an amorphous polymer) do not show any dependence of hardness with the depth of indentation whereas those for crystalline polymers (PEEK and Nylon 6) show a small decrease in the hardness with the depth of indentation. This may be due to the presence of a transcrystalline layer on the outer surfaces of the crystalline polymers. The hardness of semicrystalline polymers shows a strong

dependence upon the degree of crystallinity of the polymer (see later). It is observed that the microhardness of polymers depends upon parameters such as temperature, density and microstructure. In addition there are significant time dependent effects. This indicates that microhardness of polymers may be related to these internal (material) and external (ambient) variables.

CORRELATION BETWEEN MICROHARDNESS AND OTHER PHYSICAL AND MECHANICAL PROPERTIES

The microhardness technique when applied to polymers is an effective way of monitoring changes in their physical and mechanical properties. As in the case of metals, it has been shown^{7,8} that for polymers the microhardness (H) is linearly related to the plastic yield stress (σ) with the ratio H/σ approaching 3 for crystalline (plastic) polymers. Tabor¹⁰ showed that for metals which are generally almost entirely plastic in their nature, that the ratio H/σ is equal to 3. Figure 4 shows data for the microhardness as a function of the yield stress for polyethylene. The plot in the inset shows the variation of the ratio H/σ with the degree of crystallinity. The data show that the ratio H/σ approaches 3 only when the polymer has a high degree of crystallinity. The non-crystalline part in the polymer plays a major role in providing the elastic response of the material.

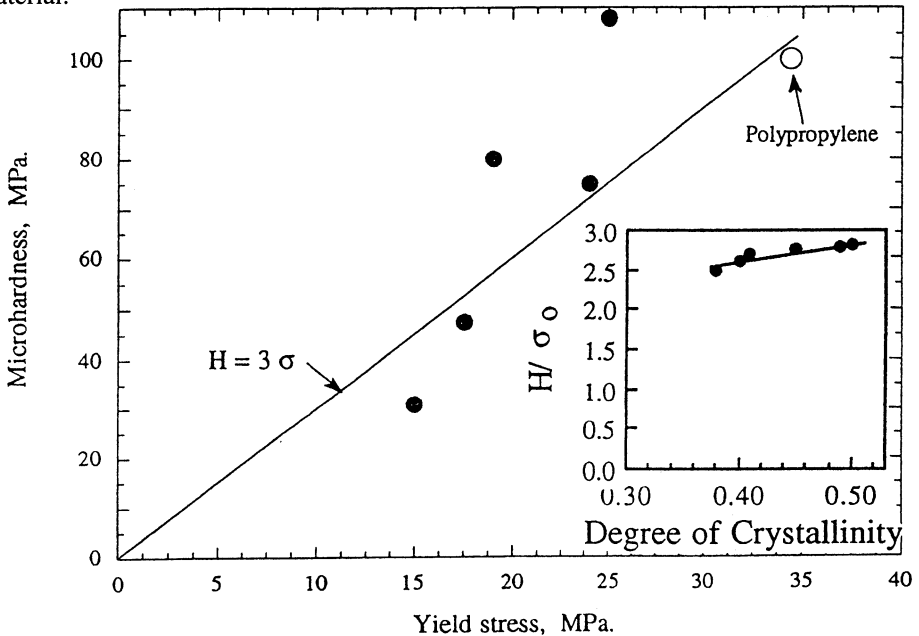


Figure 4: Microhardness as a function of yield stress for polyethylene • [ref. 6] and polypropylene O (see ref. 7). The figure also shows the straight line $H = 3\sigma$ from Tabor's relation.

The elastic modulus of polymers can be related to the microhardness by a power law relation of the form⁹;

$$H = aE^b \quad (7)$$

where a and b are constants. Figure 5 shows a logarithmic plot of the hardness against the elastic modulus for polymers. The data do show that the equation (6) is followed for these polymers.

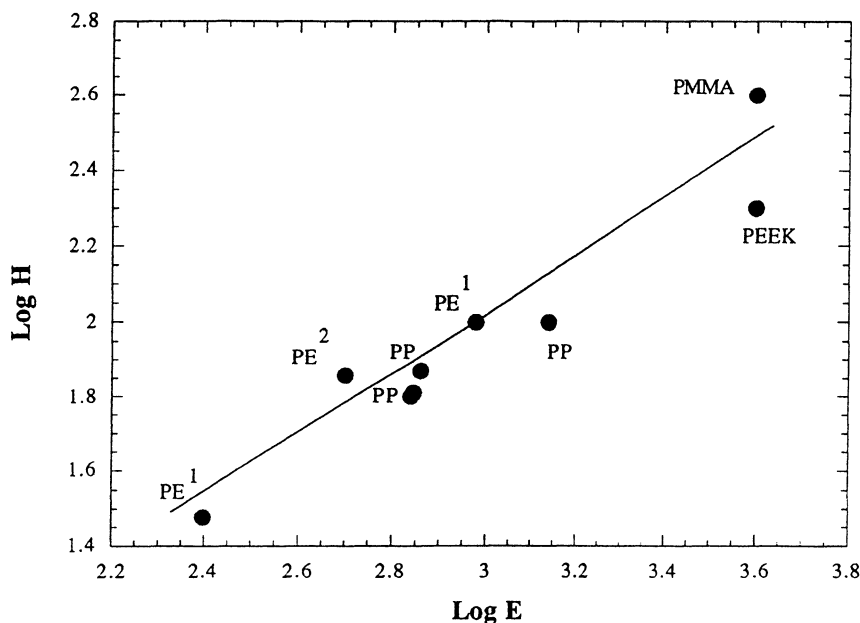


Figure 5: A log-log plot of the hardness as a function of elastic modulus for polymers. The data reported here are for PMMA (ref. 9), PEEK (ref. 9), polypropylene (PP) (ref. 7), PE¹ (molecular weight = 2×10^6) (ref. 8) and PE² (molecular weight = 170 000) (ref. 8).

The microhardness of polymers has also been related to various microstructural parameters. The main factor which determines the hardness of polymers is the distribution and the amount of crystalline and amorphous phases present in the polymer. Balta Calleja⁸ has shown that a rule of mixtures may be used to describe the microhardness of a polymer with crystalline and amorphous phases present. According to this rule,

$$H = H_C\beta + H_a(1 - \beta) \quad (8)$$

where H_C and H_a are the hardnesses of the crystalline and amorphous phases respectively and β is the volume fraction of the crystalline phase.

REFERENCES

1. See for example *The Science of Hardness Testing and its Research Applications*, ASM publication (eds. J.H. Westbrook and H. Conrad) (1973).
2. Chiu, C.H., Lautenschlager, E.P., Greener, E.H., Childress, D.S. and Healy, K.E., (1995) *J. Appl. Poly. Sci.*, **58**, 1661-1668
3. Briscoe, B.J., Sebastian, K.S and Adams, M.J., (1994) *J. Phys. D: Appl. Phys.* **27**, 1156-1162 .
Also see British Standard 903 Part 57 (1987)
4. Johnson, K.L. (1985) *Contact Mechanics*, Cambridge University Press, Cambridge
5. Briscoe, B. J. and Sebastian, K.S. (1996) *Proc. Roy. Soc. Lond. A*, 452, 439-457.
6. Sebastian, K.S., PhD Thesis, (1994) Department of Chemical Engineering & Chemical Technology, Imperial College, London, UK.
7. Lorenzo, V., Perena, J.M. and Fatou, J.G., (1989). *J. Mat. Sci. Letters*, **8**, 1455-1457.
8. Balta Calleja, F.J., (1985) *Adv. Polym. Sci.*, **66**, 117-148.
9. Briscoe, B.J. , Sebastian, K.S and Sinha, S.K., *Phil. Mag.*, **74(5)**, 1159-1169.
10. Tabor, D. (1951) in *Hardness of Metals*, Clarendon Press.

26: The Hopkinson Bar

D J Parry

INTRODUCTION

Most materials show a significant change in mechanical behaviour as the rate of strain (the deformation rate) is increased¹ (see **High Strain Rate Effects**). This is particularly evident at the high strain rates ($>10^2 \text{ s}^{-1}$) which occur under impact or explosive loading conditions. For polymeric materials, both the elastic modulus and the flow stress can increase substantially with strain rate. The split-Hopkinson pressure bar (SHPB) technique is the best established method for determining these dynamic properties of solids at high strain rates in the range of about 10^2 to 10^4 s^{-1} (see refs. 2 and 3). In its various forms, the SHPB technique can produce stress/strain/strain rate data in compression, tension and torsion.

THE SPLIT-HOPKINSON PRESSURE BAR TECHNIQUE

The most frequently used version of the SHPB technique is the compression system, in which a small disc of the material being investigated is sandwiched between two long, high-strength, steel bars called the loading and transmitter pressure bars (figure 1) (see also **Tensile and Compressive tests**).

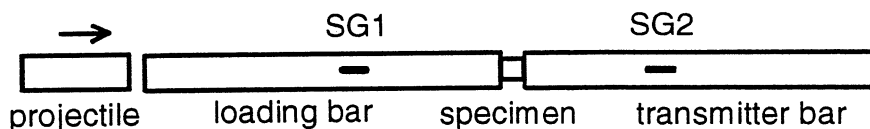


Figure 1: The basic SHPB arrangement.

The free end of the loading bar is subjected to axial impact by a projectile fired from a gas-gun, the projectile usually being made of a rod of the same material and diameter as the pressure bars. The impact generates an approximately flat-topped trapezoidal, elastic stress pulse which travels along the loading bar at about 5 km s^{-1} ($5 \text{ mm } \mu\text{s}^{-1}$) to the test specimen where it is partly reflected and partly transmitted. On each bar there are strain gauges (SG1 and SG2), usually positioned at equal distance from the

specimen, which record the loading (or incident) pulse strain ϵ_I , the reflected pulse strain ϵ_R , and the transmitted pulse strain ϵ_T . The mechanical behaviour of the specimen can be obtained by analysing these pulses, as described in the next section.

SHPB pulse analysis

Elementary plane-wave propagation theory shows that the engineering values of the specimen stress σ_s , strain ϵ_s , and strain rate $\dot{\epsilon}_s$, are given by

$$\sigma_s = (A_B / A_s) E_B \epsilon_T \quad (1)$$

$$\epsilon_s = -(2c_B / L) \int_0^t \epsilon_R dt \quad (2)$$

$$\dot{\epsilon}_s = -(2c_B / L) \epsilon_R \quad (3)$$

L , A_s are the original length and cross-sectional area of the specimen, A_B , E_B and c_B are respectively the cross-sectional area, Young's modulus, and axial wave speed for each pressure bar. By measuring ϵ_T and ϵ_R as a function of time t , the stress/strain/strain rate properties of the specimen can then be found.

It can be seen that the stress in the specimen is directly proportional to the transmitted strain pulse (equation 1) and the strain rate is directly proportional to the reflected strain pulse (equation 3). The strain can be obtained (from equation 2) by numerical integration of the reflected strain pulse using, for example, a simple trapezium method with a sampling interval of $1\mu s$. In practice, the strain gauge circuitry (see **Transducers**) is usually arranged so that the incident and transmitted pulses are recorded as positive quantities. This is done to ensure that the use of equations 1, 2 and 3 leads to the specimen stress and strain being positive in compression.

True stress and strain

In the above derivation of engineering stress and strain (see **Stress and Strain**), the increase of the area of the specimen and the decrease of its length as it deforms in compression have been ignored. Taking these factors into account gives the more realistic true stress σ and true strain ϵ in terms of the engineering values:

$$\sigma = \sigma_s (1 - \epsilon_s) \quad (4)$$

$$\epsilon = -\log_e (1 - \epsilon_s) \quad (5)$$

From equations 4 and 5 it can be seen that since σ_s and ϵ_s are both taken as positive quantities, then σ and ϵ are also positive while $\sigma < \sigma_s$ and $\epsilon > \epsilon_s$ as expected.

A TYPICAL SHPB SYSTEM

In a typical compressive SHPB system, as developed by the present author⁴, the disc specimen is about 8 mm in diameter, and 4 mm thickness, while the bars are made of maraging steel. Each bar is 1 m long and 12.7 mm diameter. The specimen faces in contact with the bars are usually lubricated to reduce frictional effects, which can cause overestimation of the flow stress. The duration of the loading pulse is equal to the time it takes for an elastic compressive wave to travel to the free end of the projectile and return as a tensile wave. For a 25 cm length projectile the pulse duration is about 100 μs . The projectile is fired from the gas gun at speeds up to about 40 ms^{-1} , the impact generating a stress pulse of amplitude up to about 800 MPa.

In figure 1, SG1 and SG2 are usually *pairs* of etched-foil strain gauges (2 mm in length) mounted axially in diametrically opposite positions on the bars. Each pair is wired in series prior to being connected to a bridge circuit. This procedure eliminates any signals due to flexural waves and doubles the output signals due to the axial stress pulses. The gauge signals are transferred to the input channels of a digital storage oscilloscope and then passed to a microcomputer for analysis and storage.

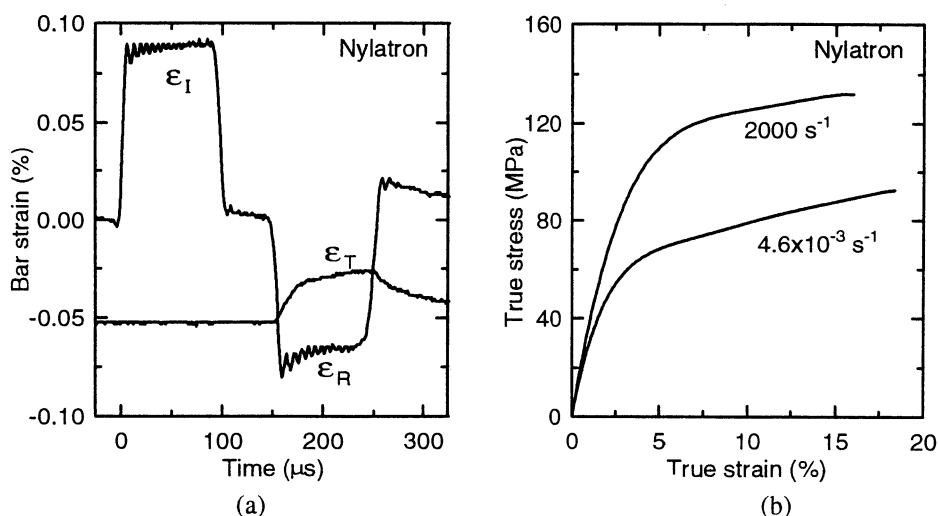


Figure 2: (a) Digital storage oscilloscope traces for a high strain rate test on nylontron. (b) Stress-strain plots for nylontron at low and high strain rates.

Figure 2(a) is an example of an oscilloscope record of pressure bar strain against time for an SHPB test on nylatron (a thermoplastic), with a projectile impact speed of 11 m s^{-1} . The upper trace (from SG1) shows the compressive incident pulse ϵ_I (positive going) followed by a tensile reflected pulse ϵ_R (negative going during the loading part), both of which are present in the loading bar. The lower trace (from SG2) shows the compressive transmitted pulse ϵ_T (positive going) recorded in the transmitter bar. The transmitted pulse starts at virtually the same time as the reflected pulse because of the equidistant siting of the strain gauges with respect to the specimen. Figure 2(b) shows a plot of the true stress against true strain for the experiment corresponding to figure 2(a), as well as for a quasistatic experiment carried out with a conventional screw machine. The substantial increase in flow stress with strain rate is clearly evident.

FURTHER CONSIDERATIONS

The high frequency oscillations shown on the incident and reflected pulses in figure 2(a) are called Pochhammer-Chree oscillations. They are a result of the short risetime impact of the projectile on the loading bar. It is possible to reduce these oscillations by using a three-bar system in which a third bar is inserted between the loading bar and the projectile⁵. This extra bar is made of a lower strength steel than the main bars and has the effect of dampening the high frequencies associated with the pulse.

REFERENCES

1. Harding, J. (1987) *Materials at High Strain Rates*, Elsevier Applied Science, London.
2. Lindholm, U.S. (1971) *Techniques in Metals Research* 5 part 1 (ed R F Bunshah), Interscience, New York, pp. 228-240.
3. Wasley, R.J. (1973) *Stress Wave Propagation in Solids*, Marcel Dekker, New York
4. Parry, D.J. and Griffiths, L.J. (1979) A compact gas gun for materials testing. *J. Phys. E: Sci. Instrum.*, **12**, 56-58.
5. Parry, D.J., Walker, A.G., and Dixon, P.R. (1995) Hopkinson bar pulse smoothing. *J. Phys: Measurement Science and Technology*, **6**, 443-446

27: Impact strength

P S Leever

INTRODUCTION

It is well known that plastics components are often more prone to failure under impact than under slowly-applied or constant load. This tendency is promoted by low temperatures and the presence of a sharp notch, and is of particular concern for tough, unreinforced crystalline thermoplastics, in which a sudden blow can precipitate brittle fracture more typical of a glassy polymer like PMMA. Impact tests (usually Charpy or Izod - see **Impact and Rapid Crack Propagation**) are widely used for such materials, and 'impact strength' data are widely quoted in material specifications. This is partly because such materials are often selected for components such as bumper bars or blow-moulded containers, which are likely to suffer impact. The popularity of impact strength data owes more, however, to the ease and speed with which tests can be conducted, and to a widespread (and incorrect) belief that impact performance somehow characterises the overall susceptibility of a polymer to brittle behaviour. In fact, it is important to treat impact strength data warily even for their primary purpose.

ENERGY ABSORPTION IN IMPACT

Whether measured by Charpy, Izod or tensile-impact methods, impact strength is primarily an index of resistance to *fracture*. The focus of attention is the transition in behaviour from 'tough' (where the energy expenditure required to create fracture surface is large) to 'brittle' (where it is small), see **Ductile-Brittle Transition**. Since early impact test methods were unable to record a load/time trace, they were designed to estimate the total energy absorbed by the specimen during a test, and it became common to express the 'strength' as the ratio of absorbed energy to fracture surface area.

This definition of impact strength makes it very difficult to distinguish a material in which fracture initiates at high load but propagates with little more energy absorption, from one in which fracture initiates at low load but subsequently requires more driving energy. Since the weighting between initiation and propagation effects differs from geometry to geometry, so do impact strength results. Moreover, the energy absorbed by the fracture surface in a polymer may be very small indeed and can easily be mislaid amongst other energy losses within the system. Although the initial impact speed is specified (usually 2-5 m/s), the displacement rate changes in an uncontrolled way during the test and with it changes the kinetic energy. Differences in specimen size and geometry also mean that a given impact speed may yield a wide range of strain rates or notch-loading rates. The overall effect of these and many other uncertainties is that

materials rank differently according to different test methods as well as under different external factors such as temperature.

FACTORS AFFECTING IMPACT STRENGTH

The principal factors affecting impact strength are temperature, thickness and notch radius¹. Whereas temperature is a genuine 'extensive' parameter for the material thickness and notch radius are geometric features of the test. However, impact strength is too crude a concept to allow this sort of distinction. The impact speed being fixed, notch root radius becomes the determining factor for strain rate at the notch root. Strain rate (as well as the constraint, which depends on the thickness) will strongly affect the yield stress and hence the ability of the material to blunt the crack during loading. Reducing the notch tip radius and increasing the thickness both favour brittle fracture and tend to reduce impact strength. The effect of increasing temperature on impact strength is often decisive. Again, this probably arises partly from the strong reduction in yield stress, and partly from the reduction in tensile modulus - which, for a given impact speed, reduces the loading rate. Thermoplastics usually show a temperature independent plateau in impact strength at low temperatures (corresponding to brittle fracture) with a sharp upswing at a temperature which marks the transition to tough behaviour. The sharper the notch, the lower the plateau strength and the higher the temperature needed to induce a brittle tough transition (see **Ductile-Brittle transition**). However, the notch-sensitivity of polymers varies immensely: tough, crystalline polymers such as the engineering thermoplastics generally have most to lose, although rubber **toughening** or short-fibre reinforcement bring significant improvements.

IMPACT FRACTURE TOUGHNESS

The sensitivity of impact strength to notch sharpness is one of the strongest arguments for using a linear elastic fracture mechanics (LEFM) approach. Although the use of an instrumented striker is an advantage (see **Falling Weight Impact Tests**), Charpy and Izod configurations can still be used, but the initial notch is replaced by a crack which is made to be as sharp as possible.

The real difference lies in the processing of results. In essence, the impact strength is multiplied by a factor which depends only on geometry and crack length² to yield an impact fracture resistance G_c (and hence, an impact fracture toughness K_c). Each material should show the same G_c or K_c in any geometry, allowing the use of impact data in design calculations. It has never been possible to use impact strength data in this way. In practice, however, recent results for tough polymers re-emphasise the strong dependence of impact fracture toughness on impact speed. This was, of course, to be expected (the data could otherwise be measured statically!) but it also re-introduces geometry dependence, since different impact speeds translate into different 'effective'

crack loading rates in different geometries.

In summary, whilst progress has been made in identifying material properties which characterise impact strength, their use in design remains undeveloped. Conventional impact-strength data remain useful for comparing grades or variants of a single specified polymer, but different polymers can only be compared properly by exploring a wider range of temperature, notch radius or specimen thickness.

REFERENCES

1. Turner, S (1983) *Mechanical Testing of Plastics* (2nd edition) George Godwin (London).
2. ISO/TC61/SC2. ISO Draft Standard "*Plastics - Determination of fracture toughness G_c and K_{Ic} - Linear elastic fracture mechanics (LEFM) approach*".

28: Impact and rapid crack propagation Measurement Techniques

P S Leever

Some plastics which show outstanding ductility under slowly-applied loads can fail in a brittle manner under impact. This tendency is enhanced by low temperatures and by the presence of a sharp notch, and it is of particular concern for the tough crystalline thermoplastics which have earned most respect as engineering materials. For this and other reasons (including their speed and ease of use), impact tests are accorded a status comparable to tensile tests in specification data for plastics.

Unfortunately, there is a gap between the information which impact tests are expected to provide and that which they actually deliver. **Falling Weight Impact Tests** realistically simulate service impact events, but do not provide geometry independent data. The widely used Charpy and Izod tests claim to provide a measure of 'strength', but it is geometry specific and cannot be used for design. **Fracture mechanics** versions of these tests provide results which are more consistent, but still appear to be test-dependent. Finally, Rapid Crack Propagation tests measure the resistance of the material to the fast fracture process which often follows impact crack initiation, but may be over conservative as a measure of impact strength.

CLASSICAL IMPACT BEND TESTS

The ISO 179 Charpy impact test¹ used for plastics differs little from that developed for steels at the turn of the century. In essence, it subjects a beam (usually 10 x 10 x 80 mm, resting on 62 mm span supports) to fast flexural displacement at a point opposite a central notch (Fig. 1). The notch may be omitted but, if used, it must conform to standard dimensions of depth (usually 20% of the thickness) and root radius. The use of a pendulum striker, and the practice of recording the energy which it loses during impact (and which, therefore, is assumed to be absorbed by the specimen) hark back to an era which preceded high-rate test machines and high-frequency load instrumentation. After correction for friction and air resistance and division by the ligament area, this energy becomes a force per unit length of notch front; termed 'notch(ed) impact strength' or, if unnotched, just 'impact strength'. The ratio of notched to unnotched strength is occasionally quoted as the 'relative notch impact strength'. The impact strength may be quoted in J/m or, e.g. J/10 mm, or as an energy per unit area (kJ/m²).

The (ISO 180) Izod impact test² method has remained more popular in the USA. The specimen is similar in geometry, but is clamped as a cantilever built-in at the notch plane (Fig. 1) and struck a fixed distance above it. Amongst several difficult features of this method are the accuracy with which the notch must be aligned with the top surface of

the clamp, and the choice of a clamping force which will hold it there during impact. Some materials are sensitive to this force, but the standard neither specifies it nor commits itself unequivocally to a method for controlling it.

Both test methods are number amongst those politely termed '*ad hoc*' and respected more for their familiarity than for their scientific stature. One of many uncertainties is that the initial energy of the pendulum is loosely specified, and anything between 20% and 90% of this energy may be lost during impact, so that the character of the test may change significantly during its duration. Numerical results for impact strength may be appended or replaced by a descriptive term ('complete break', 'hinge break', 'partial break' or 'non break') which is often more informative. In fact, possibly the most informative way to use either method is to test many specimens across a range of temperatures and thereby identify transition temperatures which separate these failure types.

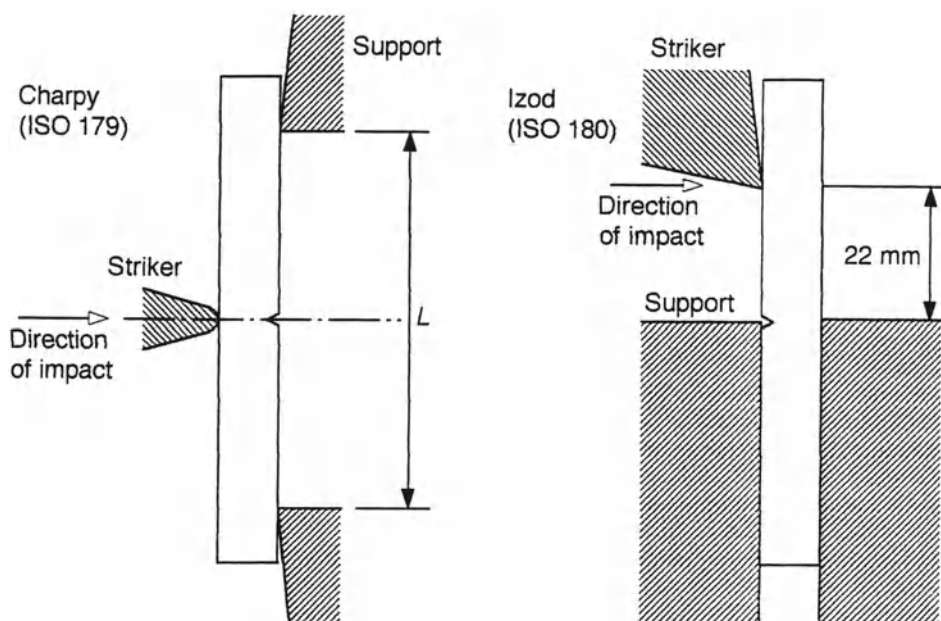


Figure 1: Standard notched impact bend test methods: (a) Charpy ISO 179, (b) Izod ISO 180.

IMPACT FRACTURE TESTS

Impact fracture tests embody the precepts of linear elastic fracture mechanics: the initial presence of a sharp notch, and the use of a Fracture Mechanics analysis to yield a fracture toughness or fracture resistance. G_c , the energy per unit area of fracture surface, is determined at the moment of fracture initiation (usually identified as peak load). Even for a perfectly brittle, linearly elastic material showing a 'sawtooth' load/time trace, G_c is not equal to the absorbed energy U_e divided by the ligament area, but there is a closed relationship

$$G_c = U_e/BW\Phi \quad (1)$$

where BW is the *gross* cross-sectional area of the specimen and Φ is a tabulated function of crack depth³. For a sharply-notched ISO 179 specimen, $\Phi \approx 2$, so that G_c is about half of the impact strength, though it is expressed in the same units. Some further details of the method are given elsewhere (see **Falling weight impact tests**).

The philosophical advantage of resorting to fracture mechanics is that, in principle, fracture data become portable to other geometries (indeed, the draft standard procedure⁴ averages G_c over a range of crack lengths, itself guaranteeing some geometry independence). Whilst this is probably true for brittle plastics such as PMMA, recent evidence shows that for tough thermoplastics G_c remains profoundly sensitive to impact speed.

RAPID CRACK PROPAGATION TESTS

'Complete break' impact tests have usually failed by a Rapid Crack Propagation (RCP) event, or by a succession of them separated by crack arrests. The initiation of such a crack jump can be characterised by G_c , but the subsequent propagation phase is inherently uncontrolled and unsteady. The study of RCP in itself demands test methods which stabilise and sustain it under a constant, measured driving force G_D . The objective is to extend the relationship between fracture resistance and crack speed from the slow crack growth region (less than about 10 mm/s) up to hundreds of m/s. It is now believed that the minimum value of G_D and the minimum value of impact G_c are equivalent, and a true material property.

Several rapid crack propagation test methods were inspired by the Robertson crack-arrest test for steels, in which a crack was injected into a wide, uniformly-stressed plate from a super-cooled and impact-loaded 'tab' which extended from half-way down one side. This basis is particularly suitable for tough plastics in which initial notches are quickly blunted on loading, making it difficult to set off RCP. A 'Modified Robertson' method using a pressurised pipe specimen rather than a plate, was the first rapid crack propagation test to be adopted (in Belgium) to specify plastic pipe.

Another approach is embodied in the High Speed Double Torsion test⁵. The double

torsion test is used for its ability to sustain constant-speed slow crack growth under a slow displacement rate. The high speed version merely applies a much faster displacement rate, using a free striker. This option is less attractive for other slow crack growth specimens because they have more complicated dynamical characteristics. Although plastics with non-linear-elastic behaviour and strong crack-speed sensitivity make analysis difficult, the High Speed Double Torsion method has yielded the first data on fracture toughness as a function of crack speed in tough polymers.

REFERENCES

1. ISO 179: 1993 Plastics - Determination of Charpy impact strength, International Organisation for Standardisation (ISO)
2. ISO 180: 1993 Plastics - Determination of Izod impact strength, International Organisation for Standardisation (ISO).
3. Williams, J.G. (1987) *Fracture Mechanics of Polymers*, Ellis Horwood (London)
4. ISO/TC61/SC2. ISO Draft Standard, Plastics - Determination of fracture toughness G_c and K_{Ic} - Linear elastic fracture mechanics approach. International Organisation for Standardisation (ISO).
5. Ritchie, S.T.K. & Leever, P.S. (1993) The High Speed Double Torsion Test, in *Impact and Dynamic Fracture of Polymers and Composites,ESIS 19* (Eds. Williams, J.G. and Pavan, A.), Mechanical Engineering Publications, London, 137-146.

29: Manipulation of Poisson's Ratio

K E EVANS

INTRODUCTION

Poisson's ratio is the ratio of the transverse compressive strain in a material to the applied longitudinal tensile strain. Alternatively, it may be described as related to the principal off-diagonal element of the elastic stiffness matrix. It is a fundamental property that affects most aspects of the mechanical properties of materials including toughness, sound propagation, thermal shock and critical buckling failure. As such, any method that enables the manipulation of Poisson's ratio is as likely to have important technological consequences as the many attempts to improve stiffness.

Nevertheless, until very recently, Poisson's ratio has not been a quantity that has received much attention. Many textbooks still quote the Poisson's ratio of most materials as being about 0.3 with some anomalies, such as rubber approaching 0.5. Despite the fact that it has been known, for over 150 years, that the Poisson's ratio of isotropic materials might have any value between -1 and 0.5, it was assumed that, for no obvious reason, it was always close to 0.3.

FOAMS

The position began to change in 1987 when a paper was published demonstrating a foam with a Poisson's ratio of -0.7^1 . This large negative Poisson's ratio was of interest because it had been achieved with an isotropic material. It is well known that anisotropic composites can be produced with either very large positive or negative Poisson's ratios² but this does not necessarily produce the benefits associated with the isotropic case.

The foam was given a negative Poisson's ratio by first taking a conventional foam and triaxially compressing it at temperature so as to permanently deform its internal microstructure. After cooling the foam, this new deformed microstructure contained collapsed, or re-entrant cells which, when stretched, attempted to revert to their original shape and thus expanded in all directions when stretched in only one. By compressing different foam specimens to different extents it is possible to produce a set of foams with a wide range of Poisson's ratios.

Given the nature of the material - an open-celled foam - it may be argued that the negative Poisson's ratio was produced by a manipulation of structure rather than material and hence was not really an intrinsic material effect. However, such a network may be embedded in a composite, and provided the relative stiffness of the network is high enough, the resultant composite will also have a negative Poisson's ratio³.

MICROPOROUS POLYMERS

In 1989, it was shown that expanded PTFE (e-PTFE) had a large negative Poisson's ratio⁴. As this material is highly anisotropic it can (and does) have a Poisson's ratio as large as -12. This property has ramifications in a number of applications of e-PTFE, notably as a gasket material and as a prosthetic artery. By duplicating the microstructure of e-PTFE, it has been possible to produce negative Poisson's ratios in both polyethylene⁵ and polypropylene⁶. Indeed, by suitable control of the processing conditions, a considerable range of Poisson's ratio has been achieved between -12 and +6.

All of these materials have in common a complex microstructure of nodules and fibrils, the interconnectivity of which operates to produce varying degrees of lateral motion - much like an umbrella opening - when longitudinal strain is applied. The benefits of manipulating the Poisson's ratio in polyethylene has been demonstrated in changes in its indentation resistance⁷. This is expected to have important ramifications on the wear behaviour of, for example, UHMWPE in hip joints.

Further examples of the benefits of manipulating Poisson's ratio at the microstructural level include the development of novel piezo-composites for optimising electromechanical coupling in novel actuator materials.

MOLECULAR AUXETICS

In 1991, a paper proposed the first molecular architecture that might enable the manipulation of Poisson's ratio⁸. This architecture in its most conventional form mimicked a two-dimensional honeycomb where the cells were some 1.5 nm across. By manipulating the shape of the cell, various positive Poisson's ratios are achievable. Alternatively, by changing the connectivity of the junction points of the cells, a bow-tie form could be produced that has a negative Poisson's ratio. These negative Poisson's ratio materials are referred to as auxetic materials. Again, by manipulating the cell shape, a range of different negative Poisson's ratios is achievable⁹.

So far it has not been possible to synthesise this network. However, progress has been made in creating a three-dimensional version¹⁰ - in effect, a molecular foam - from which an auxetic equivalent should be achievable. The approach used here is to create a very regular 3-D polymer network by using highly co-ordinated reactions. An alternative approach is to create a polymer gel with a much more irregular structure where, by controlling the degree of swelling and subsequent shrinkage of the gel, a variation in Poisson's ratio can be achieved. A polymer gel with a high dilatancy has been produced¹¹ but the exact value of its effective Poisson's ratio is not known.

Most recently, an alternative approach to achieving an auxetic polymer has been suggested using a liquid crystal polymer containing hinged units which, when the polymer stretches, hinge outwards to widen the molecule as it elongates. X-ray evidence indicates that this structure increases in volume when stretched but the Poisson's ratio

has not yet been measured.

CONCLUSION

Finally, consideration should be given to why Poisson's ratio has not been treated as a parameter that may be manipulated until so recently. The obvious answer is a prevalence in nature of so many materials with a restricted range of Poisson's ratios between 0.25 and 0.35. As has shown in this article, the manipulation of Poisson's ratio is a result of the deformation of a complex architecture which may well be both unusual and uncommon in nature. One area where such architectures may be found is in biological materials and indeed there is evidence that skin has a negative through-thickness Poisson's ratio. However, there is as yet insufficient data to confirm whether Poisson's ratio is naturally manipulated in biological polymers.

REFERENCES

1. Lakes, R. (1987) *Science*, **235**, 1038
2. Tsai, S.W., Hahn, H.T. (1980) *Introduction to Composite Materials*, Technomic Publishing, Lancaster, USA.
3. Evans, K.E., Nkansah M.A., Hutchinson, I.J., (1992) *Acta Metall. Mater.*, **40**, 2463.
4. Evans, K.E., Caddock, B.D., (1989) *J.Phys.D.Appl. Phys.*, **22** 1883,
5. Alderson, K.L., Evans, K.E., (1992), *Polymer*, **33** 4435
6. Pickles, A.P., Alderson, K.L. Evans, K.E., (1996), *Poly.Eng.Sci.*, **36**, 636.
7. Alderson, K.L., Pickles, A.P., Neale, P.J., Evans, K.E. (1994), *Acta.Metall.Mater.*, **42** 2261.
8. Evans, K.E., Nkansah, M.A., Hutchinson, I.J., Rogers, S.C. (1991), *Nature* **353**, 124.
9. Evans, K.E., Alderson, A., Christain, F.R. (1995) *J.Chem. Soc. Faraday Trans.*, **91**, 2671.
10. Wu, Z., Moore, J.S., (1996) *Angew Chem. Int.Ed. Engl.*, **35**, 297.
11. Hirai, T., Nemoto, H., Hiral, M., Hayashi, S., (1994) *J.Appl.Poly.Sci.*, **53** 79.

30: Measurement of Creep

D R Moore

Creep experiments involve the application of a constant stress and the subsequent measurement of strain as a function of time at some constant temperature. The loading configuration can be uniaxial tension, uniaxial compression, flexure, torsion or some combination of these modes (see **Tensile and Compressive Testing, Flexural and Torsion Testing**). This section will cover the first four of these configurations.

UNIAXIAL TENSILE CREEP.

A tensile creep apparatus is used to obtain the time dependent compliance or modulus function at a specific temperature. The equipment is required to apply a constant load to a uniform cross section specimen and then to measure the change in axial dimensions of the specimen. The creep function (the change of axial strain with time) is seldom necessary at strains larger than a few percent (i.e. $\epsilon \sim 0.03$) and therefore strain (ϵ) can be simply defined as

$$\epsilon = \Delta l / l_0 \quad (1)$$

Where l_0 is a gauge length in the specimen and Δl is the increase in this length caused by the application of the stress. In order to obtain accuracy, consistency and resolution in the measurement of strain it is necessary to use an extensometer (see **Transducers**) attached to the specimen, rather than use a "cross-head" movement detector often available on universal testing machines. The method of detection of length change can be via an electrical transducer or by an optical device. It is usual to be able to detect strains of about 10^{-3} (i.e. 0.1%) for polymers, and often with resolution upto one hundredths of this strain. Therefore, if the gauge length were to be 100 mm (a typical value) then increments of length increase should be detectable better than about 0.1 mm. The extensometer will need to be attached to the test specimen and for polymers with relatively low levels of stiffness, there is a need for this device to be low in mass and non-indenting.

Application of load should be along the axial length of the specimen, without distortion of the specimen and without friction in the moving parts of the apparatus. The time taken to apply the load can also be critical. It should be applied smoothly to avoid dynamic transients in stress and should be applied in a time such that strains are not monitored within 10 times this time. For example if strains need to be monitored from 100 seconds after application of the constant load then the load must be established within 10 seconds.

In evaluating the creep behaviour of a glassy polymer, with a short term modulus of

3 GPa, then a 0.01 strain is achieved with the direct application of 75 Kg. (assuming a specimen of cross section 4 mm by 6 mm). This is difficult to achieve by direct loading and a lever device is usual to assist the application of load (lever arm ratios of 5:1 are common). When fibre reinforced polymers are tested, where the modulus can increase by a factor of three, then the use of a lever loading arm becomes a practical necessity. Universal testing machines do not require such devices but have limitations in the achievement of specimen axial alignment. When dealing with polymers at test temperatures above their glass-rubber transition (e.g. polyethylene and polypropylene at 23 °C) then the modulus will have reduced by an order of magnitude (to around 0.3 GPa) and direct loading of the specimen is necessary to ensure minimum friction of the moving parts. Consequently, some versatility is required in the design and engineering of the creep apparatus.

UNIAXIAL COMPRESSIVE CREEP.

Many of the design requirements for an apparatus for uniaxial compressive creep are similar to those discussed for tensile creep. There are, however, some special considerations in the design of the test geometry. The usual long slender tensile specimen (length to transverse dimension ratio l/t of about 40) will tend to buckle at small loads. This is overcome by reduction of this l/t ratio, but if this ratio becomes too small then large frictional forces are generated between the specimen and load bearing anvil system (see **Tensile and Compressive Testing**). For example, if the specimen has a square cross-section of dimension t then the applied stress σ_A generates a much larger true stress σ_t in the specimen, given by

$$\sigma_t = \sigma_A (1 + \mu l/4t) \quad (2)$$

With μ being the coefficient of friction between specimen and anvil. In practice, the use of a grease between specimen and anvil can reduce this frictional term and allow a sensible choice of specimen dimensions.

CREEP IN FLEXURE.

The bending of a beam provides a simple method for the determination of modulus E through the measurement of bending stiffness F/δ

$$F/\delta = kEI \quad (3)$$

Where F is a constant applied force (for the creep experiment), δ is a measured displacement of a beam specimen (measured as a function of time for creep) and I is the second moment of area for the beam. For example, for a uniform rectangular prismatic

beam of length w and thickness b loaded in three point bending where the support span is S then modulus as a function of time $E(t)$ is obtained by measuring the time dependent central displacement $\delta(t)$ for a constant applied force:

$$E(t) = F S^3 / \delta(t) b w^3 \quad (4)$$

Equation 4 stems from linear elastic theory and therefore when the central displacements become large (i.e. greater than half the specimen depth) then the geometric configuration becomes non-linear and major modification to this expression become necessary. Consequently, this approach is only suitable for low strain determinations of creep: typically less than 0.5%.

CREEP IN TORSION.

Small strain creep experiments in shear can be obtained by torsion of a rectangular beam type specimen (see **Torsion and Bend Tests**). For example, some workers have used the same beam geometry for bending and torsion. Shear modulus, as a function of time $G(t)$ can then be determined by application of a constant torque T and measurement of the angular twist of the specimen θ

$$G(t) = T l / k \theta \quad (5)$$

Where l is the length of the specimen subjected to torque, k is a shape factor related to the width a and thickness b of the specimen and these have been calculated for small strain deformations by Nederveen and van der Vaal. Equation 5 applies for only small deformations (strains less than 0.005) but provides a helpful method for obtaining the creep function for shear modulus.

REFERENCES.

1. Thomas D.A. and Turner S. (1969) *Experimental technique in uniaxial tensile creep testing in Testing of Polymers*, Vol 4 (ed. Brown, W.E.) Interscience
2. Bonnin J.M., Dunn C.M.R., Turner S. (1969). A comparison of torsional and flexural deformations in plastics, *Plast & Polym* 517,
3. Nederveen C.J., van der Vaal C.W. (1967) A torsion pendulum for the determination of shear modulus and damping around 1Hz, *Rheologica Acta*, 6, 4.

31: Measurement of Poisson's Ratio

K E EVANS

INTRODUCTION

Poisson's ratio is defined as

$$\nu_{xy} = \frac{-\epsilon_y}{\epsilon_x} \quad (1)$$

Where ϵ_y is the transverse strain resulting from an applied longitudinal strain ϵ_x . The minus sign is included so that ν_{xy} is positive for most materials since, under tension, most materials contract laterally and vice versa (see **Manipulation of Poisson's Ratio** where negative Poisson's ratio, or auxetic, materials are described).

Since most materials have a Poisson's ratio much less than one (~ 0.3 is very common) then lateral strains are always considerably less than longitudinal strains. Since the direct measurement of strain is always difficult in the elastic region, any errors will be compounded in calculating the Poisson's ratio. Strictly speaking, Poisson's ratio is a constant and is defined in the limit of small strain. The combination of these various issues makes the direct measurement of Poisson's ratio a difficult problem. Until recently ν_{xy} has been assumed to be fairly constant for a wide range of materials. However, interest has been recently revived with the production of materials with a wide range of different Poisson's ratio, many of them polymers¹.

Another important issue is that Poisson's ratio is often strain dependent. For such materials it is more appropriate to refer to a Poisson's function

$$\nu_{ij} = -\frac{\Delta\epsilon_j}{\Delta\epsilon_i} \quad (2)$$

where Poisson's function is defined by the gradient of the ratio of strains, in direct analogy to the tangent modulus.

MEASUREMENT TECHNIQUES - STATIC

The normal and most straightforward method for measuring Poisson's ratio is by measuring lateral strain whilst conducting a normal mechanical tensile test². Under such circumstances lateral and longitudinal strain may be measured either by LVDTs, clip gauges, or by applying strain gauges (see **Transducers**). In the former two cases there may be problems in obtaining sufficient accuracy to measure Poisson's ratio. In the

latter case there can be problems with bonding the strain gauge and the strain range will be limited so it is unlikely that Poisson's function can be measured. Normally engineering strains are calculated. However, this has recently been shown to produce highly anomalous results in strain dependent materials and true strain is preferable³.

Optical extensometry may also be used and this often has the advantage of covering a wider strain range, where non-linearity is important. It is often the only technique that may be used with soft or biological polymers. Direct video extensometry with magnifications of the order of 200 x may be sufficient. Otherwise interferometric techniques may be required for higher accuracy⁴

Some papers infer a value for Poisson's ratio from a measurement of tensile modulus, E and shear modulus, G using the formula⁵

$$\nu = \left(\frac{E}{2G} \right) - 1 \quad (3)$$

However, this assumes that the material is isotropic (seldom exactly true) and that the shear modulus has been accurately measured (often difficult). This technique is not advised.

MEASUREMENT TECHNIQUES - DYNAMIC

Dynamic mechanical tests are also often used to measure Poisson's ratio. The most common technique measures the speed of sound waves passing through the test sample in various directions and from this information, providing the density is known, a complete set of elastic constants can be obtained⁶.

For isotropic materials this is a relatively convenient method as there are only two unknown independent variables (E and ν , say). However, for anisotropic materials (e.g. drawn polymers or reinforced polymers) it is not uncommon to have at least nine unknown variables. A further problem with this technique is that the sound waves must be propagated through different (preferably orthogonal) directions. Ideally a cubic specimen with the corners cut off⁷ provides the best test geometry but this is often not available. Most specimens commonly come as thin sheet and it is often not possible to measure with sufficient accuracy through the thickness.

A further problem with the method is that many materials, particularly polymers, have highly strain-rate dependent properties. Acoustic techniques commonly work at frequencies anywhere between 0.5-5.0 MHz. Hence the elastic constants obtained at these frequencies may be very significantly different to the static properties. Finally, since the technique relies on vibrating the sample at small strains, it is not possible to obtain strain-dependent values.

CONCLUSION

Other techniques have been developed, such as laser Brillouin spectroscopy⁸ or acoustic microscopy for small samples or laser Doppler vibrometry⁹ for rough samples or simple dilational methods¹⁰ measuring volume changes.

However, to avoid any ambiguity, the direct measurement of true lateral and longitudinal strain, in order to obtain the strain dependent Poisson's function, is to be preferred.

REFERENCES

1. Lakes, R., (1993) *Adv. Mater.* **5**, 293
2. ISO 527-1 (1993), *Plastics Determination of Tensile Properties*
3. Alderson, K.L., Alderson, A., Evans, K.E. (1997), *J.Strain Analysis*, **32**, 896.
4. Chen, G.P., Lakes, R.S. (1991), *J.Mat.Sci.*, **26**, 5397.
5. Migwi, C.M. Darby, M.I., Yates, B. (1994), *J.Mat.Sci.* **29**, 3430
6. Read, B.E., Dean. G.D., (1978) *The Determination of the Dynamic Properties of Polymers and Composites*, Adam Hilger Ltd., Bristol..
7. Ashman, R.D., Cowin, S.C., Van Buskirk, W.C., Rice, J.C. (1984), *J.Biomech.*, **17**, 349.
8. Yeganeh-Haeri A., Weichner, D.J., Parise, J.B. (1992) *Science*, **257**, 650.,
9. Dubbleday, P.S., (1992) *J.Acoust.Soc.Am.*, **91**, 1737.
10. Rinde, J.A. (1970) *J.Appl.Poly.Sci.*, **14**, 1913.

32: Molecular Weight Distribution and Mechanical Properties

T Q Nguyen and H H Kausch

INTRODUCTION

After the chemical structure, the polymer chain length and its distribution are undoubtedly the next most important molecular parameters controlling the physical, mechanical and processing properties of plastic materials. Change in material properties with increasing molecular weight (MW) without a change in chemical composition is well-exemplified by the series of n-alkanes. For low MW paraffins, the load bearing capacities are nearly zero since short chains in the bulk material may easily slip past each other when subjected to mechanical stress. In higher MW polyethylene (PE), the increase in the number of weak van der Waals interactions per chain can effectively immobilize the macromolecule in an entanglement network. Depending on MW and its distribution (MWD), PE can exist under a variety of formulations, each one with tailored properties for specific applications. The different commercial grades include low MW resins ($\sim 10^3$ daltons) used as hot melt adhesives ultra-high MW polymers ($\sim 10^6$ daltons) aimed at demanding applications in which high draw ratio (gel-spinning) or high **wear** and **fatigue** resistance (hip prostheses) are required, and bimodal MWD products with unique mechanical and processing properties, employed in the fabrication of large diameter PE pipes.

PROPERTIES CORRELATABLE WITH MWD

Physical properties

glass transition temperature
softening temperature
phase diagrams in solution
adsorption.

Mechanical properties

elasticity modulus (uncrosslinked)
tensile strength
elongation at break
low temperature toughness
flexural strength
impact strength

tear strength
 fatigue life
 hardness
 scratch resistance
 coefficient of friction
 resistance to environmental stress cracking

Rheological and processing properties

melt viscosity ($\propto M^{3.4}$)
 energy storage in melts ($\propto M^7$)
 creep
 stress relaxation and internal loss (rubbery region)
 melt fracture
 die swelling
 drawability
 film forming properties

Clearly, the relation between MW and MWD with mechanical properties is of great technical importance and has attracted much research interest since early in the history of polymer science. In 1936 Douglas and Stoops reported that the tensile strength (σ_b) of vinyl chloride-vinyl acetate copolymers could be expressed as a linear function of $1/M$. This empirical dependence was later confirmed by Flory¹ who extended its applicability to polydisperse samples. Stated in general terms, the equation originally proposed by Flory could be reformulated as

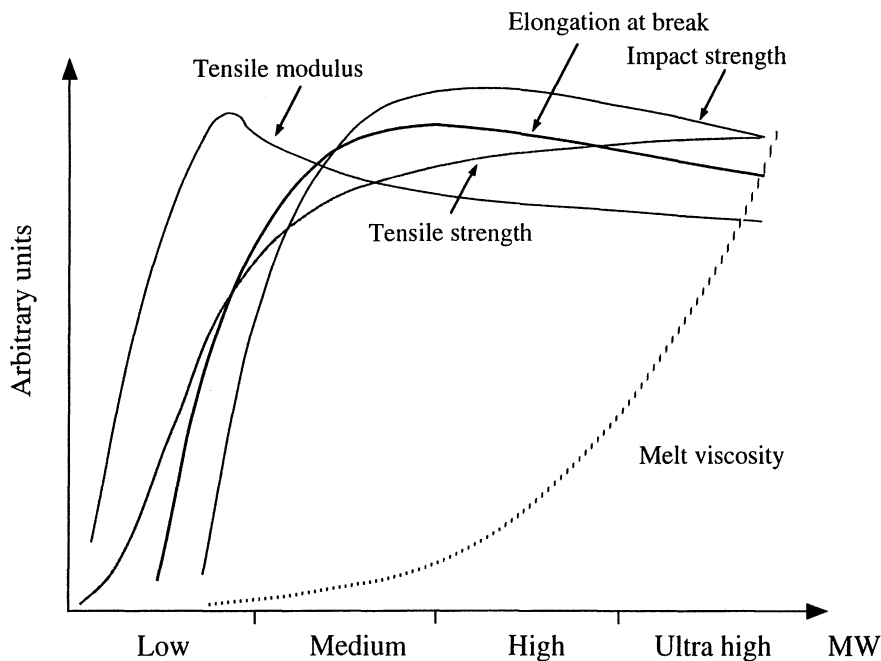
$$P = A_p - \frac{B_p}{\overline{M}_p} \quad (1)$$

where P is the property, A_p and B_p are positive constants and $\overline{M}_p$ some average MW which has to be defined with respect to the property. At the molecular scale, chain ends constitute a major point of weakness in transmitting covalent bond strength. In addition, chain ends are less constrained and can become more easily activated than inner segments. Therefore, a logical starting point was to associate mechanical properties with the number-average $\overline{M}_n$. This MW average still remains the preferred correlation parameter in conjunction with mechanical properties of polymer systems².

EFFECT OF MW AND MWD ON SELECTED MATERIAL PROPERTIES

Mechanical properties of polymer materials generally improve with the degree of polymerization (Figure 1). However, since melt viscosity increases even faster with MW ($\propto M^{3.4}$), a compromise must be established between engineering performance and processing requirements. As a general rule, the plastic with the lowest MW should be

selected, as long as it meets the minimum end product property requirements. One practice which has proven to be successful in several instances consists in using bimodal MWD materials, obtained either by blending two homopolymers of widely different MWs or by polymerization in tandem reactors. Bimodal grades usually retain the strength and stiffness of the high MW fraction while conserving the crack resistance and processability of the lower MW component.



Schematic representation of MW-mechanical properties relationship

Figure 1: Schematic representation of MW-mechanical properties relationships.

STRESS-STRAIN PROPERTIES

The **stress-strain** test is probably the most widely used technique for the determination of mechanical properties. From the stress-strain behaviour, four important material qualities can be derived:

a) The Young's modulus (E) characterizes the resistance of the material to low strain deformation ($< 1\%$). For glassy polymers, the tensile moduli increase sharply with MW before levelling off to a plateau value almost independent of polymer structure at ca. 3.5 GPa. Beyond the critical MW, it is observed that MW and MWD have no major

influence on modulus excepted when very low MW species (telomers) are present. The modulus depends, however, on the state of chain orientation and increases linearly with the draw ratio. In the high MW region, the elastic modulus tend to decrease as a result of misalignment of long polymer chains in the direction of stress. If these long polymer chains can be preferentially aligned by some special process such as gel-spinning, then exceptionally high modulus material can be produced. The most notable example is ultra oriented PE fibres with a typical room temperature Young's modulus of 200 GPa (highest theoretical estimate 324 GPa).

b) The yield strength and brittle strength (see **Yield and Plastic deformation**). The yield strength of amorphous polymers is generally found to be either weakly dependent or independent of MW. In semi-crystalline polymers like in PE, the yield strength increases linearly with the density, and sometime with the MW. These trends appear, however, to be second-order effects resulting from a change in the degree of **crystallinity** with MW. Brittle failure occurs if the polymer breaks at low elongation before reaching the yield point. Unlike the yield strength, which seems not to depend directly on MW, the brittle strength decreases substantially with a reduction in MW. For many polymers, a good correlation in the form of equation 1 has been obtained between the brittle strength and $\overline{M}_n$. As well as the material properties, the **ductile/brittle transition** is also largely dependent on external test conditions such as specimen size, notch radius, strain rate, mode of loading, temperature and physical ageing. Keeping all these conditions constant, as a general rule, lowering MW of the sample will cause a ductile test specimen to fail in a brittle mode. Also, high MW grades usually retain ductility at lower temperatures. For semicrystalline polymers such as HDPE, low temperature brittle properties can be improved by lowering the degree of crystallinity.

c) The tensile strength, σ_b , required to rupture the sample is one of the most widely studied fracture parameters in relation to MW and MWD. Measurements on many glassy polymers have shown that σ_b is near zero at very low MW. As the MW increases σ_b rapidly increases and eventually reaches a constant level at sufficiently high MW. It is now widely recognized that the strength of glassy polymers is related to long range entanglements that serve to restrict chain slippage during loading. This entanglement network can exist only above a critical MW, denoted as M_C . Experimentally, $M_C \sim 2 M_e$, the minimum MW for entanglement usually determined from polymer melt viscosity. Based on these considerations, it is possible to rewrite equation (1) as

$$\sigma_b = \sigma_{\infty} \left(1 - \frac{M_0}{\overline{M}_n} \right) \quad (2)$$

where σ_{∞} is the strength of a polymer of infinite MW and M_0 ($\sim M_C$), the extrapolated threshold MW as σ_b goes to 0. The question of whether or not other MW averages, such as $\overline{M}_w$, $\overline{M}_v$ or any specifically defined average, could give better correlation with the tensile strength has not been settled yet. In fact, it has been suggested that the use of a modified number average MW, $\overline{M}_n^*$ in which all polymer fractions with $M < M_0$ have

been excluded from the calculations could give a better correlation with broad MWD samples. In semicrystalline samples, MWD influences the crystallisation rate and even the morphology and state of orientation of the crystallites. When crystal content and structure are held constant, the tensile strength increases with MW as with amorphous polymers. In some experiments in which flexural strength was determined in parallel with tensile strength, perfectly similar curves are obtained for both properties as a function of polymer MW.

(d) The ultimate elongation (ϵ_b) indicates the maximum strain that a material can withstand before rupture. For most amorphous polymers below the **Glass Transition** temperature T_g , the breaking strain follows the same trend as the tensile strength. In particular, ϵ_b , improves with the increase in $\overline{M}_n$ (eq. 2) and with a narrowing in MWD. The ultimate elongation above T_g (drawability) shows a more complex dependence on MW, temperature and strain rate. With PE, for instance, it has been observed that for each MW, at a given strain rate, there exists a narrow temperature window where the maximum draw ratio could be obtained³. These findings are rationalised in terms of a $\overline{M}_i$ molecular weight average with a value situated between $\overline{M}_w$ and $\overline{M}_z$. The notion of $\overline{M}_i$ average was introduced by Graessley (1967) to describe the entanglement friction factor in polydisperse systems:

$$\overline{M}_i = \left[\int_0^\infty M^{5/2} w(M) dM \cdot \int_0^\infty M \cdot w(M) dM \right]^{2/7} \quad (3)$$

With elastomeric materials, the propensity for crystallization at high strains can modify the elongation characteristics. As with glassy polymers, low MW fractions depress ϵ_b . On the other hand, long polymer chains can crystallise at relatively low strains, resulting in a reduction of ϵ_b in high MW samples. The net effect is a maximum in the elongation curve vs. MW. For many semi-crystalline polymers, the elongation at break is found to increase with MW but decreases with density, again as a result of change in crystallinity.

IMPACT STRENGTH

The **impact strength** is a measure of a material ability to resist breakage under high-speed loading conditions (see also **Impact and Rapid Crack Propagation, Falling Weight Impact Tests**). Impact results are often imprecise due to change in velocities and loading modes. Because large number of samples are required for repetitive testing, the materials used are generally poorly unfractionated, rendering results interpretation difficult. Even with these imprecisions, it is agreed that impact strength shows a similar behaviour as found with ultimate elongation properties, i.e. a rapid increase with MW above a critical value, a levelling off in the intermediate MW range, and a gradual decrease in the ultra-high MW region. This parallelism is understandable because the

total energy required to break is a function of the ability of the polymer to elongate.

FAILURE PROPERTIES

The fracture toughness (K_{IC}) and the fracture energy (G_{IC}) are two important parameters for the characterisation of crack propagation in polymer materials (see **Fracture Mechanics**). The experimental shape of G_{IC} plotted as a function of MW is sigmoidal in several glassy polymers such as PMMA, PS and PC. It is widely recognized that the energy required to propagate a crack goes mainly into the growth of a craze at the crack tip (see **Crazing**). Stable crazes are not observed below a critical MW, $M_C \sim 2 M_e$. In this low MW range, the fracture energy increases with $M^{1/2}$ in accord with theoretical calculations based on craze geometry. Above M_C , the fracture energy rises rapidly according to a power law in $M^{2.3}$ before eventually reaching a plateau at higher MW. In the high MW region, G_{IC} can be fitted with an empirical equation of the form of Eq.2. Modeling the crazed material as a highly anisotropic network of springs, Kramer et al⁴ have predicted that G_{IC} should vary as the number of entangled strands per unit craze area. In the presence of short chains with $M < M_C$, the theory predicts a rapid decrease in G_{IC} with the volume fraction of the high MW component. In this case, a strict dependence of G_{IC} on $\overline{M}_n$ is not expected.

Crack healing or welding could be envisaged as the reverse process of crack propagation. Since crack healing involves mass transport by diffusion across the interface, a large dependence on MW is expected⁵. Based on the reptation theory, it has been predicted that K_{IC} and the average interdiffusion distance increase with time as $(t/M)^{1/4}$ whereas the time required for complete healing (t_∞) should scale with MW as M^3 .

FATIGUE LIFE

The fatigue life (see **Fatigue**) is determined by stressing specimens at various stress levels, frequencies and amplitudes until failure occurs. Although the polymer MW has long been recognised as a leading factor in determining the fatigue life of the sample, the exact influence of MWD has been much less investigated. Comparison between fractions and blends of PS led some investigators to conclude that the fatigue strength is controlled by $\overline{M}_n$ rather than by $\overline{M}_w$. In semicrystalline samples, decreasing the degree of crystallinity, in addition to increasing the MW, can extend the fatigue life by several orders of magnitude.

ENVIRONMENTAL STRESS CRACKING (ESC)

Environment cracking and crazing, frequently encountered in stressed polymers in presence of certain liquids at room temperature, has its origins in the weakening of intermolecular forces in the region of crack growth (see **Environmental Effects**). In glassy polymers, MW has negligible influence on ESC resistance (at least, in the initial stage of craze formation). This contrasts with polymer orientation which constitutes the major modification which can improve craze resistance. MW and MWD have a predominant influence, however, in semicrystalline plastics such as polyethylene. This improved resistance with MW can be explained by the increase in concentration of tie molecules which hold the lamellae together. Polymer MW also has an indirect influence on ESC resistance by changing the degree of **crystallinity**. The more crystalline the material, the lower its ESC resistance, because fewer tie molecules hold the semicrystalline regions together. As a result, at constant MW, a quenched material has a better ESC resistance than an annealed one.

CONCLUSIONS

The effects of polymer MW and MWD on material properties is a long standing problem in polymer science. Although the importance of MW and MWD on mechanical performance has long been recognised, quantitative correlation between these parameters has always been a difficult endeavour. Early studies are plagued with inadequate MW and MWD characterisation. The situation has now considerably improved with the development of automatic osmometer, sensitive light scattering photometer and gel permeation chromatography (see **MWD characterisation by GPC**). Even so, correct evaluation of mechanical test results constitutes the most difficult part in this type of investigation. In addition to MW and MWD, mechanical properties are controlled by a large number of structural and external factors. Some of these variables, such as chain orientation, crystalline structure and morphology, are not independent so a change in MW or MWD can affect the other parameters. The specific effects of MW and MWD can be determined only if all the other variables are held constant or allowed for quantitatively. With respect to the MWD, the interpretation of a given property in a polydisperse sample can be undertaken only if the contribution of each MW fraction to that property is properly taken into account. With a better understanding of the micromechanisms of polymer deformation (and their dependence on MW), a quantitative representation of the effects of MW and MWD on mechanical properties seems to be in hand in the near future.

REFERENCES

1. Flory, P.J. (1945) *Tensile strength in relation to molecular weight of high polymers*. *Journal of the American Chemical Society*, **67**, 2048-2050.
2. Nunes, R.W., Martin, J.R. and Johnson, J.F. (1982) *Influence of molecular weight and molecular weight distribution on mechanical properties of polymers*. *Polymer Engineering and Science*, **22**, 205-228.
3. Termonia, Y. and Smith, P. (1992) *Kinetic model for tensile deformation of polymers. Part IV: effect of polydispersity*. *Colloid & Polymer Science*, **270**, 1085-1090.
4. Sha, Y., Hui, C.Y., Ruina, A. and Kramer, E.W. (1995) *Continuum and discrete modelling of craze failure at a crack tip in a glassy polymer*, *Macromolecules*, **28**, 2450-2459.
5. Kausch, H.H. and Tirrell, M. (1989) *Polymer interdiffusion*. *Annual Review in Materials Science*, **19**, 341-377.

33: Molecular Weight Distribution - Characterisation by GPC

T Q Nguyen, H H Kausch

INTRODUCTION

The MWD is probably the single most fundamental property of a polymer (see **Molecular Weight Distribution and Mechanical Properties**). Depending on the application, MW of polymer materials can encompass an extremely large range extending from several hundreds (paints, coatings, functionalised polymers) to a few million daltons (UHMWPE, high performance fibres). Unlike in the case of small molecules, the assignment of an unequivocal MW to a macromolecular material is not straightforward. Due to the kinetics of polymerization, no synthetic polymer has a unique MW. Because polymers exist with a range of chain lengths and conformations, it is usual to quote a series of MW averages like the number average ($\overline{M}_n$), the weight average ($\overline{M}_w$) or the viscosity average ($\overline{M}_v$), each quantity representing one moment of the MWD. Evidently, complete information on the polymer system can be obtained only if the whole MWD can be determined. Routine MWD analysis is generally performed by Gel Permeation Chromatography (GPC), although several emerging techniques like Field-Flow Fractionation and Matrix Assisted Laser Desorption/Ionisation time-of flight mass spectrometry show great potential for future developments. Some important MW averages are defined by the expressions:

$$\overline{M}_n = \sum_i n_i M_i / \sum_i n_i \quad (1)$$

$$\overline{M}_w = \sum_i n_i M_i^2 / \sum_i n_i M_i \quad (2)$$

$$\overline{M}_v = \left(\sum_i n_i M_i^{a+1} / \sum_i n_i M_i \right)^{1/a} \quad (3)$$

where n_i is the number of molecules with molecular weight M_i and a the Mark-Houwink exponent. The ratio $\overline{M}_w / \overline{M}_n$ known as polydispersity index, is a measure of the width of the MWD.

GEL PERMEATION CHROMATOGRAPHY

Gel Permeation chromatography (GPC) also known as Size Exclusion Chromatography (SEC) is an isocratic liquid chromatography technique first described by Porath & Flodin for biomacromolecules (1959), then by Moore for organo-soluble polymers (1963). Due to its technical importance, GPC has benefited from continuous development since its discovery and has now evolved as a state-of the-art method for determining MWD.

SEPARATION MECHANISM

The heart of any chromatographic system is the column in which separation occurs. GPC columns are packed with porous beads of uniform size with diameter from 15 μm to 3 μm . The porosity distribution should be in the same size range as the dissolved macromolecules to be separated. Column packing may be organic (gels of PS crosslinked with DVB) or inorganic (porous glass or silica). To cover the whole range of molecular sizes found in synthetic polymers, it is necessary to connect several columns in series, each one packed with a gel of different porosity. Alternatively, a mixture of gels of various porosities could also be used.

There is now a general consensus that separation in GPC arises from the steric exclusion mechanism. Steric exclusion is based on the decrease in the statistical number of available conformations of a flexible polymer chain in proximity to the liquid-gel interface. The domain next to the pore walls, therefore, represents a region of low entropy for the polymer chains. In other words, the polymer chains try to avoid approaching at a distance less than about one hydrodynamic radius (R_h) separating the center of mass of the molecular coils from the interface. Unlike other chromatographic techniques which rely on enthalpic interactions, the origins of the partition of macromolecules between the solvent inside the pores and the mobile phase are purely entropic in GPC. The total solvent volume in a GPC column is the contribution from interstitial volume (V_0) and the pore volume (V_p). The accessible volume V_{acc} for a macromolecule inside the pore is given by:

$$V_{acc} = K_{GPC} \cdot V_p \quad (4)$$

From this relation, the polymer elution volume (V_e) can be written as

$$V_e = V_0 + V_{acc} = V_0 + K_{GPC} \cdot V_p \quad (5)$$

Evidently, the partition coefficient (K_{GPC}) changes with the size of the macromolecule. For macromolecules with a size larger than the pore diameter, $K_{GPC} = 0$ whereas $K_{GPC} = 1$ for small molecules like those of the solvent which can have access to the totality of pore volume. As a result, the largest macromolecules which are excluded from the gel elute first at V_0 , whereas the smallest ones (total permeation) elute at $V_0 + V_p$.

CALIBRATION AND MULTIDETECTION IN GPC

Calibration constitutes an essential step in GPC characterisation. As with any chromatographic technique, GPC is a secondary analytical tool and necessitates some calibration procedure to convert the experimental chromatogram (detector signal plotted as a function of elution volume) into a molecular weight distribution. There are essentially three techniques of calibration:

(a) The "classical" technique consists in injecting narrow polymer standards (generally PS) of known MW to establish the calibration curve $\log(M) = f(V_e)$. Instead of narrow standards, it is also possible to calibrate with a "broad standard" with at least two well-characterised MW averages ($\overline{M}_w$, $\overline{M}_n$, or $\overline{M}_v$).

(b) Universal calibration: One persistent problem encountered in GPC-MW calibration is the dependence of the calibration curve on polymer structure. Since GPC separates polymers according to their molecular sizes, all macromolecules having identical hydrodynamic volume should elute with the same V_e regardless of the chemical structure or degree of branching. Based on this principle, Benoit *et al.* (1967) proposed the use of the product $[\eta] \cdot M$ instead of M as the key calibration parameter. Polymer solution theory predicts that molecular volume of Gaussian coils may be expressed in terms of $[\eta] \cdot M$ through the Flory-Fox relation:

$$[\eta] \cdot M = \Phi \langle R^2 \rangle^{3/2} \quad (6)$$

$\langle R^2 \rangle$ is the mean-square end-to-end distance, the constant Φ has a value of $2.86 \cdot 10^{23}$ in a theta solvent and $\sim 1.7 \cdot 10^{23}$ in good solvents according to the Ptitsyn-Eizner equation. The plot of $\log([\eta] \cdot M) = f(V_e)$ is known as the "universal calibration" curve. Once established for a given polymer (for example, PS standards), the "universal calibration" curve should remain valid for any other polymer or copolymer under purely steric exclusion separation. Generally, enthalpic effects can be minimized with a proper selection of the solvent which must be good for the polymer and have at the same time a solubility parameter δ close to those of the stationary phase. Even with this precaution, enthalpic interactions with the stationary phase may be difficult to avoid with some highly polar or charged polymers and represent a source of difficulties in the GPC characterisation of hydrosoluble polymers.

(c) Multidetector GPC: Classical GPC with only one concentration detector (DRI, IR or UV spectrophotometer, densitometer, evaporative light scattering) is limited in its ability to determine absolute MWD of polymers of different chemical structures. It was soon realised that the association of a concentration detector with a molecular size

sensitive detector (on-line viscometer, low angle laser light scattering (LALLS) photometer) could relieve much of the problem of calibration imprecision. The primary data which can be obtained from viscometric detection is the intrinsic viscosity distribution, $[\eta] = f(V_e)$. This information can then be converted to MWD with the universal calibration method. In addition, molecular size can also be obtained by utilizing the Flory-Fox equation. Light scattering (LS) is the only technique capable of providing absolute MW information without any *a priori* assumption. With the use of multiangle light scattering detector (MALLS), the polymer radius of gyration can also be determined. The definite advantage of LS over the other modes of detection is its exemption from retention calibration. As such, the experimental MWD is not dependent on extraneous factors like flow rate variations, column overloading, axial broadening or non-steric effects. One main drawback of LS is the lack of sensitivity for low MW fractions. The use of a triple detection scheme, DRI-Viscometry-LS, is gaining in popularity and can correct from the weakness of each individual mode of detection.

ANALYSIS OF COMPLEX POLYMERS

A polymer is defined as complex when it has more than one distributed property. A linear homopolymer like PS is simple because it is heterogeneous in only one property which is the MW. Branched polymers and copolymers, on the other hand, have broad distributions in at least two different properties. Characterisation of complex polymers require information from several detectors with at least one detector signal per property to be determined.

DETERMINATION OF LONG CHAIN BRANCHING

Multidetector GPC is the best suited tool for the study of long-branched polymers. Long chain branching determination is based on the reduction of hydrodynamic volume with increasing degree of branching. Since a branched polymer has a lower intrinsic viscosity than its linear homologue, differences in branching will show up in comparisons of their Mark Houwink plot. Quantitative measurements of branching can be obtained from the Stockmayer-Fixman *g* factors defined as the ratio of a branched polymer molecule's (b) unperturbed mean square radius of gyration to that of a linear polymer (l) with the *same* composition and MW.

Experimentally, *g* factors can be calculated from MW and intrinsic viscosity measurements using the relation

$$g = \frac{\langle R_g^2 \rangle_{b,M}}{\langle R_g^2 \rangle_{l,M}} = \left(\frac{[\eta]_{b,M}}{[\eta]_{l,M}} \right)^{1/x} \quad (7)$$

where *x* is the branching structure factor having a value of 0.5 for star branched polymers, 1.5 for comb-like branched polymers and $0.5 < x < 1.5$ for intermediate branching.

ANALYSIS OF COPOLYMERS

Tailoring novel high performance properties to plastic materials are generally accomplished not by new polymer synthesis but by copolymerization, grafting or blending of well known macromolecules (see **Alloys and Blends**). A linear copolymer with only two repeating units constitutes a highly complex system and poses real challenges to the analytical chemist. Disregarding the sequence length distribution and stereoregularity distribution, two parameters remain to be considered: the combined MW-chemical composition distribution. Analysis of copolymers MWD by GPC is a complex endeavour and requires supplementary chemical composition information from selective detectors like Diode Array, FTIR or NMR. However, the analysis of samples with multiple heterogeneities with a single separation technique has its limitations. A powerful combination, HPLC-GPC orthogonal chromatography, shows great promise in the differentiation of chemical heterogeneities from structural heterogeneities. Since separation in HPLC is dominated by enthalpic interactions, it perfectly complements the entropic nature of the SEC retention mechanisms in the characterization of copolymers and blends.

OTHER METHODS OF MWD CHARACTERIZATION

Despite its widespread acceptance, GPC suffers from some inherent drawbacks, such as non-exclusion effects for polar samples, limited peak capacity, shear degradation in the ultra-high MW range, lack of chemical structure information, and dissolution requirement for the polymer. Among other alternative tools for polymer MWD characterisation, field-flow fractionation (FFF), matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry and dynamic thermomechanical analysis of polymer melts can offer useful complements to the GPC technique.

REFERENCES

1. Yau, W.W., Kirkland, J.J. and Bly, D.D. (1979) *Modern size-exclusion liquid chromatography*, John Wiley & Sons, New York.
2. Barth, H.G. and Mays J.W. (eds.) (1991) *Modern Methods of Polymer Characterization*, John Wiley & Sons, New York.

34: Monte Carlo Techniques

C. Chui and M. Boyce

INTRODUCTION

The use of numerical methods to investigate the thermo-mechanical behaviour of polymers has become increasingly widespread in recent years as computational resources become more efficient and cost effective. Analytical techniques, while providing insights into scaling laws obeyed by these systems, suffer in their inability to incorporate or infer microscopic material details. Numerical models which capture the discrete nature of material structure offer the possibility to observe the microstructural features governing macroscopic response. Of course, the level of detail incorporated in any numerical model imposes limits on computationally accessible length/time scales. Monte Carlo methods appear to be ideally suited to attack one of the fundamental problems of polymer physics: determining the consequences of polymer chains sampling a large number of configurations on the macroscopic behaviour.

One specific Monte Carlo technique, pioneered by Metropolis et al.¹, provides a systematic method for efficiently sampling probability distributions derived from statistical thermodynamics. The Metropolis algorithm stochastically “marches” the model through the most probable regions of configuration space, thereby providing information regarding the system's statistically representative behaviour. This approach is in contrast to deterministic methods such as molecular dynamics, which uses Newton's equations of motion to sample a representative path in momentum and configuration phase space².

DEFINITION OF MONTE CARLO

In their most elementary form, Monte Carlo methods refer to a set of numerical techniques which use probability theory to infer information from problems which are inherently statistical in nature. Generally, these methods numerically generate a large number of realisations of a system from which statistical analysis is applied to infer desired properties. One simple example involves determining the expectation value of the sum of a pair of rolled die. Of course this trivial example is treatable analytically, but consider if one attempted to infer the expectation value by throwing two die, summing the values, and averaging the results over a large number of throws. The expectation value through this ‘experiment’ is estimated by:

$$\langle \text{SUM} \rangle \approx \frac{1}{N} \sum_{i=1}^N (X_i + Y_i) \quad (1)$$

the angular brackets denote the expectation value

N is the number of throws

X_i and Y_i are the values of the two die for the i th throw

A Monte Carlo algorithm simulates the die throws through the repeated use of a random number generator. For random numbers uniformly distributed between 0 and 1, the algorithm assigns different die values to six evenly spaced intervals in the range 0 to 1. A way to generalize the above example is to say that Monte Carlo techniques specify algorithms which sample probability distribution functions, the consequences of which are inferred from statistical analysis of the numerically generated system realizations. All problems amenable to Monte Carlo methods can be cast in this framework. The Metropolis algorithm is one such method which samples the distributions derived from statistical mechanics.

MONTE CARLO IN THE CONTEXT OF STATISTICAL MECHANICS

The methods discussed in the following sections focus on systems which can only attain a finite number of states. This discretization of phase space is appropriate for numerical methods since the models are evolved in discrete steps. Rigorous derivations of these results are presented in many excellent texts^{3,4}. The constant particle-number/volume/temperature ensemble (NVT) is described by the classic Boltzmann probability mass function:

$$P_i = \frac{\exp\left(\frac{-H_i}{kT}\right)}{\sum_i \exp\left(\frac{-H_i}{kT}\right)} \quad (2)$$

P_i is the probability that the system samples the i th phase space coordinate

H_i refers to the Hamiltonian associated with the i th phase space coordinate

kT denotes the product of Boltzmann's constant with the absolute temperature

The quantity in the denominator is typically called the *NVT* partition function, which is denoted as Z . For simple material models, closed form expressions for Z can be obtained from which all thermodynamic quantities are directly calculated. More generally, the ensemble average of any property can be explicitly determined using equation

$$\langle A \rangle = \frac{\sum_i A_i \exp\left(\frac{-H_i}{kT}\right)}{\sum_i \exp\left(\frac{-H_i}{kT}\right)} \quad (3)$$

A_i is the value of the property calculated from the i th state

$\langle A \rangle$ is the expectation value of the property for the system

Underlying the distribution and properties are assumptions which limit their applicability to equilibrium ensembles which sample a very large number of states. In practice, the equilibrium restriction is followed by investigating processes for which the characteristic relaxation time of the system is much shorter than the characteristic relaxation time of the process of interest. Typical algorithms sample enough states to meet ensemble size requirements and obtain reasonable results.

IMPORTANCE SAMPLING AND THE MARKOV CHAIN

Two basic ingredients which belong in any practical Metropolis algorithm are importance sampling and the Markov chain⁵. These mathematical devices enable the algorithm to perform sampling of desired distributions efficiently. Importance sampling helps the algorithm focus effort on states which contribute most to sums while reducing effort on states which contribute very little, thereby enabling much more efficient use of the configuration space sampling points than simple random sampling techniques.

The Markov chain provides a means by which the Metropolis algorithm can systematically perform importance sampling through the use of probabilities which govern the transition of one state to any nearby state. By making specific choices for these transition probabilities, the Markov chain is guaranteed to eventually produce a distribution of states consistent with those derived from statistical mechanics.

Interestingly, the partition function is not required for the algorithm to proceed, thus producing the rather odd situation of sampling on a distribution which is not even known! This seemingly great saving is earned at the cost of not actually having the partition function available to calculate other thermodynamic functions such as the configurational contribution to the Helmholtz free energy or the thermodynamic entropy.

THE METROPOLIS ALGORITHM

All of these parts come together in what is known as the Metropolis algorithm which can be summarised in a few simple steps. For the *NVT* ensemble, the procedure is:

- 1) Generate an initial state.
- 2) Calculate the system's configurational Hamiltonian (i.e. the analogue to potential energy).
- 3) Randomly select a degree of freedom and perturb its 'position'
- 4) Compute the change in the Hamiltonian, ΔH , due to the perturbation
- 5) If the Hamiltonian decreases, accept the perturbed configuration as a new configuration, store the desired properties, and return to step 3. Else go to step 6.

- 6) Generate a random number from a uniform distribution over the interval 0 to 1.
- 7) If the random number generated is less than $\exp(-\Delta H/kT)$, then accept the perturbed configuration as the new configuration, store the desired properties, and return to step 3. Else take the old configuration as the new configuration, store the desired properties, and return to step 3.

In theory, the algorithm ensures that the perturbed configurations will eventually sample states with a frequency consistent with the Boltzmann distribution. Since the algorithm typically requires some number of cycles before reaching the equilibrium sampling condition, accumulation of property data is not performed until most important thermodynamic quantities (i.e. energy, pressure, etc.) appear to reach a statistical steady state condition. Exactly when the steady state is reached is often difficult to determine, particularly at low temperatures when the algorithm converges quite slowly. Occasionally, trial configurations which are tailored for the conditions of a particular system (i.e. moves which take advantage of system kinematics) may significantly speed up the rate of convergence. Conditional probabilities other than those specified by the Metropolis algorithm may also help increase efficiency.

EXAMPLE OF APPLICATION TO A SERIES OF HARMONIC SPRINGS

The application of the Metropolis Algorithm can be illustrated through a simple one dimensional example involving a series of particles connected via identical harmonic (i.e. linear) springs with spring constant, C . By considering an imposed displacement on one end of the spring 'chain' with the other fixed, the resulting configurations attained by the remaining springs can be determined in several ways. For systems with no thermal energy ($T=0K$), the configuration is uniquely determined by the force balance of the springs and is calculated by constructing a set of linear equations which can be solved to obtain the athermal equilibrium displacements. In this case, the particles are evenly spaced within the domain (Fig 1).

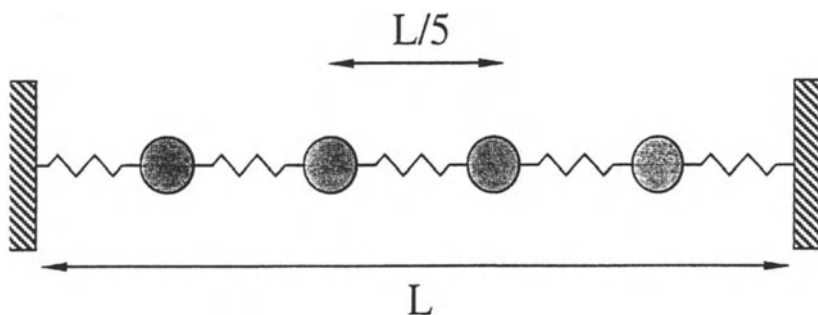


Figure 1: Athermal equilibrium configuration of particles connected by identical harmonic springs.

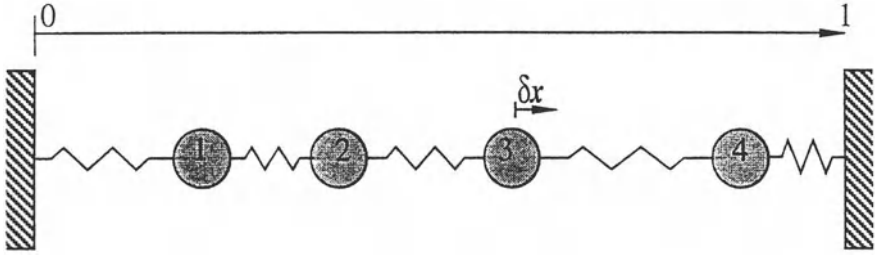


Figure 2: Example of configuration sampled during Metropolis algorithm. Particle 3 is being perturbed by a displacement, δx .

For systems at finite temperatures, the configurations sampled by the particles can only be determined in a statistical sense. Molecular dynamics techniques perform the configurational sampling by assigning masses to the particles correlating the initial velocity distribution to the kinetic energy representative of the temperature, and integrating Newton's equations. The Metropolis method would follow the procedure outlined in the previous section:

- 1) Randomly assign particle positions consistent with the constraints imposed on the systems (i.e. the end particles have fixed displacements, all particles are situated between the end points of the "chain")
- 2) Compute the total potential energy of the system by adding up the individual contributions from each of the springs.
- 3) Randomly select a particle and perturb its position by an amount δx (figure 2).
- 4) Calculate the energy change, ΔH , of the spring network due to the perturbation
- 5) If the energy decreases, accept the perturbed particle position as the new position, store any desired information and return to step 3. Else go to step 6.
- 6) Generate a random number from a uniform distribution over the interval 0 to 1
- 7) If the random number generated is less than $\exp(-\Delta H/kT)$, then accept the perturbed particle position as the new position, store any desired information, and return to step 3. Else count the old particle position as the new position, store the desired information, and return to step 3.

After looping through the steps a sufficient number of times, the system reaches a statistical "equilibrium" identical to that found from integrating Newton's equations. An example of a potential energy versus number of algorithmic loops curve is shown in figure 3 for the system depicted in figure 2. After reaching statistical steady state, the particle positions oscillate around their athermal equilibrium values (figure 4).

SAMPLING ON OTHER ENSEMBLES

Other ensembles, such as the constant particle-number/pressure/temperature (NPT) and constant particle-number/volume/energy (NVE) ensembles have probability mass functions analogous to equation 2. The algorithm as described above applies only to the NVT ensemble, but distributions corresponding to other ensembles are also capable of being sampled through slight modifications of the Metropolis technique. By selecting appropriate transition conditional probabilities, the Markov chain can be made to converge to a distribution consistent with the desired ensemble. For example, the NPT ensemble suggests that volume be used as an additional degree of freedom with the system configuration and volume being perturbed during each loop of the Metropolis Algorithm and enthalpy being the governing quantity. An alternative approach to sampling the NPT ensemble is to use the Metropolis algorithm as originally designed for the NVT ensemble coupled with closed loop feedback control to determine the appropriate system volume. That is, the system's internal pressure is computed periodically and the volume is adjusted in order to eliminate the difference between the internal and externally imposed pressure. This has the advantage over the NPT algorithm in that the volume changes applied are not random in nature, thus saving computational effort. Details regarding modifications necessary to sample distribution for other ensembles are discussed in reference 5. Variations on these methods are applied to simulate the mechanical behaviour of amorphous polymers in an accompanying article **Monte Carlo Techniques Applied to Polymer Deformation**.

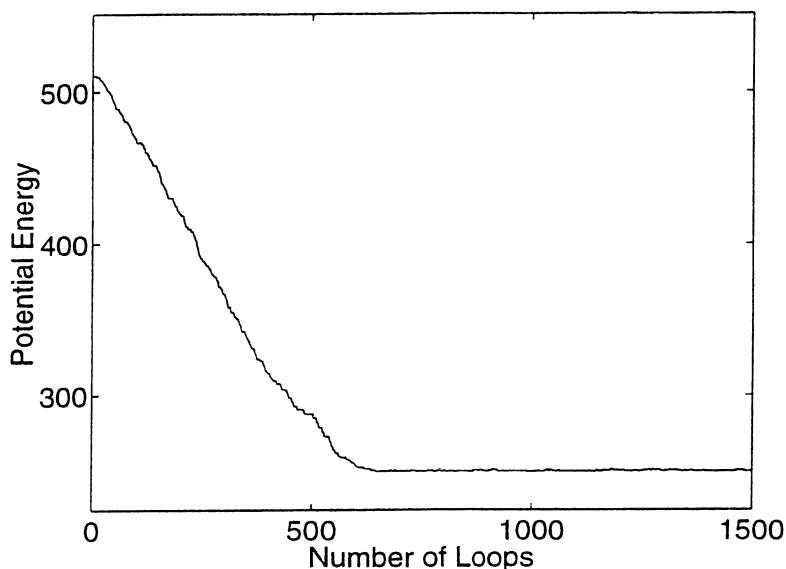


Figure 3: Example of potential energy evolution during Metropolis algorithm for the 4 particle system depicted in figure 2.

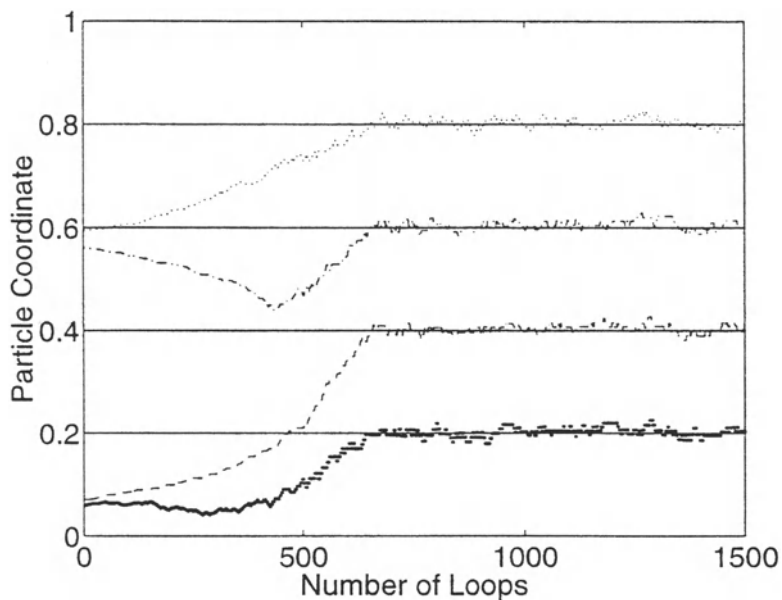


Figure 4: Evolution of particle co-ordinates during Metropolis algorithm for system depicted in figure 2. The straight lines represent the athermal equilibrium positions. After a sufficient number of loops, the particles oscillate around the equilibrium co-ordinates.

REFERENCES

1. Metropolis et al. (1953) Equation of State Calculations by Fast Computing Machines, *J. Chem. Phys.* **10**, 1087-1092
2. Haile, J.M. (1992) *Molecular Dynamics Simulations*, Wiley & Sons
3. Rushbrooke, G. (1949) *Introduction to Statistical Mechanics*, Oxford University Press
4. Hudson, J. (1996) *Thermodynamics of Materials - A Classical and Statistical Synthesis*, Wiley & Sons, Inc.
5. Heerman, D. W. (1986) *Computer Simulation Methods in Theoretical Physics*, Springer-Verlag

35:Monte Carlo Techniques applied to Polymer Deformation

Clarence Chui and Mary Boyce

INTRODUCTION

The deformation of amorphous polymers at low temperatures (i.e. "glassy polymers") is generally a non-equilibrium process (see **Amorphous Polymers**). The picture usually invoked to describe a glassy polymer is that of an entangled network structure trapped in a liquid-like state away from equilibrium. At these temperatures, the rates at which many of the relaxation processes occur in the material are much lower than typically imposed deformation rates¹. Application of techniques such as the Metropolis Monte Carlo method for these types of systems requires special considerations which are briefly discussed in the following sections.

APPLICATION OF THE METROPOLIS ALGORITHM TO NON-EQUILIBRIUM CONDITIONS

Through reinterpretation of the Metropolis algorithm, many of the techniques introduced in the article introducing Monte Carlo techniques can be extended to non-equilibrium situations (see **Introduction to Monte Carlo Techniques**). Even without modification, the algorithm provides valuable qualitative information about system kinetics. Consider a case where the algorithm is applied to a system which is initially far away from equilibrium. The relationship between any desired property and the number of states sampled in the Markov chain for a complex system before achievement of an approximate steady state condition is schematically illustrated in figure 1. The qualitative form of this relationship, while not representative of any real time dynamics, nonetheless mimics the forms found for many kinetic processes.

When discussing system kinetics in the manner described above, it is often useful to introduce a random variable as an artificial time measure so that relative comparisons of the rates of processes can be made. This general technique is commonly called 'Dynamic Monte Carlo'². Dynamic Monte Carlo methods are physically appealing in that transitions which require large energy increases correlate to processes occurring at relatively low rates, while transitions which decrease energy correspond to those occurring at relatively high rates.

OPERATIONAL DETAILS REQUIRED TO SIMULATE POLYMER DEFORMATION

Many different types of polymer representations are possible in constructing models of amorphous polymer deformation. The level of detail incorporated in these various models varies from descriptions of electronic degrees of freedom to simple bead-spring representations of polymer chains. Several of these approaches are discussed extensively in reference 3. Although the details of these various models are quite different, most require attention to four features:

- 1) Specification of local interactions.
- 2) Chain/Network generation.
- 3) Preparation of the system through annealing and quenching to obtain a desired initial state.
- 4) Application of prescribed macroscopic deformation conditions

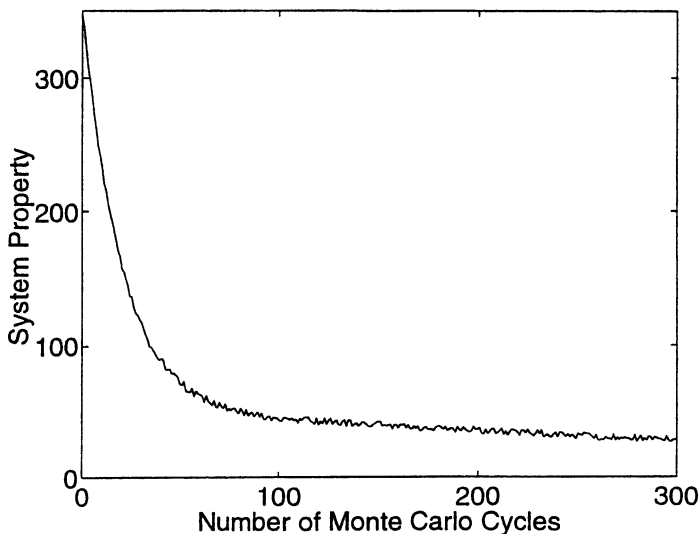


Figure 1: Illustration of system "kinetics" obtained from the Metropolis algorithm.

Local Interactions

Polymeric materials generally possess microstructures made up of long molecular chains consisting of many repeating monomers. The strong covalent bonds generally govern the spacing between atoms along the backbones of these chains and are typically much more rigid than other degrees of freedom such as valence angle bending and bond torsion⁴. Due to the rather complex structure possessed by polymeric materials, relatively simple interactions are often employed in order to reduce the computational burdens of the

model. One of the most common models used to represent this characteristic structure is the poly-bead model which represents the structure as beads connected by springs on a linear chain (fig 2).

The springs mimic the connectivity and response of the covalent backbone bonds found in linear polymers. Nonbonded interactions are incorporated to mimic the long range attraction and short range repulsion between beads from different chains and beads far separated along the same chain. These Van der Waals type interactions are of great importance in systems below the glass transition temperature since it is their presence which controls much of the deformation response through hindrance of chain motion. More detail can be incorporated by accounting for bond angle (i.e. valence angle) fluctuations and dihedral angle torsion potentials as well as chemical side groups.

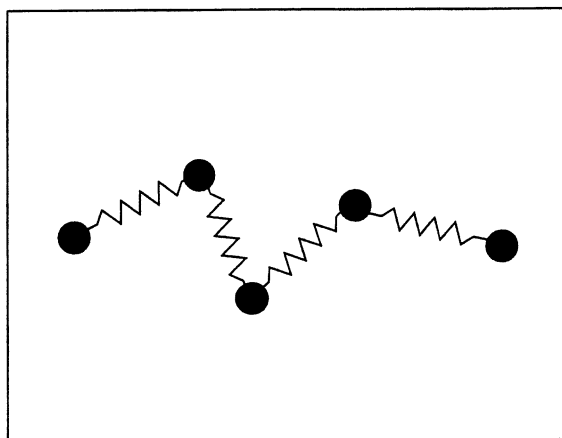


Figure 2: Schematic of polybead chain.

Chain/Network Generation

After specifying the local interactions, an initial configuration is generated in one of many possible ways. To reduce the finite size effects of the system, a periodic cell is often used to define the simulation domain. The cell is periodic in the sense that particles which exit one boundary have image particles which enter the system from the opposite boundary. Most generation techniques attempt to construct initial structures which are near equilibrium in order to reduce the amount of time required to evolve the system to the desired initial state. The algorithms often rely on some form of a random walk chain growth process with many variations of the procedure biasing the selected growth directions by the bonded and non-bonded energies⁵. Crosslinking can be introduced by connecting the chain ends of a large number of chains to common beads which act as effective crosslinking junctions⁶. More elaborate schemes attempt to mimic the polymerisation process explicitly through the use of kinetic algorithms⁷.

Annealing and Quenching

The initially generated structures are not in equilibrium and must be relaxed before deformation is applied. Annealing and quenching are critical in that they strongly affect the initial state of the network structure and thereby determine the subsequent properties of the system. This is especially true at low temperatures where the Metropolis algorithm samples very limited regions of phase space. Annealing procedures involve performing static energy minimisations or constant volume Metropolis evolution at high temperatures during which the range of interaction of the nonbonded potentials is incrementally increased from zero to the desired value. Once the full effects of excluded volume are introduced, the system is run under constant pressure conditions at 'high' (i.e. liquid) temperatures until equilibrium is attained. The system is then quenched by continuing the Metropolis algorithm while decreasing the Boltzmann temperature until the desired temperature is reached after which the system is evolved at that temperature until all important thermodynamic measures approach a steady state condition. The exact cooling schedule required to obtain a reasonably low energy initial state is an area of active research in the field of optimisation⁸. Typical schedules have the form:

$$kT = d/(\log M) \quad (1)$$

where kT is the Boltzmann temperature, d is an empirical constant and M is the number of Monte Carlo steps. Equation 1 is usually adequate for obtaining a system in the rubbery state. Unfortunately, the equilibration step for systems at glassy temperatures may take an inordinate number of Monte Carlo cycles before a satisfactory initial state is obtained. The process can be expedited by applying moderate levels of compressive stress, thereby enhancing packing of the system, followed by equilibration under stress free conditions. This 'over relaxation' allows the system to anneal from a very compact state to the desired open glassy structure. A similar effect is found if the system is undercooled before being equilibrated at the desired operating temperature.

Imposing Deformation

After obtaining the desired initial state, deformation is applied to determine the system's mechanical response. Boundary driven methods simply apply incremental boundary shifts during the simulation. The periodic nature of the model forces particles which exit the simulation cell during a shift to reappear on the opposite side, creating artificially high density regions near contracting boundaries and sparse regions near dilating ones. By allowing the system time to relax before applying the next shift, these density 'shocks' diffuse out of the affected regions thus bringing the system to a more realistic energy state. At high temperatures, the characteristic number of Monte Carlo cycles required to remove these shocks is small enough that boundary shifting can be applied fairly rapidly. At low temperatures however, the density shocks and shifts occur at the same 'time' scale, thereby creating a rather artificial situation where material is

continuously accumulating near contracting boundaries. An alternative method employs incrementally affine deformation jumps of the system followed by several relaxation steps resulting in overall inhomogeneous behaviour. This procedure eliminates density shock development but mimics unrealistic kinematic conditions during each strain jump. The use of small jumps offers a reasonable compromise.

EXAMPLES OF POLYMER DEFORMATION

Figures 3 through 5 illustrate the responses obtained from networks composed of 250 chains with each chain consisting of 50 particles. By deforming the network at various strain states, strain rates, and temperatures, the sensitivity of the behaviour to mechanical and thermal constraints is explored. Figure 3 depicts the periodic cell boundaries and bond vectors for one such network before and after significant deformation. The response of the network generally suggests that constraints which reduced the mobility of the chains relative to the rate at which deformation is applied tend to elevate the network stresses, a finding consistent with experimentally observed behaviour¹. Figure 4 shows the response of the network under uniaxial compression, uniaxial tension, and plane strain compression conditions. The constraint stresses required to enforce the plane strain condition elevates the observed flow stress of the network while the negative hydrostatic pressures of uniaxial tension tend to reduce it.

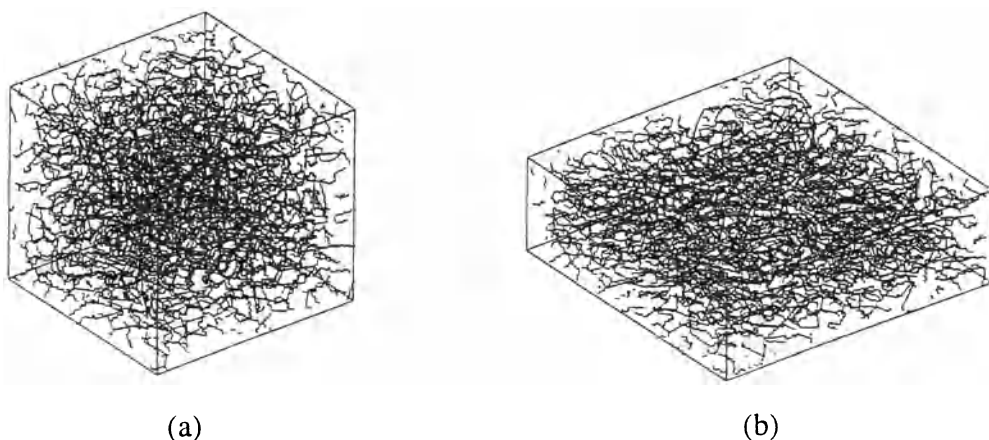


Figure 3: Plot of periodic cell and network bond vectors: (a) undeformed configuration, b) after -0.7 true strain under uniaxial compression conditions.

The development of deformation induced anisotropy is clearly captured by the model as shown by the large strain behaviour (i.e. strain > 0.5) which indicates that strain hardening occurs much sooner during uniaxial tension than in uniaxial compression. The three-dimensional nature of orientation evolution is apparent when comparing the

textures generated from different states of deformation. Figure 5 displays pole figures obtained by monitoring the orientation intensity of locally defined chain segment vectors relative to the direction of loading. Figure 5a shows the initially uniform distribution of the vector orientation, as indicated by the relatively uniform intensity. Under uniaxial compression conditions, the vectors tend to rotate away from the direction of loading and towards the transverse directions (fig 5b). The dark ring around the pole figure perimeter indicates an increase in intensity for orientations away from the direction of loading with the circular pattern suggesting that the vectors are distributed in an axisymmetric manner. Uniaxial tension results (fig 5c) show the vectors rotating towards the direction of loading in an axisymmetric pattern while the plane strain compression pole figure (fig 5d) indicates rotation away from the loading axis towards the free direction (X2 axis). Pole figures monitoring the intensity of orientation relative to transverse directions also display distinguishing features of texture development and help establish a general trend of rotation of local quantities towards the direction of material stretching. These results are consistent with experimental measurements of molecular orientation obtained, for example, using birefringence and X-ray diffraction, and thus illustrate the possibility of observing microstructural evolution with deformation and correlating this evolution to various aspects of macroscopic mechanical behaviour.

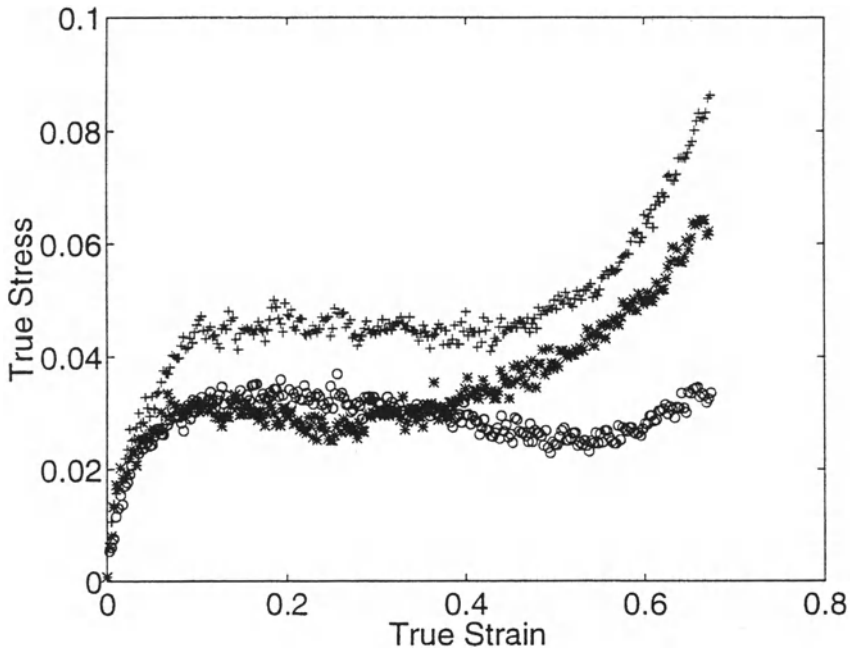


Figure 4: Response of network under uniaxial compression, uniaxial tension, and plane strain conditions (o uniaxial compression, + plane strain compression, * uniaxial tension).

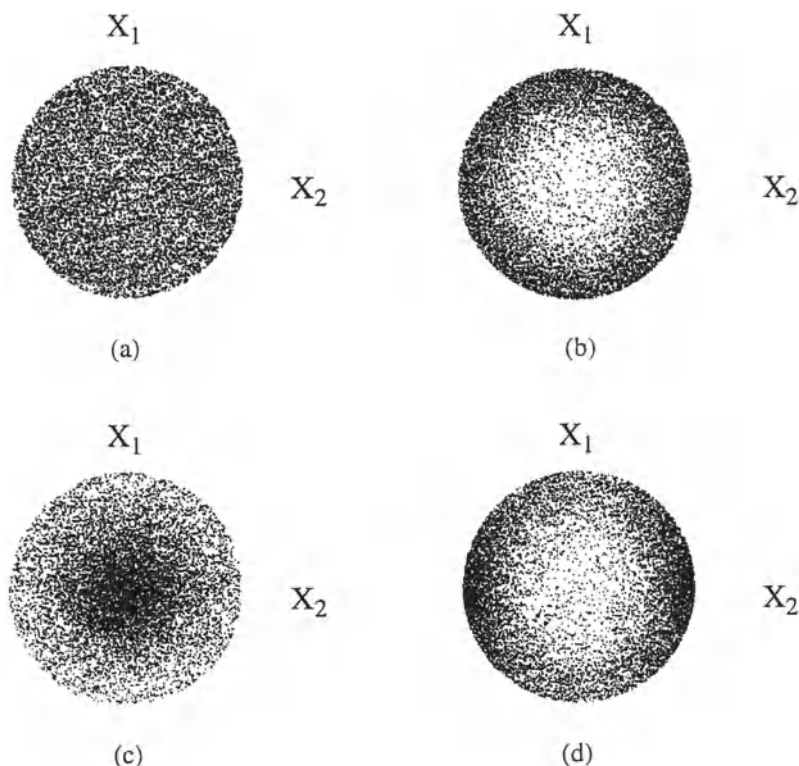


Figure 5: Pole figures showing orientation intensity relative to the direction of loading: (a) Initial intensity distribution, (b) distribution after -0.7 true strain in uniaxial compression (c) distribution after 0.7 true strain in uniaxial tension (d) distribution after -0.7 true strain in plane strain compression.

CLOSING REMARKS

The examples discussed above show that Monte Carlo methods are useful tools for investigating the mechanical behaviour of polymers. Like other discrete simulation techniques, these types of models are able to explicitly investigate parametric dependencies not necessarily accessible by experimental methods. Detailed information regarding particle kinematics can be analysed to identify specific mechanisms or classes of mechanisms by which polymers accommodate deformation. This article acted to illustrate how Monte Carlo techniques can be used to study deformation of a monodisperse polymer network.

The extensions to studying a wide variety of influences on polymer behaviour are numerous and thus Monte Carlo techniques provide an exciting opportunity to study the

complex interactions in polymers which give rise to mechanical properties.

REFERENCES

1. Haward, R., (1973) *The Physics of Glassy Polymers*, Applied Science Publishers, Ltd.
2. Bortz et al., (1975) A New Algorithm for Monte Carlo Simulation of Ising Spin Systems, *J. Comput. Phys.*, **17**, 10,
3. Binder, K. (ed), (1995) *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, Oxford University Press
4. Flory, P. (1969) *Statistical Mechanics of Chain Molecules*, Wiley and Sons, Inc.
5. Theodorou, D. and Suter, U. (1985) Detailed Molecular Structure of a Vinyl Polymer Glass, *Macromolecules*, **18**, 1467
6. Chui, C., (1997) Ph.D. Thesis, MIT, Cambridge USA
7. Duering, E., Kremer, K., and Grest, G., (1993) Dynamics of Model Networks: The Role of the Melt Entanglement Length, *Macromolecules*, **26**, 3241
8. Bertsimas, D. and Tsitsiklis, J., (1993) Simulated Annealing, *Statistical Science*, **8**, 10

36: Neutron Scattering

A. R. Rennie

INTRODUCTION

Neutrons for scientific and engineering investigations are produced either in nuclear reactors or particle beam accelerators. Neutron scattering is a tool employed to determine the structure of materials using methods similar to those used with X-rays (see **X-ray Scattering Methods**). There are, however, several distinctive features of the technique which bring sufficient benefits to outweigh the rarity and cost of neutron beams. The advantages fall in three main areas: first, the scattering of neutrons depends on nuclear forces, is not correlated with atomic number and can vary strongly between isotopes of the same element. Structural studies with light elements such as hydrogen are possible. In particular there is a large difference between normal hydrogen and deuterium which has permitted labelling of molecules or parts of molecules. Secondly, the neutrons are massive particles and energy transfer between the sample and the neutron beam can be measured readily. This permits spectroscopic measurements to measure thermal motion in materials with the benefit that the information about dynamics relates to specific atomic or molecular distances within the material. Thirdly, neutrons interact weakly with many materials. Sample can be measured in air and containers can be made out of fused quartz, many metals and other materials. This permits measurements on materials in 'service' conditions of temperature, load or chemical environment. Benoit and Higgins¹ have described the application of neutron scattering to polymers both as regards structural measurements and studies of molecular motion. Structural studies using various types of radiation are described by Hukins².

In scattering experiments it is usual to measure the intensity, I as a function of scattering angle θ , and wavelength, λ , under well defined conditions of sample illumination. These are related to the wavelength transfer, Q by

$$Q = (4\pi/\lambda) \sin(\theta/2) \quad (1)$$

The vector Q relates to the distance scale probed; roughly $I(Q)$, the scattered intensity as a function of the magnitude Q , measures the correlations at a distance given by $|2\pi/Q|$ in the direction defined by Q . If dynamic properties are to be explored by measurement of energy transfer, E , data is reported as $I(Q,E)$. This will represent energy loss (or gain) for the particular distance and direction defined by Q . The application of neutron scattering to studies of mechanical properties of polymers usually relates to fundamental investigations of molecular models. A major area of activity has been the study of molecular size in the bulk of solid polymeric materials. The ability to determine shape (size in different directions) and distortion under tensile load and shear has been of considerable importance in studies of deformation. Dynamic properties and motion

have been explored in both molten and solid polymers.

SMALL-ANGLE SCATTERING

Scattering at small angles is used to study structures larger than the spacings of individual atoms or small molecules. In contrast to diffraction which is largely concerned with scattering from an ordered arrangement of atoms or molecules a major use of small-angle scattering has been to determine the size and mass of isolated particles. The principles are similar to those for light scattering studies of polymers in solution but with the use of isotopic contrast for some molecules, the method can be applied to bulk polymers. It can be shown that for any spherical object:

$$I(Q) = \text{const.} \exp(-Q^2 R_g^2 / 3) \quad (2)$$

for $QR_g < 1$ where R_g is the radius of gyration of the scattering objects. This provides a simple, model independent way of determining the size of polymer molecules. The deformation of molecules can be observed by measuring the small-angle scattering in different directions under applied stress. Analysis of the full scattering pattern can yield further detailed information about the conformation of polymer molecules. In more complex systems such as copolymers and polymer blends (see **Alloys and Blends**), the extent and range of phase separation can be determined.

A number of experiments have been performed that test molecular models for polymer deformation and flow in elastomers, molten polymers, amorphous and semi-crystalline solid polymers as well as solutions (see e.g. reference 4). For example, experiments have shown at what level the deformation of an elastomer sample is affine. The anisotropy of the molecules and entanglements in deformed samples of melts and elastomers leads to relaxation at different speeds in different directions and some highly anisotropic molecular conformations known from the appearance of the small-angle scattering as 'butterfly patterns'. Other experiments have measured the molecular deformation in semi-crystalline polymers such as polyethylene. The range of applications is now very large: apparatus has been constructed for dynamic elongational strain in the neutron beam at frequencies up to 10 Hz as well as for studies under static load and on quenched samples. Shear cells have also been constructed for polymer melts and solutions.

DIFFRACTION AND WIDE-ANGLE SCATTERING

Scattering at wide angles provides information on crystal structures and local molecular order. In many materials measurements of crystal strain have been used to map stress distributions in samples under load or after yield. This type of experiment is not frequently applied to polymeric materials as the deformation mechanisms rarely correspond to simple crystal strain but often to molecular flow and rearrangement.

Crystallisation under strain can be measured but these measurements are more frequently made using X-ray diffraction.

DYNAMIC NEUTRON SCATTERING

In order to understand the mechanical behaviour of polymeric materials, considerable effort has been made to determine what happens at a molecular or sub-molecular level at the **glass transition**. Other relaxation processes (see **Relaxations in Polymers**) observed in dynamic mechanical tests can be associated with particular molecular motions (see **Dynamic Mechanical Analysis**). The spectroscopy that can be performed with neutrons can provide very detailed information in this area (refs. 1 and 4). Even measurements on normal hydrogenous polymers can give data on length scales and times of molecular motions. This type of experiment has been used to test models of the co-operativity associated with the glass transition. It can also give information about the role of **plasticisers** in modifying polymer properties. Other experiments, particularly using spin-echo spectroscopy to look at large distances and molecular diffusion times, have been directed at understanding reptation which provides a theoretical basis for understanding flow and diffusion of entangled polymers.

REFERENCES

1. Higgins J.S and. Benoit H.C (1994) *Polymers and Neutron Scattering* Oxford Univ. Press,
2. Hukins D.W.L (1981) *X ray Diffraction by Disordered and Ordered Systems* Pergamon, Oxford.
3. Brumberger H. (Ed.) (1995) *Modern Aspects of Small-Angle Scattering* Kluwer, Dordrecht.
4. Richter D. and Springer T. Eds. (1988) *Polymer Motion in Dense Systems* Springer, Berlin.

37: Non elastic deformation during a mechanical test

C. Gauthier

The mechanical behaviour of glassy polymers has been extensively investigated and their constitutive equations determined over a wide temperature and strain range. In this article some thermodynamic and kinetic aspects of polymer behaviour, based on experimental features of the non elastic deformation of these polymers, will be discussed.

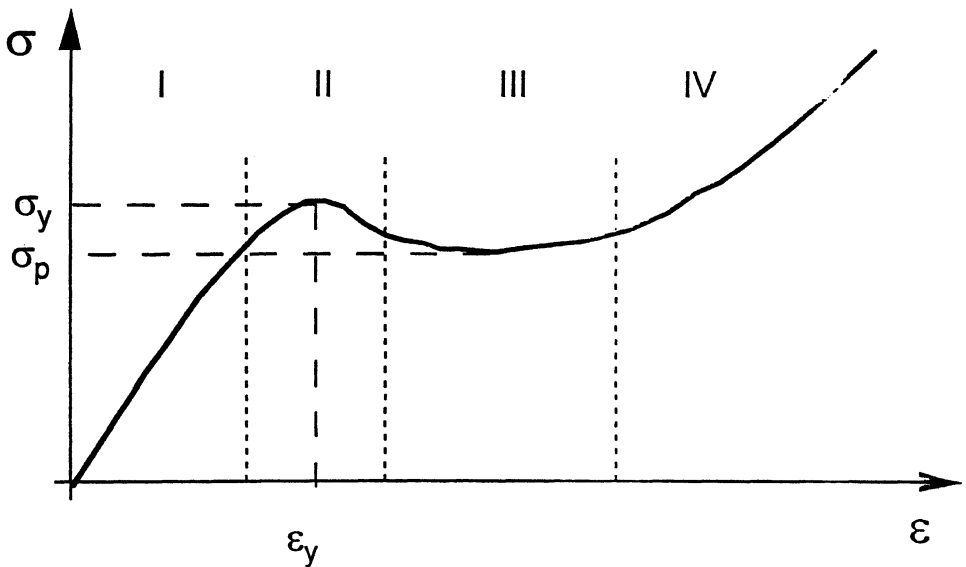


Figure 1: Schematic stress - strain curve of a glassy polymer strained at a constant rate.

The typical stress-strain behaviour of glassy polymers strained with a constant crosshead speed below T_g is shown in Figure 1. This curve exhibits four typical regions. At first, the curve consists of a nearly straight section corresponding to the elastic followed by the viscoelastic response of the polymer. The initial slope of the curve is near the Hookean modulus but already corresponds to a partly relaxed response. The decrease of this slope coincides with the development of inelastic deformation, i.e. non linear behaviour. The second part of the curve is associated with the yield process: the stress reaches a maximum often called yield stress (σ_y) and then decreases towards a minimum value, the plastic flow stress (σ_p). The third part corresponds to the region where the stress is minimum and almost independent of strain (steady state regime).

Then, when stress increases again, strain hardening appears due to macromolecular orientation. Finally strain hardening becomes gradually more important prior to break. From a study of the recovery processes in glassy polymers (see **Recovery of glassy polymers**), the nature of the components of non elastic deformation (anelastic and plastic components here written respectively ϵ_{an} , and ϵ_{pl}) can be clarified. The stress strain curve can then be described by considering the evolution of these components during the mechanical test.

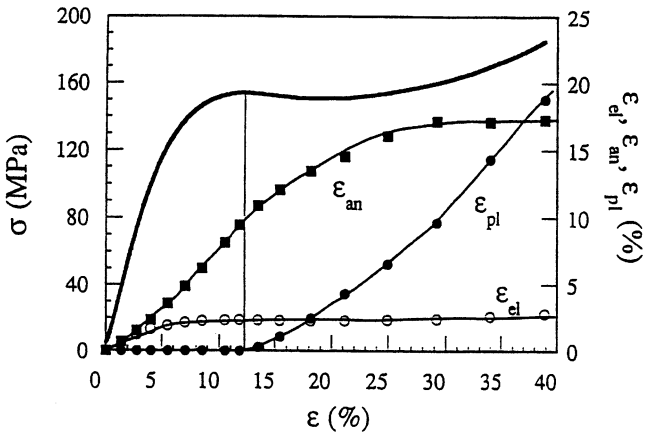
EVOLUTION OF THE ANELASTIC AND PLASTIC COMPONENTS DURING A MECHANICAL TEST

A treatment of about 1h at $T_g - 20^\circ\text{C}$, on a sample strained at a temperature T_{def} far below T_g , allows the total recovery of ϵ_{an} while ϵ_{pl} , remains in the sample. After such a treatment, the residual strain is equal to the plastic component of the strain (ϵ_{pl}). That means that we can determine experimentally ϵ_{pl} as a function of the applied strain (ϵ_t). The purely elastic deformation can be calculated from $\epsilon_l = \sigma_t/E_u$ in which E_u is the unrelaxed modulus measured at very high frequency or at very low temperature (see **viscoelasticity**). Then, the value of the anelastic component can be deduced from

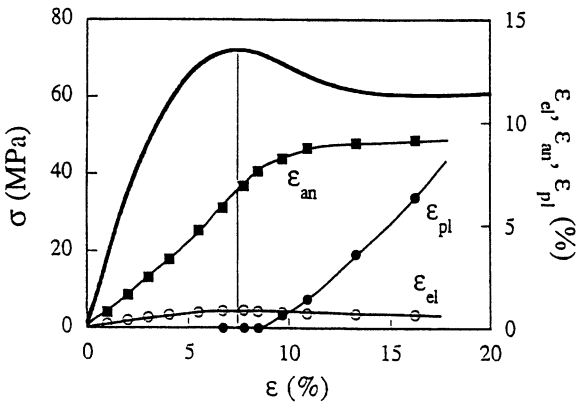
$$\epsilon_{an} = \epsilon_t - \epsilon_l - \epsilon_{pl} \quad (1)$$

Figure 2 presents the respective contributions of anelastic and viscoplastic strain in the case of PMMA strained at 20°C in plane strain compression. It can be observed that ϵ_{an} onsets from the very beginning of the test and keeps growing even beyond the maximum stress. Then, ϵ_{an} , tends towards a constant value ($\epsilon_{an\ sat}$) when the stress reaches its minimum value. The value of $\epsilon_{an\ sat}$ varies with the polymer (Figure 2 a and b) and also with the temperature of the test: $\epsilon_{an\ sat}$ decreases when the test temperature increases and it is expected to become negligible above T_g . On the other hand, the plastic component onsets around the maximum stress and then increases continuously as the strain increases.

It must be emphasised that the stress peak occurs when a large increase of anelasticity is taking place before ϵ_{pl} is detected. This highlights the main role played by the anelastic component in the yielding process, until the strain reaches a value of about 0.3. The plastic strain becomes the main component of the deformation only in the minimum stress zone corresponding to the stationary regime. In fact, the anelastic component is necessary to create plastic strain. Indeed, Oleynik² shows that a prestrained sample heated near T_g (in order to eliminate ϵ_{an} , but still featuring ϵ_{pl}), when deformed a second time, requires a certain amount of ϵ_{an} , before creating further ϵ_{pl} .



a



b

Figure 2: Evolution of the components of the deformation during a mechanical test: a) PMMA strained at 20°C (biaxial compression, strain rate = $2 \cdot 10^{-3} \text{ sec}^{-1}$) b) PC strained at 20°C (uniaxial compression, strain rate = $2 \cdot 10^{-3} \text{ sec}^{-1}$)

THERMODYNAMIC APPROACH

During sample deformation, a large amount of energy ΔU is stored in the sample and this energy can be measured. During the test, the mechanical work done by the stress (W) can be calculated and the heat (Q) dissipated in the process can be measured. The difference between the two values $\Delta U = W - Q$ gives the internal energy stored in the deformed sample. The evolution of W , Q and ΔU during the compression test of a PMMA sample is illustrated in Figure 3a. Up to strains 15-20%, the main part of W is converted to stored energy ΔU . This energy increases from the very beginning of the deformation and levels off at a value of about 14 Jg^{-1} for PMMA, 10 Jg^{-1} for PS and 8 Jg^{-1} for PC. The similarities in the evolution of ΔU and ϵ_{an} , with both quantities levelling

off , points to direct link between ΔU and ϵ_{an} .

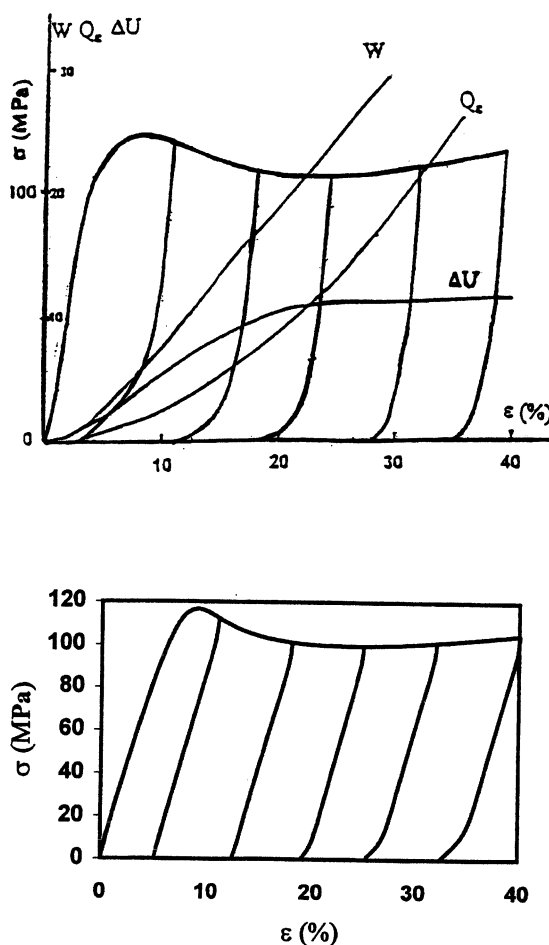


Figure 3: a) Experimental stress strain uniaxial compression test for PMMA (uniaxial compression 14°C, strain rate = $7.10^{-4} \text{ sec}^{-1}$). Evolution of mechanical work (W) dissipated heat (Q) and stored energy (ΔU) with strain. b) Simulated stress strain uniaxial compression test for PMMA (uniaxial compression 14°C, strain rate = $7.10^{-4} \text{ sec}^{-1}$).

ANALYSIS BASED ON MOLECULAR PROCESS

The process of non-elastic deformation of glassy polymers is summarised in Figure 4. Under external stress σ , the nucleation and development of specific defects (shear

microdomains, smd) occurs in isotropic glassy matter (arrow from (1) to (2) in Figure 4). These smd are the elementary carriers of the macroscopic anelastic strain (ϵ_{an}) in a deformed glassy sample. The nucleation of smd increases the internal energy (ΔU). Consequently, this stored energy results in a draw back force involving strain recovery in a temperature range from $T_{def} < T < T_g$. When unloaded, the system returns to the equilibrium state by clearing the barrier from (2) to (1). With the constriction of smd, the microstructural state of the undeformed material is recovered. With further deformation, smd ultimately merge (arrow (2) to (3)) and the stored elastic energy is dissipated. This last process is responsible for the appearance of the plastic component of macroscopic strain which can only be recovered heating above T_g . Quantitative analysis of the experimental data using such a framework has been performed and an example is illustrated in Figure 3b. Computer simulated $\sigma(\epsilon)$ curves for loading and unloading regimes show good accordance with experiments, both, qualitative and quantitative for a broad range of applied strain with one set of parameters (see **Monte Carlo Techniques Applied to Polymer Deformation**).

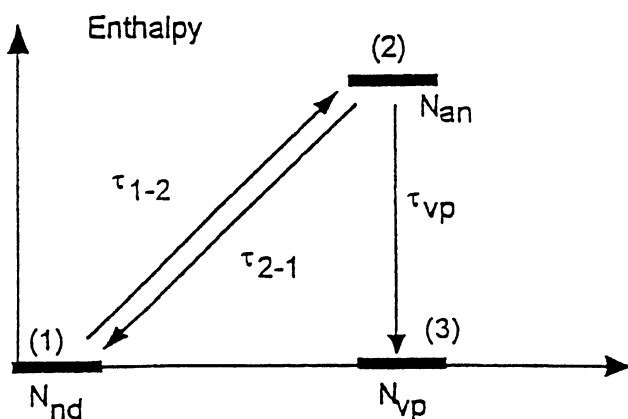


Figure 4: Schematic representation of deformation mechanisms operating in glassy polymers.

REFERENCES

1. David, L., Quinson, R., Gauthier, C. and Perez, J. (1997) *Polym. Eng. Sci.*, **37**, 1633
2. Oleinik, E.F. (1989) *Prog. Coll. Polym. Sci.*, **80**, p140-150
3. Gauthier C., David L, Ladouce L, Quinson R, Perez J, (1997) *J. Appl. Polym. Sci.*, **65**, 2517

38: Plasticisers

G. M. Swallowe

Plasticisers are small molecules, usually low vapour pressure liquids, of molecular weights in the region 100-1000 which form solutions within the polymer. They are dissolved predominately in the amorphous regions of the polymer and act to reduce the yield stress and increase the toughness of the material. They also reduce the modulus and T_g. Plasticisers find their main use as a means of increasing the flexibility and toughness of a polymer for such applications as tubing and films. They are also sometimes added as a processing aid to reduce internal friction and lower melt viscosity.

Plasticisers are used mainly in thermoplastic materials but small amounts are sometimes added to thermosets in order to improve the impact resistance. Poly(vinyl chloride) PVC is virtually useless without the addition of plasticisers since the pure material forms a brittle corrosive mass which is rapidly degraded by UV. However PVC is capable of taking up large quantities of a whole range of plasticising molecules to produce extremely useful engineering plastics. Plasticisers are drawn from a large range of organic molecules including esters of carboxylic acids, hydrocarbons and halogenated hydrocarbons, ethers, polyglycols etc. Even a molecule as simple as water acts as a plasticiser for nylons.

PLASTICISING MECHANISM

The most popular theory of plasticiser action proposes that the plasticiser molecules act as lubricants which force apart the chains in the amorphous regions of the polymer and allow them to slip over each other more easily. An alternative 'gel theory' proposes that the plasticiser molecules form weak bonds with the polymer chain and in this way reduce the number of points of attachment between the chains. Loose attachments give rise to rigidity and their replacement with bonds to individual plasticiser molecules increases flexibility and decreases the flow stress. Evidence for the gel theory comes from nmr observations that even at very high concentrations (50% by weight) some systems have no completely free plasticiser.

An alternative free volume theory proposes that the plasticising action is due to the increase in free volume (see **Glass Transition**) in the system caused by the plasticiser molecules loosely bonding to the chains. The free volume can be considered to be the 'empty space' in the polymer calculated as the difference between the actual volume per unit mass of polymer and the fully crystalline value. Since it is virtually impossible to make a fully crystalline polymer there will always be some free volume. A large fraction of the free volume in the polymer is generated by chain end groups so the greater the number of end groups the greater will be the free volume. The loosely bonded plasticiser molecules effectively form extra end groups and rapidly increase the free volume. Classical viscosity theory (see **Time-Temperature Equivalence**) relates viscosity to

free volumes with an increase in free volume leading to a reduction in viscosity. The theory therefore proposes that the reduction in viscosity and modulus is due to the free volume increase. It is likely that aspects from all three theories play a part in plasticising effects.

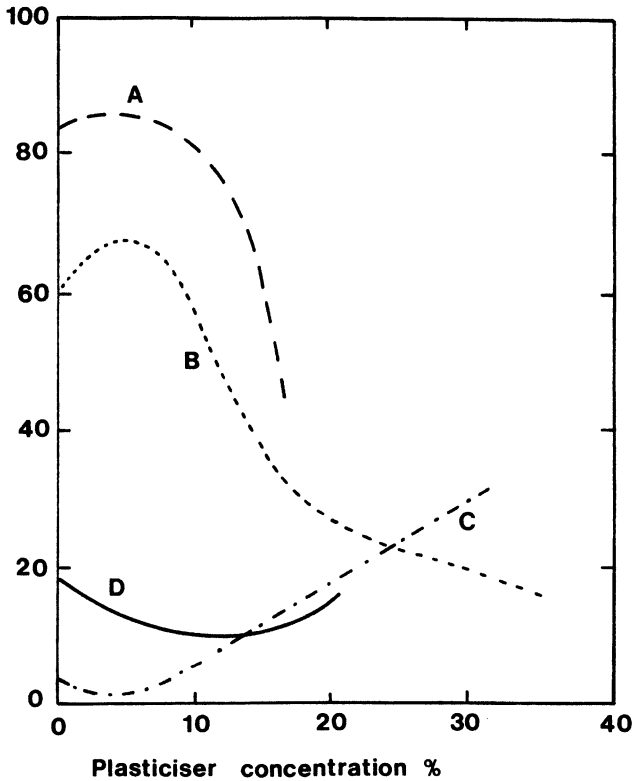


Figure 1: Schematic diagram of the effect of plasticiser concentration on Mechanical Properties. Curves: A (---) modulus; B (.....) Tensile Strength; C (- · - · -) Elongation to Break; D (—) Impact Strength.

MECHANICAL EFFECTS

The main mechanical effects of plasticisers are illustrated in the schematic diagram, Figure 1, which is based on the effects of the addition of a plasticiser to PVC. It is evident that there is a reduction in modulus and tensile strength and an increase in elongation to break and more modest changes to impact strength. It can also be seen in Figure 1 that the addition of small amounts of plasticiser can lead to *increases* in modulus and tensile strength and a *decrease* in elongation to break. This effect is called antiplasticisation and is believed to be due to an increase in **crystallinity** caused by the

increased mobility of chain segments on addition of plasticiser. When a large amount of plasticiser has been added the crystallites are believed to redissolve and normal plasticising action take place. The minimum concentration required for plasticising action is known as the plasticiser threshold concentration and it varies with the plasticiser/polymer combination.

Plasticisers lower T_g . The T_g of the plasticised polymer may be estimated from the expression

$$\log\left(\frac{T_g}{T_{g1}}\right) = \frac{W_2 \log(T_{g2} / T_{g1})}{W_1 (T_{g2} / T_{g1}) + W_2} \quad (1)$$

where W_1 and W_2 are the weight fractions of plasticiser and polymer in the combination and T_{g1} and T_{g2} are the glass transition temperatures of the pure plasticiser and polymer. Plasticisers increase the temperature range of the glass transition region and also the useful temperature range over which the polymer may be used i.e. the difference between T_g and the softening temperature.

COMPATIBILITY

In order to provide effective and long lived plasticisation the plasticiser must be compatible with the polymer and must be retained in high concentrations for a long time. Early plasticised polymers often became rapidly brittle through the loss of plasticiser due to volatility. This problem can be overcome by using higher molecular weight plasticisers with a very low vapour pressure and predicted lifetimes based on plasticiser loss now frequently range from 30 to 100 years. However degradation by UV or other **environmental effects** can shorten this predicted life span.

Chemical compatibility from the point of view of a polymer/plasticiser system refers to the ability of the materials to mix to form a homogeneous composition. Solubility is controlled primarily by ΔH the heat of mixing and this is given by

$$\Delta H = n_1 \phi_2 V_1 (\delta_1 - \delta_2)^2 \quad (2)$$

where n_1 is the mole fraction of solvent, ϕ_2 the volume fraction of solute, V_1 the molar volume of the solution and δ_1 and δ_2 the solubility parameters of the solvent and solute respectively. δ may be estimated from the expression $\delta = \Delta E/V$ with ΔE the energy of vapourisation per mole and V the molecular volume (see also **Alloys and Blends** and **Adhesion**). However, the molecular weights involved are so high that measurements of heat of vapourisation are impractical.

Factors, other than solubility, which control compatibility include hydrogen bonding, dipole moment, viscosity etc. A combination of a suitable solubility parameter δ and a similar dielectric constant (which is a measure of dipole moment and intermolecular

forces) will often pinpoint likely candidates for compatible plasticisers. Fuller information on plasticisers may be found in the references below.

REFERENCES

1. Sears, J.K. and Darby, J.R., (1982) *The Technology of Plasticizers*, Wiley
2. Gould, R.F. (ed.) (1965) *Plasticization and Plasticizer Processes, Advances in Chemistry Series No. 48*, American Chemical Society
3. Ritchie, P.D. (ed.) (1972) *Plasticisers, Stabilisers, and Fillers*, Iliffe

39: Poisson's Ratio

K E EVANS

INTRODUCTION

The Poisson's ratio of a material, ν_{xy} , is normally defined as

$$\nu_{xy} = \frac{-\epsilon_y}{\epsilon_x} \quad (1)$$

Where ϵ_x is an applied longitudinal strain and ϵ_y is the resulting orthogonal, lateral strain. Since most materials contract when stretched, the minus sign is a convention to ensure that most materials have a positive value for ν_{xy} .

In this article the basic relationships resulting from the derivation of Poisson's ratio from linear, small-strain elasticity theory will be summarised. Then attention will be given to the problems associated with polymers - in particular strain dependent and strain-rate dependent behaviour - and how they may be dealt with (see **Stress and Strain**).

POISSON'S RATIO FROM CLASSICAL ELASTICITY THEORY

Poisson's ratio arises from the stiffness matrix of classical elasticity theory which, for a generally anisotropic material, assuming diagonal symmetry of the stiffness matrix, has 21 independent constants¹. As a result of the symmetry of the stiffness matrix we have

$$\nu_{xy}E_y = \nu_{yx}E_x \quad (2)$$

Given that the stiffness matrix must be positive definite then the extreme bounds on the value of Poisson's ratio are given by

$$\nu_{xy} \leq \left(\frac{E_x}{E_y} \right)^{1/2} \quad (3)$$

Hence for an orthotropic material Poisson's ratio may be large positive or negative and indeed values as large as -12 have been measured².

By applying the constraints imposed by the symmetry of a particular material, the

bounds on ν_{xy} are further reduced. In the isotropic case

$$-1 \leq \nu \leq 1/2 \quad (4)$$

In this special case, any two of the four elastic constants, Young's modulus E , shear modulus G , bulk modulus K and Poisson's ratio ν , may be treated as independent. The others are then interrelated by such relations as

$$G = \frac{E}{2(1 + \nu)} \quad \text{and} \quad (5)$$

$$K = \frac{E}{3(1 - 2\nu)} \quad (6)$$

The fundamental importance of Poisson's ratio in determining the mechanical properties of any material can be found by a cursory examination of any standard text on mechanical properties. Properties that depend on Poisson's ratio include plane strain fracture toughness, indentation resistance, sound wave propagation, thermal shock resistance and critical buckling.

In general, Poisson's ratio has been treated as a parameter that varies little from polymer to polymer. However, the recent discovery that it can be varied over a considerable range of values³ leads to the possibility of designing materials with varying Poisson's ratios (see **Manipulation of Poisson's Ratio**).

POISSON'S RATIO IN POLYMERS

There are three added problems in dealing with Poisson's ratio in polymers: anisotropy, strain dependence and strain rate dependence of mechanical properties. Formally, the first of these can be dealt with within the context of classical elasticity theory. However, the large increase in independent variables from two in the isotropic case to, say, nine in the orthotropic case produces a very considerable increase in practical difficulties, most especially in the complexity and tediousness of the measurements needed to fully characterize a material. However, this issue has to be addressed. It is not unusual, for example, for researchers using computational methods such as finite element analysis to design plastic components, to be unable to find data on all the necessary elastic constants to fully characterize the material. This issue continues to be a problem.

By definition, Poisson's ratio is a constant. However, many polymers are not perfectly elastic. Even if they are stiff in the elastic region, this region may not be linear, in which case, it is necessary to define a strain dependent Poisson's function⁴ :

$$\nu_{ij} = -\frac{\Delta \epsilon_j}{\Delta \epsilon_i} \quad (7)$$

defined by the gradient of the change of strain. This is equivalent to the need to use the tangent modulus to define non-linear stiffness. It is also important, under such circumstances, that true strains, rather than engineering strains, be used; otherwise considerable and important errors can occur⁵. These issues are particularly important for relatively soft polymers and biological polymers⁶.

Many polymers are not just anelastic, they are also plastic. Under such circumstances it is important that one is aware that one is dealing with an effective Poisson's ratio. For example, the value obtained may differ in a tension test to that obtained in a compression test and it is important to define the value and range of strain that the single value may be applied to. In the general case, Poisson's function must be used and practical techniques for dealing with this issue now exist⁵.

Finally, it is necessary to deal with the problem of **viscoelasticity**. As is well known⁷ the Young's modulus and shear modulus of a viscoelastic material can be represented as

$$E^* = E' + iE'' \quad (8)$$

and

$$G^* = G' + iG'' \quad (9)$$

Assuming we have an isotropic material, this gives

$$\nu^* = \nu' + i\nu'' \quad (10)$$

where

$$\nu' = \left[(E'G'' + E''G') / 2(G'^2 + G''^2) \right] - 1 \quad (11)$$

$$\nu'' = (E''G' - E'G'') / 2(G'^2 + G''^2) \quad (12)$$

The important point to note here is that in any standard 'static' test ν' is measured and it might be assumed that this is independent of the imaginary components. However, ν' contains the imaginary components of E'' and G'' . Hence the apparent elastic response may reflect the time dependent characteristics in a more complex way than either E^* or G^* ⁸.

REFERENCES

1. Lempriere B.M. (1968) *AIAAJ*, **6**, 2226,.
2. Evans K.E., Caddock B.D., (1989) *J.Phys.D.Appl.Phys.*, **22**, 1883,.
3. Neale P.J., Pickles A.P., Alderson K.A., Evans K.E, (1995) *J.Mat.Sci.*, **30**, 4087.
4. Beatty M.F., Stalnaker D.O, (1986.) *J.Appl.Mech.*, **53** , 807,
5. Anderson K.L., Alderson A., Evans K.E, (1997) *J.Strain Analysis*, **32**, 896.
6. Caddock B.D., Evans K.E, (1995) *Biomaterials*, **16**, 1109.
7. Ferry J.D, (1970) *Viscoelastic Properties of Polymers*, 2nd Ed., Wiley, N.Y.
8. Rigby Z., (1967) *Appl.Poly.Symp.*, **5**, 1.

40: Polymer Models

D. J. Parry

TIME DEPENDENT BEHAVIOUR

If an ideal elastic solid is subjected to a step increase in stress, the strain increases suddenly and then remains constant. However, if a polymer is subjected to a step increase in stress, there will be a time-dependent continuous increase in strain after the initial elastic response; this behaviour is called **creep**. The time constant associated with this process is called the retardation time. Alternatively, if a step increase in strain is applied, then the stress decreases with time; this is stress relaxation. The time constant in this case is called the relaxation time. These time constants can be related on a microscopic level to the fundamental molecular structure through various activation processes. However, many features of time-dependent polymer behaviour can be described by using simple phenomenological models (see **Viscoelasticity**).

LINEAR VISCOELASTIC MODELS

The simplest of these models are based on a linear (Hookean), massless spring of elastic modulus E and a linear (Newtonian) dashpot of viscous constant η . For the spring, the stress σ and strain ϵ are related by $\sigma = E\epsilon$; for the dashpot, the stress is related to the strain rate by $\sigma = \eta d\epsilon / dt$, where t is time. The dashpot enables time dependency to be modeled. Some of the more common simple models are outlined below.

The Maxwell model

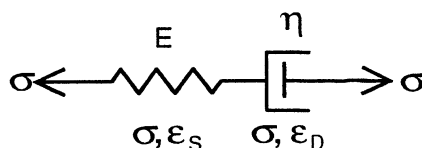


Figure 1: The Maxwell model.

Figure 1 shows the Maxwell model in which the spring and dashpot are in series. The stress is the same for each element and the strains add, i.e. the total strain is $\epsilon = \epsilon_s + \epsilon_D$. Differentiating gives the stress-strain relationship:

$$\frac{d\epsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad (1)$$

The Kelvin (or Voigt) model

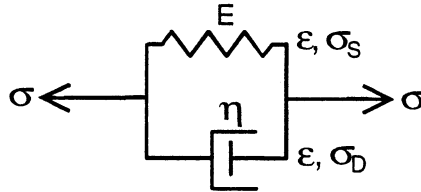


Figure 2: The Kelvin model.

The Kelvin model is shown in figure 2. The spring is in parallel with the dashpot and so the strain is the same for each element while the stresses add, i.e. the total stress is $\sigma = \sigma_s + \sigma_D$. The stress-strain relationship is then:

$$\sigma = E\epsilon + \eta \frac{d\epsilon}{dt} \quad (2)$$

The standard linear solid

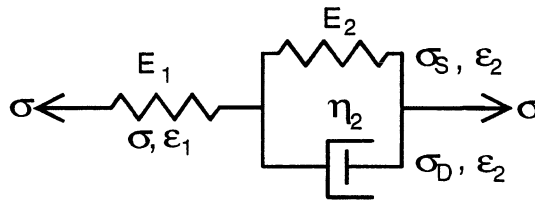


Figure 3: The standard linear solid.

One form of the standard linear solid, as illustrated in figure 3, combines a Kelvin model in series with a spring. Using the same procedures as above leads to the following stress-strain relationship:

$$E_1 E_2 \varepsilon + E_1 \eta_2 \frac{d\varepsilon}{dt} = (E_1 + E_2) \sigma + \eta_2 \frac{d\sigma}{dt} \quad (3)$$

An alternative, equivalent, version of the standard linear solid is that of a Maxwell model in parallel with a spring.

ACCURACY OF THE MODELS

A guide to how accurately the models predict real polymer behaviour can be seen by comparing the strain-time response of a typical solid polymer with that of the models when subjected to creep loading and unloading.

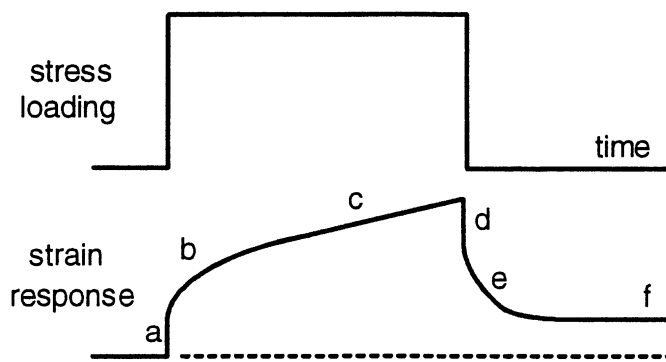


Figure 4: Stress loading/unloading and the strain response for a solid polymer.

Figure 4 shows that for a real material there are several distinct regions. In the loading part, region (a) corresponds to an instant elastic response, (b) is a retarded (primary creep) region in which the strain grows exponentially with time, while (c) is a linear viscous (secondary, or infinite creep) region in which the strain rate is constant. The unloading response consists of an instant elastic part (d), a retarded part (e), and finally a region (f) corresponding to a permanent strain.

The Maxwell model predicts regions (a), (c) and (f), but not (b) and (e). The Kelvin model is satisfactory for regions (b) and (e), but not for the rest. The standard linear solid successfully predicts the shapes of all the regions except for (c) and (f). Clearly, a more complex model is needed to predict the actual response. A four element representation consisting of a Maxwell model in series with a Kelvin model does predict

all the response regions but still has only one time constant (retardation time). Since real materials can have a large number of retardation times in regions (b) and (c), the most accurate representation of the strain response can only be realised by having a generalised model with a continuous spectrum of retardation times. The same arguments apply to the use of models to represent stress relaxation.

REFERENCES

1. Crawford, R.J. (1987) *Plastics Engineering*, Pergamon Press, Oxford.
2. Ward, I.M. and Hadley, D.W. (1993) *An Introduction to the Mechanical Properties of Solid Polymers*, John Wiley and Sons, London.

41: Recovery of Glassy Polymers

C. Gauthier

From a very general point of view, when a sample is submitted to an external force, it undergoes a deformation. That deformation is termed reversible if it disappears when the force is removed. When reversibility is total and instantaneous, the deformation is elastic. Actually, at low value of strain, the behaviour of a polymer is viscoelastic. The recovery process is then partly delayed with time: this component of the deformation is called anelasticity. Beyond a certain limit, a part of the deformation becomes irreversible. This permanent deformation is called plastic. In metals, the threshold, also called the plastic limit, is quite easy to determine. However, in polymers, the plastic limit is more difficult to estimate due to a polymers viscoelastic nature and the existence of anelasticity (see **Viscoelasticity**). Conventionally, the different components of strain are illustrated via a creep test (see Figure 1 and **Creep**).

Several studies have shown that amorphous polymers subjected to large deformation (up to more than 50%) in the glassy state can recover their whole deformation at a temperature above T_g . This recovery leads us to question the usual distinction of the two non elastic deformations: anelastic and plastic. The aim of this article is to clarify this aspect by illustrating the recovery process as a function of time and temperature.

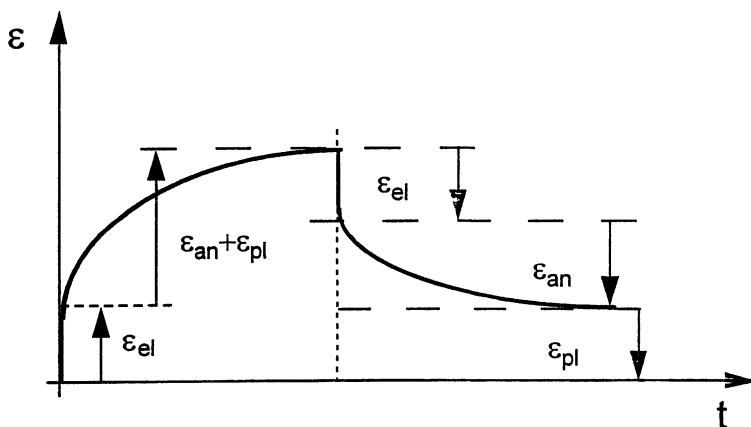


Figure 1: Schematic representation of strain versus time during a creep test: components of the deformation: elastic (ϵ_{el}) anelastic (ϵ_{an}) and plastic (ϵ_{pl})

STRAIN RECOVERY TESTS - EXPERIMENTAL PROCEDURE

The tensile test is the simplest method to evaluate the mechanical behaviour of solids. But in polymers, as advised in standard textbooks, it is better to use compression and

shear tests in order to avoid heterogeneous deformation due to plastic instability phenomena such as necking. The uniaxial compression test consists of loading a homogeneous sample, of fixed cross section, at constant cross head velocity (e.g. 0.1 mm min^{-1}). The test is performed on cylinders with dimensions of the order $L=22 \text{ mm}$, $\varnothing = 8 \text{ mm}$ so as to avoid buckling effects and to minimise barrelling (see **tensile and compressive testing**). The strain is measured by means of an extensometer fixed on the sample.

In order to study recovery the cross-head of the apparatus is stopped at a certain level of deformation (ϵ_i), and immediately moved in the opposite direction at a constant rate (e.g. 1 mm min^{-1}). During this active unloading, data are still recorded until the load becomes equal to zero. In practice, several samples are deformed up to different strain values and then unloaded. After a given recovery time (t_{rec}), the residual strain (ϵ_r) is obtained by measuring the length of the deformed part of the sample using, for example, a LVDT transducer (see **Transducers**).

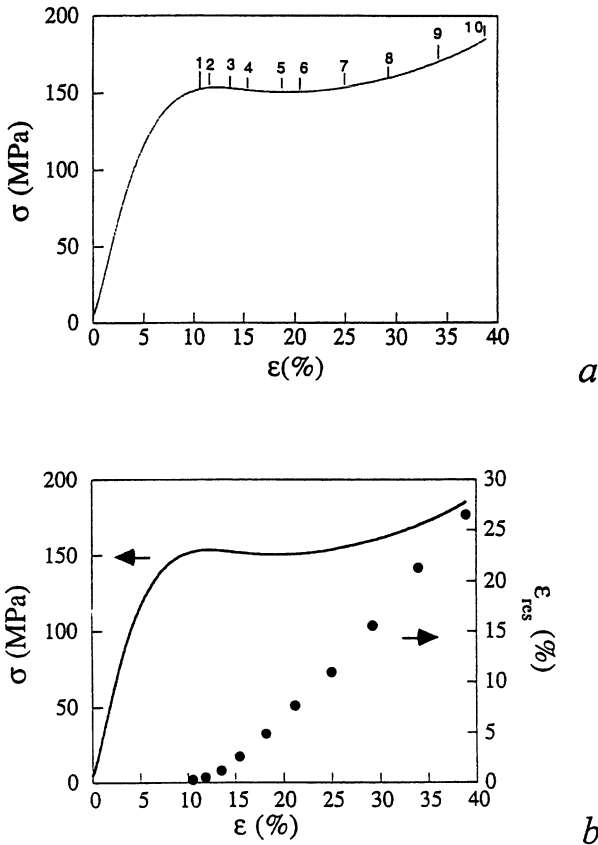


Figure 2: Determination of residual deformation (ϵ_{res}) for different applied strain levels (ϵ_i) (PMMA, 20°C) a) Stress strain curve, positions of the applied strains for ten different samples b) Residual strain after 15H at 20°C versus applied strain.

Influence of time and temperature

In short, the residual strain ϵ_{res} is recorded after different values of time t_{res} for different applied strain levels (ϵ_i). Figure 2 illustrates the data from such a test. The curve ϵ_{res} versus ϵ_i depends on the time and temperature of the recovery process. Obviously, for a given applied strain, the residual strain decreases as the recovery time increases. In addition, the recovery kinetics depends on recovery temperature (T_{rec}). At a temperature well below T_g of the polymer, the residual strain decreases slowly with time. However, the strain recovery kinetic is fast for T_{rec} Close to T_g . For example, in the case of PMMA strained to 19% at 20°, the residual strain measured after 15 h decreases quite regularly at temperatures up to 100°C; however at higher temperatures the recovery rate accelerates and recovery becomes total at 120°C. From the isothermal recovery curves, it is possible to build a strain recovery master curve by applying a time temperature reduction scheme (see **Time-Temperature Equivalence**), i.e. by shifting the isotherm data. along the log time axis. The thermal activation effect on the recovery process is then clearly shown.

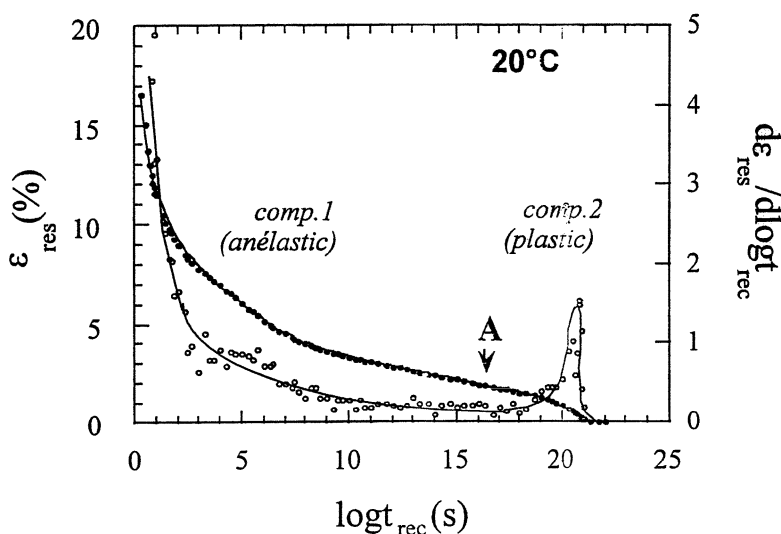


Figure 3: Recovery master curve for PMMA strained to 19% at 20°C

Strain recovery master curve

Figure 3 illustrates the strain recovery master curve obtained for PMMA strained to 19% with a reference temperature equal to 20°C and also the derivative of that master curve. Firstly, the large time scales involved should be noted. From this curve, it can be estimated that at 20°C, the time for the total recovery of the PMMA strained up to 19% corresponds to ten billion years. From the derivative curve, one can estimate the

characteristic time distribution of the non elastic deformation recovery. At least qualitatively, two contributions to the recovery process can be distinguished. We can see that at $T = 20^{\circ}\text{C}$, the first component extends from the very beginning of the recovery experiment to times around 10^{15}s . Note that the unloading time employed (a few seconds) prevents the recovery process being followed at time shorter than about 10s. The second component is less distributed (only two decades) around 10^{19}s at 20°C which corresponds to about one billion years (at 115°C the corresponding deformation is totally recovered in a few minutes).

Considering the characteristic time distribution of these two components, they can be attributed to the two components of the non elastic deformation. Due to the fact that the second component recovers only after very long times whereas the first one is mostly recovered after normal observation times, these components can be conventionally called plastic and anelastic deformation respectively. However, at temperatures near T_g , the relative recovery times of the plastic component also become very short and both cannot be distinguished anymore.

Finally, it can be added that non elastic strain recovery can also be investigated by applying a linearly increasing temperature to the sample. For example, Oleynik³ and co-workers have shown the existence of two distinct components during the strain recovery of several polymers strained at temperatures far below T_g .

CONCLUSION

The non elastic strain recovery in glassy amorphous polymers is a two stage process. Each stage corresponds to a particular component of the non elastic deformation which can be clearly identified when the temperature is less than $T_g - 30^{\circ}\text{C}$: (i) an anelastic component which recovers over a large time scale (at least 10 decades) ranging from very short times to some 10^{15}s in PMMA at 20°C , and (ii) a plastic component which recovers over a range of about two decades after around one billion years for PMMA at 20°C . Nevertheless, this second component can recover in a few hours at temperature close to T_g . The use of a thermal treatment will allow the elimination of the anelastic part of the deformation (plastic deformation remaining unmodified). This thermal treatment consists of 1 hour at $T_g - 20^{\circ}\text{C}$ corresponding to point A on Figure 3 in the case of PMMA, the example illustrated here.

REFERENCES

1. Ward I.M and Hadley D.W. (1993) *Mechanical properties of solid polymers*, Wiley, New York
2. Quinson R., Perez J, Rink M., Pavan A, (1996) *J. Mat. Sci.* **31** 4387-4394
3. Oleynick E.F., (1990) in *High performance polymers* ed. E. Baer and S. Moet, Hanser Verlag, Munscher.

42: Relaxations in Polymers

G. M. Swallowe

INTRODUCTION

Viscoelastic models of polymer behaviour incorporate a relaxation time which is defined as the ratio of the viscosity of the elements to their modulus (see the article on **polymer models**). In more complex models a relaxation time spectrum is defined since it is recognised that an adequate model of the behaviour cannot be made using a single relaxation time. The agreement between experimental observations and theory increases as the number of elements, and associated relaxation times, in the models increase and by using a large number of elements and a relaxation time spectrum good agreement can be achieved. However this is an artificial process and the use of such models tells us nothing about the molecular processes which give rise to viscoelastic response, they merely provide a means by which the response of the polymer, over the temperature, time and strain rate for which the model is valid, can be predicted. There are however 'genuine' relaxations which occur in polymers which are related to the movements of side groups and give rise to changes in the modulus and loss tangent.

α , β , γ RELAXATIONS

For an amorphous polymer a dramatic change in the modulus occurs in the region of the **glass transition** temperature T_g . This can be thought of as being due, at temperatures below T_g , to the available thermal energy falling below that required for chain segments to have the energy needed to overcome the potential barriers to movement. The system is therefore 'locked' into a glassy state. This transition is called the α transition or α relaxation. It can be readily observed by plotting the modulus or the loss tangent as a function of temperature as illustrated in the schematic diagrams in Figure 1. Figure 1a shows the change in modulus as a function of temperature, the glass transition is readily apparent as are several smaller transitions at temperatures below T_g . These are called secondary transitions or secondary relaxations and are given the names β , γ , etc. in descending order of temperature below the glass transition.

In a viscoelastic medium the modulus is time dependant (see article on **dynamic mechanical analysis techniques and complex modulus**) and there is a damping factor associated with each change in the modulus. This means that if an oscillating stress is applied to a polymer the strain in the material will lag behind the stress. This lag is frequency dependent and is expressed in radians. The angle of lag δ gives a measure of the energy loss per cycle in the region of the transition through the 'loss tangent' $\tan \delta$.

$$\tan \delta = 1/\omega\tau = E''(\omega)/E'(\omega) \quad (1)$$

with ω the frequency of oscillation, τ the relaxation time associated with the transition $E''(\omega)$ the (frequency dependant) loss modulus i.e. the quantity which measures energy dissipation in the material and $E'(\omega)$ the modulus which measures the strain in phase with the applied stress, the storage modulus. A plot of $\tan \delta$ against temperature (at a fixed frequency of oscillating stress) therefore has peaks at temperatures corresponding to the relaxations where the energy dissipation in the material has maxima. Figure 1b illustrates this process.

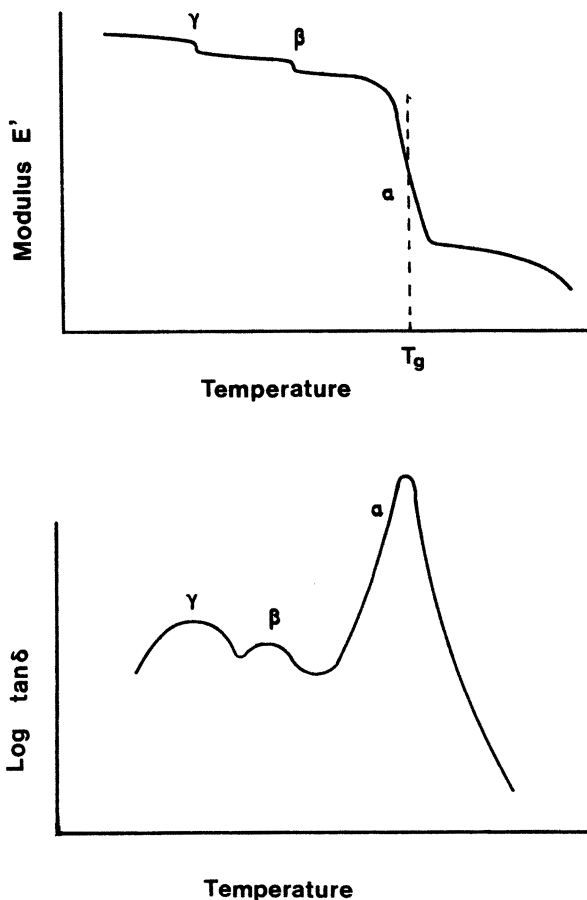


Figure 1: a) schematic of the temperature dependence of the modulus of a polymer. b) corresponding relaxations as observed in $\tan \delta$.

The glass transition is the range of temperatures at which large scale chain motion becomes possible. The molecular motions involved in the glass transition are rotational. Bulky side groups which inhibit rotation will reduce the glass transition temperature.

Secondary transitions arise as a result of freedom of motion which is still possible for side groups or short sections of the polymer backbone chain at temperatures below T_g where the activation energy for these motions is less than that required for large scale chain motion. The precise position of the secondary peaks depends on the testing frequency, in a similar way to that in which the T_g itself varies with testing frequency, or equivalently, **strain rate**. However the frequency sensitivity may vary from relaxation to relaxation and testing at a high frequency could 'drive' the β transition into the α and it would therefore no longer be apparent.

Secondary relaxations are generally due to rotational motion of side groups, either about their link to the main backbone chain or the sidegroup together with its link atom about the rest of the chain in a 'crankshaft' motion³, see figure 2.

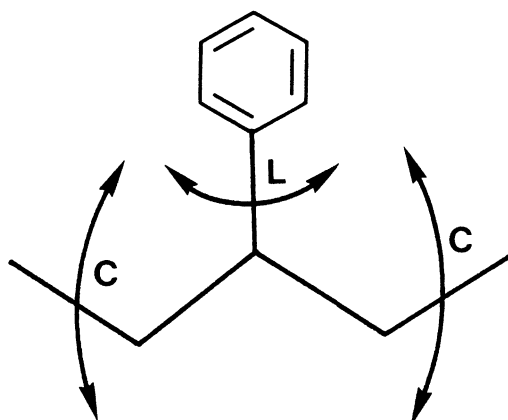


Figure 2: Schematic of rotation about a chain link L, and 'crankshaft' rotation C.

CRYSTALLINE POLYMERS

The discussion above applies to **amorphous polymers**, **crystalline polymers** can be considered to be two-part materials in which the transitions described above take place in the amorphous portion. There will in addition be relaxations which occur in the crystalline phase involving for example defects or co-operative motion of atoms along the chains within the crystallites. Interlamellar shear in which crystallites move relative to each other by shear of the amorphous regions is also possible. Study of relaxation processes is ongoing and very few crystalline polymers have yet been studied in sufficient detail for the unambiguous assignment of the peaks to particular molecular processes. More detailed discussions of the processes involved can be found in the books by Arridge¹, Ward⁴ and McCrum² et al.

REFERENCES

1. Arridge, R.G.C. (1975) *Mechanics of Polymers*, Clarendon Press, Oxford
2. McCrum, N.G., Read, B.E. and Williams, G. (1967) *Anelastic and dielectric effects in polymeric solids*, Wiley
3. Shatzki, T.F. (1962) *J. Polymer. Sci.* **57**, 496.
4. Ward, I.M. (1985) *Mechanical Properties of Solid Polymers*, Wiley.

43: Sensors and Transducers

G. M. Swallowe

Strictly speaking a sensor is a device which detects or measures a physical quantity and a transducer a device which converts energy from some physical quantity into an electrical signal. However the two terms are commonly used interchangeably and will not be distinguished in this article. From the point of view of mechanical testing the parameters that are of most importance are force (stress), strain and temperature

TEMPERATURE

Temperatures, other than ambient, are almost universally measured with thermocouples although devices such as resistance sensors are sometimes employed. Thermocouples consist of junctions between different metals and provide a DC output voltage in the millivolt range that increases with the temperature difference between the sensing junction and a reference junction held at a known temperature. Their small size and short response times, compared to thermometers, as well as the fact that they give an electrical output makes them ideal temperature sensors. The system traditionally consists of a continuous circuit with a copper wire leading from a sensitive meter to a junction with (for example) a constantan wire. The constantan wire leads to a second constantan /copper junction and then copper wire leads back to the meter. A range of thermocouples suitable for use over different temperature ranges are available with the most suitable for polymer work being the copper constantan (-200 to 350 °C) although chromel-constantan provides a larger output signal and chromel-alumel which has a smaller output but a larger useful range are also commonly employed. The traditional method of use involves inserting one junction into an ice/water mixture and the other in the region of interest and using the published thermocouple tables to calculate temperature from the output voltage. However this method has almost disappeared since the advent of solid state electronic devices which simulate the reference and also incorporate sensitive voltage measuring circuits. Using these devices the reference junction is not required and a single metallic junction is placed in the region of interest with the insulated copper and constantan wires running back to the detection instrument. If the temperature measurement is acceptable to an accuracy of a couple of degrees then no special meters are required and a simple two wire thermocouple can be used with a standard multimeter. The voltage measured by the meter is converted into a temperature using the standard tables and the ambient room temperature added to the result to yield the temperature at the thermocouple junction.

Resistive temperature transducers operate by monitoring the change in resistance with temperature of either a thin film or a coil of metal, usually platinum. Since only small changes in resistance occur the instrumentation required to reliably detect modest

temperature changes needs to be more sophisticated than that used in thermocouple circuits. Usually a bridge circuit incorporating compensation for the lead resistances will be required^{1,2}. Since a larger quantity of the sensing substance is used in a resistive sensor than in a thermocouple their response is rather slower, typically taking several seconds to respond to a 100° change. Thermistors, which are resistive sensors based on semiconductors, are more suitable than metallic resistance sensors for low temperatures i.e. in the range ~ -50 to 150 °C. The thermistor resistance change is very non-linear and because of this it does not form the basis of reliable 'do it yourself' systems but commercial systems incorporating small and reasonably rapidly responding sensors are readily available.

STRAIN

Strain measurements cover a range from small fractions of a percent in the elastic region to extension ratios of hundreds of percent in elastomers and drawn polymers. For small strains it is important to measure strain directly on the sample since the errors introduced by attempts at 'toe compensation' (see **Tensile and Compressive Tests**) will lead to serious errors in strain measurement. The most popular method of measuring small strains is by the use of strain gauges. These are small and cheap resistive elements, usually metal foil or thin wire, whose change of length with strain causes a resistance change which is then monitored. The resistance change is measured using a resistance bridge and converted to strain via the expression

$$\varepsilon = (\Delta R/R)/GF \quad (1)$$

with GF the gauge factor. The gauge factor of metal gauges is normally about 2. However the strain limit on most gauges is normally in the region of 1-3% so the resistance change is small. Semiconductor gauges, in which the sensing element is a strip of semiconductor, have a larger gauge factor (~ 50-200) so the resistance change for a given strain is much greater. However semiconductor gauges have a very small maximum strain before failure (~ 0.5%). The gauge sensing elements are normally mounted on a polyester backing which must be glued to the sample. For attachment to most materials a suitable glue that does not creep (normally an epoxy, polyester or cyanoacrylate) can be found but polymers such as polyethylene and PTFE present special difficulties and drastic surface treatments may be required before a gauge can be attached. Metal foil 'post yield' gauges which have strain limits of up to 20% are available but can be only used for one strain cycle. When measurements are carried out at temperatures other than ambient the differential thermal expansion between the gauge material and the sample will give rise to apparent strains. These can be accounted for by the use of temperature compensation techniques^{3,4}.

Most tests where strains of greater than a few percent are involved make use of extensometers. In tensile tests these clip on to the sample and measure the change in

separation of the attachment points during the test. In compressive tests they are usually used to measure the changing separation of the compressing platens. The measuring action of extensometers may be based on strain gauges, in which the displacement is transformed into the bending of an elastic beam to which the gauges are attached, or on direct resistance, inductance or capacitance changes.

The simplest (and cheapest) extensometers are linear potentiometers and these are available in precision form with a linearity (resistance against displacement) of 0.1% over displacement ranges up to several hundred mm. The alternative for displacement measurements in the range of millimeters to centimeters is the linear variable differential transformer (LVDT). The LVDT consists of three coils wound on a former in which a core of ferromagnetic material can move along the axis of the coils. The central coil is supplied with an AC signal in the range of 1 Hz to 10 MHz and the output of the other coils is monitored by the associated electronics¹. The resulting signal is linear with displacement of the core to an accuracy of $\sim 0.1\%$. LVDTs are rugged, often mounted in stainless steel cases, and resist shock and vibration. They have a large output signal and very low friction movement of the core so wear is minimal. They are however rather more expensive than linear potentiometers and the associated electronics is more sophisticated.

Capacitive transducers, which depend for their operation on the change in capacitance between a fixed plate and a movable plate attached to the sample, are also available. They are however rather less practical than resistive transducers or LVDTs and are rarely used in polymer work except for systems where sub millimeter length changes are expected e.g. thermal expansion measurements.

All the displacement measurement techniques outlined above involve fixing the extensometer to the sample in some way. This may be by gluing in the case of strain gauges or using clips for an extensometer. There is then concern that the gauges may 'reinforce' the sample and that an extensometer will change the state of stress in the sample both by the application of lateral forces and due to the stress in the region of the clips. Non contact measurement techniques are therefore gaining in popularity.

Non contact methods are based on optical observations of the sample surface. The simplest types make use of small self-adhesive targets which are placed on the sample and their separation monitored either by a video system or optical sensors which accurately follow the targets. These are essentially automated versions of a traveling microscope technique. More sophisticated techniques based on Laser Speckle Interferometry⁵ enable strain to be monitored over the whole sample surface with displacement resolutions of $1\mu\text{m}$ or less. It is based on interpreting changes in the speckle pattern observed when an expanded laser beam falls on a surface. Automated systems using video monitoring and including the interpretation software on a dedicated PC are commercially available. Techniques based on Moiré fringes³ also enable strain over the whole surface to be monitored at strain resolutions down to $\epsilon = 10^{-5}$. The Moiré technique is based on the interference effects observed when one regularly spaced grid is observed through a second similar grid. The interference pattern that arises when one grid is deformed can be related to the displacements of the other grid. Normally the Moiré technique involves one grid being bonded to the sample and the patterns are

observed through the second (reference) grid. However, projection techniques can be used which dispense with the need for a bonded grid by projecting an image of a grid onto the sample and observing the image through the reference grid.

FORCE

Force transducers come in a wide variety of designs ranging in sensitivity and range from milligrams to tonnes and with linearities varying from a few percent to $\sim 0.1\%$. Strain gauge based force transducers are almost universally used for static force measurements. For the lower end of the force range they are based on a load cell in which the force is transmitted to a beam or diaphragm and the resulting elastic bending of the beam or diaphragm element is detected by bonded strain gauges. At higher loads the direct axial compression or tension of a steel rod onto which the strain gauges are attached may be used (see **Hopkinson Bar**). Dynamic force measurements are usually made with accelerometer. This is a transducer which measures acceleration. Knowing the mass of the object to which the accelerometer is attached the force can be calculated using the relationship $F = ma$ (see **Falling Weight Impact Tests**). Accelerometers are small rugged devices whose operation is based on the fact that certain materials, piezo-electric materials, generate a voltage when compressed or sheared. The charges induced on the faces of the piezo-electric crystals under pressure can only generate minute currents and the output impedances are very high so they must be used with sensitive (and expensive) charge amplifiers. Some of the more modern devices incorporate amplifiers into the accelerometer itself giving a lower output impedance and reducing the possibility of noise pick up by the leads to the accelerometer. The devices contain a small moveable mass and a piezoelectric crystal within a sealed steel shell. Any acceleration or deceleration of the device causes the mass to load the crystal and a voltage is produced which is proportional to the acceleration. Calibration of the accelerometer/amplifier system enables the output voltage to be converted into the absolute value of acceleration of the device and hence of the mass to which it is attached. Since they depend on acceleration for their output they are only useful for dynamic measurements and find their main materials testing applications in instrumented drop weight and fracture systems. Accelerometers being essentially a mass/spring system will have a natural resonance frequency and their output will become non-linear if the operating frequency approaches the resonance frequency. They are generally available with usable frequency ranges from ~ 1 Hz to 30 kHz.

NOISE

Many experiments will involve the use of long electrical leads connected to strain gauges, extensometers, accelerometers etc. Such leads are a frequent source of noise which is picked up from mains 'hum', electrically operated machinery or other sources

of electromagnetic radiation in the vicinity. If DC measurements are being made this noise can be eliminated by the use of blocking filters which will only transmit signals with a frequency below ~ 1 Hz and the problem can be overcome. Fortunately the strain rate of most standard tests puts them in this category. Dynamic measurements are however essentially AC measurements and the frequency response of the system must be sufficiently large that the true material response (e.g. the voltage output of a transducer as a function of time) is not smoothed or distorted by filtering. Pickup can therefore be a major problem. Ensuring that wiring to/from a strain gauge is wound together and does not form any loops which can act as an aerial and, if possible, is in the form of a earthed shielded cable reduces the problem. Signal amplification as close as possible to the sensor boosts the signal relative to any noise picked up and is a major advantage, hence the development of accelerometers with built in amplifiers. Earth loops are another major source of interference. Ideally only one earthing point should be used for all equipment in an experimental setup. Disconnection of the mains earthing pin in mains powered equipment is often desirable since it eliminates earth loops, though the risk of electrical shock is increased. References 6 and 7 provide much practical advice on noise reduction.

REFERENCES

1. Carstens, J.R. (1993) *Electrical Sensors and Transducers*, Prentice-Hall
2. Sinclair, I.R. (1988) *Sensors and Transducers: A guide for Technicians*, BSP Professional Books.
3. Holister, G.S. (1967) *Experimental Stress Analysis*, Cambridge University Press
4. Beckwith, T.G., Marangoni, R.D. and Lienhard, J.H. (1993) *Mechanical Measurements 5th ed.*, Addison Wesley.
5. Jones, R. and Wykes, C. (1989) *Holographic and Speckle Interferometry 2nd ed.*, Cambridge University Press.
6. Mardugian, M. (1987) *How to control electrical noise*, Don White Consultants Inc.
7. Morrison, R. (1996) *Solving Interference Problems in Electronics*, Wiley.

44: Slow crack growth and fracture

P S Leever

INTRODUCTION

Fracture is usually identified as a 'catastrophic' event: under increasing load, an existing crack suddenly propagates rapidly and uncontrollably through the component (see **Fracture Mechanics**). However, in many polymers, and especially in thermoplastics, any cracking is usually seen after a long period of growth under constant or constantly-fluctuating stress (see **Fatigue**). The loading conditions which ultimately precipitate fracture may, therefore, be of much less practical importance than those during the preceding months or years of steady slow crack growth¹. Although slow crack growth also occurs in other classes of materials, the internal mobility of polymers makes them rather more susceptible, particularly in the presence of an active environment (see **Environmental Effects**).

SLOW CRACK GROWTH PHENOMENA

Brittle slow crack growth is seen most clearly during fracture testing of amorphous polymers. Extending a single-edge notched (SEN) plate specimen of e.g. unmodified PMMA at a constant rate usually leads to catastrophic brittle fracture. However, careful observation reveals a region of initial crack extension, leaving a different (even smoother) fracture surface than the **rapid crack propagation** which follows. For PMMA tested using a specimen with a short initial crack, steady crack acceleration is followed by an abrupt jump in speed from tens of millimetres to hundreds of metres per second.

Changing either the material or the specimen geometry may reveal strikingly different behaviour. In a tough, crystalline polymer, the initial crack may become blunt during loading, and tear in a stable manner which can be arrested by stopping the test machine. The hallmark of tearing is that separation occurs only after the crack-tip material has drawn to an extent comparable to that seen in an un-notched tensile test: the presence of the notch merely localises the spread of drawing. Tearing may or may not develop into 'unstable' brittle fracture.

The resistance of a material to crack growth is generally determined by the stress needed to cause separation at the crack tip, and the capacity of the surrounding region to absorb damage while transmitting this stress to it. The mobile, entangled-chain structure of thermoplastics is relatively easy to separate. If the separation stress does not damage the surrounding material, brittle slow crack growth proceeds. Many polymers, however, gain toughness by their ability to open up, around the separation point, into a voided structure (usually showing stress whitening) which protects it (see **Crazing**). Ductile

crack behaviour may be induced in some otherwise brittle plastics by reducing the thickness or increasing the temperature. Geometry effects are important too: slow crack growth can be deliberately stabilised by the use of a specimen designed to measure it (see **slow crack growth and fracture: Measurement techniques**).

FRACTURE MECHANICS DATA

Linear elastic fracture mechanics concepts have been useful in correlating data on brittle slow crack growth. Crack growth rate $\dot{a}$ is measured as a function of applied stress intensity factor K (or, equivalently, crack extension force G). Plotted on log/log axes (Fig. 1), the data fall on a straight line:

$$\dot{a} = A_C K^n \quad (1)$$

(A_C and n being constants) although $\dot{a} \rightarrow 0$ as K is reduced towards a lower threshold K_{th} , and $\dot{a} \rightarrow \infty$ as K approaches the fracture toughness K_C i.e. the transition to **fast fracture**. The ‘constant’ A_C differs greatly from material to material and varies with temperature and with environment. A_C increases with temperature, and data can sometimes be organised using **time-temperature equivalence** concepts to produce a master curve. In general, n is much more constant: for most polymers, it is in the range of about 5-10.

The Dugdale model provides a useful way to relate fracture mechanics data to the underlying mechanics of the crack-tip craze. By relating toughness (G_C or K_C) to the craze stress (assumed to be uniform) and the craze opening displacement (which turns out to be constant), the model has for some materials been able to explain the all-important exponent n in terms of those which govern changes in modulus and yield stress¹.

MECHANISMS OF SLOW CRACK GROWTH

The principal separation mechanism in thermoplastics is stress-activated disentanglement. At working temperatures, individual segments along the chain undergo ‘Brownian’ motion, and are restrained from diffusing through the relatively open structure only by the neighbours to which they are bonded. For an entire polymer chain to diffuse along the tube formed by its neighbours requires a high mechanical force, or the long wait needed to see random motions apparently ‘co-operate’. However, *scission*: (breakage of a primary carbon-carbon backbone bond) requires even higher forces.

In an amorphous polymer structure chains can only be grasped and unravelled between entanglement points, which are transient statistical entities rather than ‘knots’. Light crosslinking provides real, stable anchor points which resist chain slippage up to higher stresses: very tough materials can be made by lightly crosslinking thermoplastics (e.g.

polyethylene). **Crystallinity** can confer similar benefits: the strength of crystallites themselves and the density of *tie molecules* that connect them are crucial factors. More heavily crosslinked polymers must separate by scission (which requires higher stresses) but are less ductile (so that the separation stress is ‘focussed’ more efficiently onto the crack tip). Thus thermosets usually show a lower fracture resistance. The distinction between slow crack growth and environmental stress cracking is purely nominal: air, and especially moist air, may itself be an active environment. The effect of environment may be physical or chemical (see **Environmental Effects**). Physical effects arise from plasticisation (see **Plasticisers**) at a stressed crack tip by fluids or gases which diffuse into it. Especially under the extremely high levels of triaxial tension at the tip of a growing craze, a mobile species can have a powerful effect in lubricating chain motion, thereby accelerating disentanglement.

There is strong evidence that voids form not only in the wake of retreating chain ends, but also at points where chain scission has been followed by combination with a free radical. The extra mobility of chain ends has a powerful effect on chain mobility, and therefore on slow crack growth. All other things being equal, low molecular mass grades have much lower slow crack growth resistance (see **Molecular Weight Distribution and Mechanical Properties**).

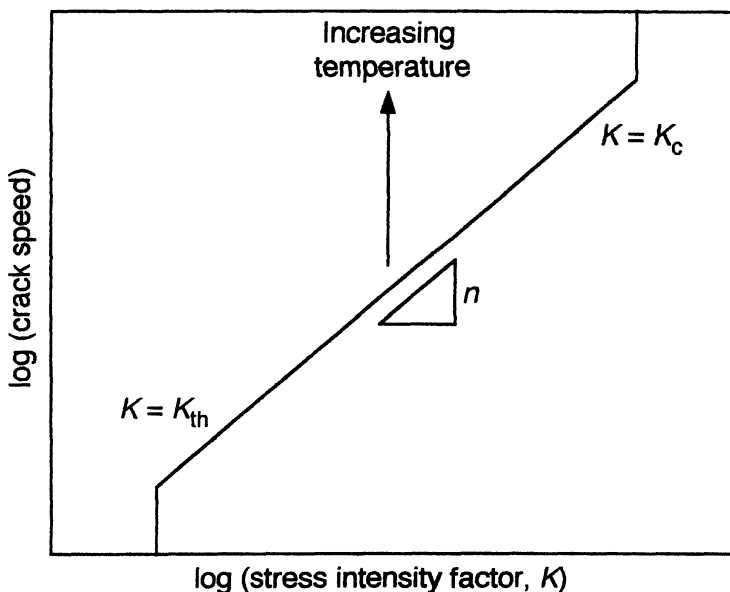


Figure 1: Schematic of typical slow crack growth for a polymer.

FROM SLOW CRACK GROWTH TO FRACTURE

Few polymers subjected to **tensile testing** fail by steady acceleration of slow crack

growth to complete separation. Some (e.g. PMMA) suffer an abrupt, almost instantaneous increase in crack speed by at least two orders of magnitude: they 'go bang'. Others such as polyethylenes, undergo a transition from slow crack growth (which is usually *very* slow) to crack blunting and nett-section yield, separating eventually by fracture of fully-oriented material. The distinction between slow crack growth and fast crack propagation is real, rather than merely a matter of degree: they are effectively demarcated by a regime of 'forbidden' crack speeds (see **Fast fracture in polymers**).

REFERENCE

1. Williams, J.G. (1987) *Fracture Mechanics of Polymers*, Ellis Horwood

45: Slow Crack Growth and Fracture: Measurement Techniques

P S Leever

INTRODUCTION

The use of **fracture mechanics** concepts to specify and characterise structural polymers remains relatively undeveloped. This is at least partly because it is impossible to attribute a unique 'fracture toughness' to materials which respond in such a complex way to temperature, environment, load history and duration of loading. When polymer components fracture, it is usually after a long period of slow crack growth, either under static or cyclically varying load. The loading conditions which ultimately precipitate fracture may, therefore, be of much less practical importance than those during the preceding months or years of steady crack growth.

To date, slow crack growth has been most widely studied for pressure-pipe materials which must sustain constant stress for 50 years or more, without developing either leaks or cracks which could be vulnerable to additional (e.g. impact) loads. This section outlines some of the ways in which such 'subcritical' crack growth can be investigated and presented as material data for predictive models.

FRACTURE MECHANICS METHODS

If a sharp crack in a polymer is held under a constant 'subcritical' loading $K < K_c$ or $G < G_c$ for a long period, the crack will generally extend at a constant rate (see **Slow crack growth and fracture**). As K is increased the crack growth rate increases exponentially. This can make measurement difficult. In, for example, a simple single-edge notched (SEN) tension specimen under constant load, K increases as the crack extends, causing rapid crack acceleration. The solution lies in the use of 'constant K ' specimens. The two most practical of these are the tapered double cantilever beam (TDCB) geometry (Fig. 1) and the double torsion (DT) geometry (Fig. 2). Each of these has the inherent property that its compliance increases linearly with crack length, rather than (as in most other geometries) more rapidly. Using linear elastic fracture mechanics concepts it is easy to show that, whether a constant-load is imposed (e.g. by a dead weight) or constant-displacement rate (by a test machine), K and therefore the crack speed should remain constant. K can be calculated from the load whilst the crack length can either be measured directly or inferred from the load-point displacement.

The TDCB specimen is an approximation to a 'contoured' DCB profile which can be shown analytically to maintain absolutely constant K but is difficult to make and rarely

used¹. The DT specimen is even simpler - merely a rectangular plate, with a crack guiding sidegroove on the underside. However, load or displacement is applied, unusually, out-of plane, by four-point bending near one end, twisting the specimen apart along its centreplane. The resulting crack front shape extends self-similarly but it is not straight through the thickness (as is approximately the case in most other geometries) but extremely curved (Fig. 2). Intersecting the lower edge more or less at right angles, it sweeps back steeply and does not even reach the upper surface. This leads to fewer interpretative problems than one might expect, but the crack speed measured on the lower surface (which is not easy to measure anyway) does not represent that along the rest of the crack front².

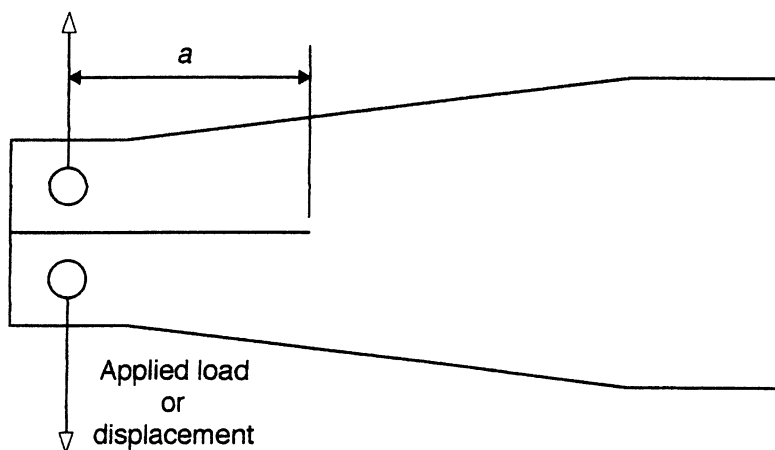


Figure 1: Tapered double cantilever beam (TDCB) specimen for slow crack growth testing.

TIME-TO-FAILURE METHODS

Slow crack growth testing is limited by a paradox: those materials which are easy to test (such as the much-studied PMMA) are, *ipso facto*, not used under long-duration loading. Materials like pipe-grade polyethylene and PVC which *are* used under long duration loading fail after such long periods that testing must somehow be accelerated. The most obvious way to do this is to increase K and extrapolate backwards; but such tough materials tend to react to this by blunting of the initial crack so that LEFM no longer applies. A more effective alternative is to increase the specimen thickness and measure time-to-failure rather than crack speed. It can be shown (approximately) that if crack speed is proportional to n then a specimen under constant load P will fail after a time proportional to $1/n$.

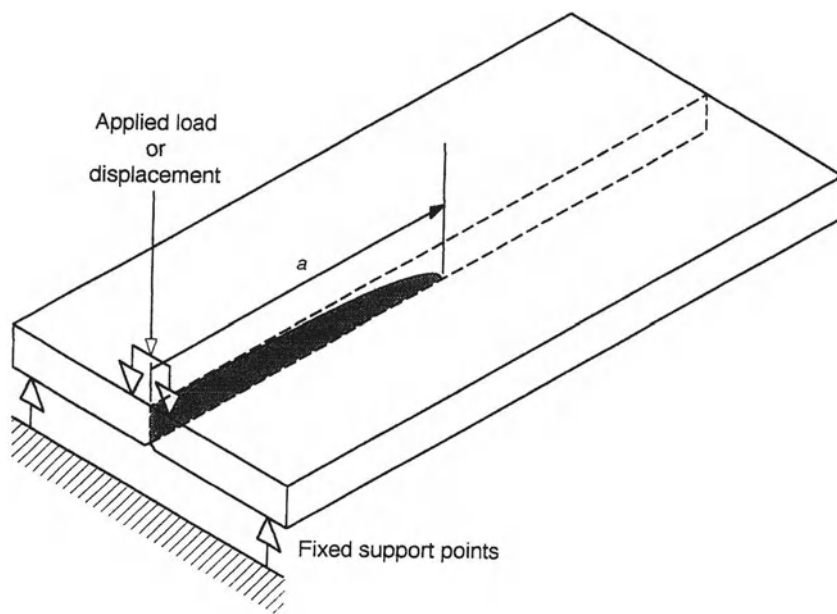


Figure 2: The double torsion (DT) test, showing a characteristically curved crack front.

A practical test employing this approach is the ‘PENT’ test³, which uses a thick plate deeply notched on three of its four faces so that the crack front is effectively as constrained as one in an infinitely thick plate. To accelerate the failure process, the temperature is raised.

REFERENCES

- 1 Williams, J.G. (1987) *Fracture Mechanics of Polymers*, Ellis Horwood (London).
- 2 Leever, P.S. & Williams, J.G. (1985) Material and Geometry Effects on Crack Shape in Double Torsion Testing. *Journal of Materials Science* **20**, 77-84.
- 3 Zhou, Z. and Brown, N. (1996) *Polymer Testing* **15**, 549-558.

46: Standards for Polymer Testing

G. M. Swallowe

There are three main types of standards 1) Measurement standards 2) Product specification standards and 3) Systems standards. Measurement standards are designed to ensure consistency in measurement and are maintained by National Laboratories where reference standards and calibrated measuring instruments are kept. These are used to provide the standards against which calibration service providers can refer their instruments and in order to provide a national calibration and certification service. Product specification standards form the largest group of standards and cover materials, testing methods, terminology, safety, dimensions and tolerances etc. The purpose of these specification standards is to provide a means of ensuring compatibility and objective comparisons between different materials and products. Systems standards cover such aspects as how to maintain and install equipment, quality inspection etc. From the point of view of this volume the most relevant standards are the group loosely defined as product specification standards. These will include standard tests for strength, ductility, thermal properties etc. Use of these standard test methods not only provides information which enables comparisons between different materials to be made but also comparisons between batches of nominally the same material from different manufacturers.

STANDARDS ORGANISATIONS

Most countries have their own standards organisations and there are now over 100 standards organisations in existence, the oldest being the British Standards Institution. The ISO (International organisation for Standards) exists to work towards harmonising world standards and the EC has its own standards organisation CEN whose primary aim is to harmonise standards throughout the EC. From a practical point of view the most important standards for polymer testing are those issued by the ASTM (American Society for Testing and Materials), the ISO, CEN, DIN (Deutsches Institut für Normung) and BSI (British Standards Institute). Standards contain details of the test methods, the dimensions of the samples that should be used, as well as a recommended number samples to test and the method of presenting the results. Included also is usually a method for conditioning samples prior to testing or a reference to a further standard for conditioning samples. ASTM standards frequently contain representative measurements from several laboratories. Specific standards are numbered with a system of letters and numbers, the letters indicating the originating standards organisation and the numbers the standard number. Lists of standards are published annually by the main standards organisations and, when required, standards are reviewed, updated or replaced. Many standards are now comparable between the different organisations and will have numbers such as BS ISO 871 which indicates both a British and International standard

(in this case for the determination of the ignition temperature of plastics). The ASTM publishes tables of equivalencies between ASTM and ISO standards. Many standards are specific to a particular polymer or form of polymer product and the number of specific polymer standards runs into many hundreds. Listed below is a selection of the more relevant general ASTM and BSI standards from the point of view of polymer mechanical testing. However these represent only a small fraction of polymer standards. For a comprehensive listing readers should consult the annual listings of their standards available from the standards organisations at the addresses listed at the end of this article.

- ASTM D256 Determining the Impact Resistance of Notched Specimens of Plastics
- ASTM D618 Standard Practice for Conditioning Plastics for Testing
- ASTM D638 Test Method for Tensile Properties of Plastics
- ASTM D695 Test Method for Compressive Properties of Rigid Plastics
- ASTM D746 Brittleness Temperature of Plastics and Elastomers by Impact
- ASTM D785 Test Method for Rockwell Hardness of Plastics
- ASTM D883 Terminology Relating to Plastics
- ASTM D1004 Initial tear resistance of Plastic Film and Sheet
- ASTM D1043 Stiffness Properties of Plastics as a Function of Temperature
- ASTM D1242 Resistance of Plastic Materials to Abrasion
- ASTM D1708 Tensile Properties of Plastics by use of Microtensile Specimens
- ASTM D2990 Tensile, Compressive, and Flexural Creep and Creep Rupture
- ASTM D3028 Kinetic Coefficient of Friction of Plastic Solids
- ASTM D4092 Terminology Relating to Dynamic Mechanical Measurements on Plastics
- ASTM D4812 Unnotched Cantilever Beam Impact Strength of Plastics
- ASTM D5023 Dynamic Mechanical Properties of Plastics Using Three Point Bending
- ASTM D5024 Dynamic Mechanical Properties of Plastics in Compression
- ASTM D5026 Dynamic Mechanical Properties of Plastics in Tension
- ASTM D5045 Plane Strain Fracture Toughness and Strain Energy Release Rate
- ASTM D5420 Impact Resistance of Flat, Rigid Plastic Specimen by Means of a Striker Impacted by a Falling Weight
- ASTM D5628 Impact Resistance of Flat, Rigid Plastic Specimen by Means of a Falling Dart
- ASTM D5936 Specification for Multipurpose Test Specimens Used for Testing Plastics
- ASTM D5938 Guide Describing the General Principles for Determination of Tensile Properties of Plastics
- ASTM D5941 Determining the Izod Impact Strength of Plastics
- ASTM D5942 Determining the Charpy Impact Strength of Plastics
- ASTM D5943 Determining Flexural Properties of Plastics

- BS 2782 Methods of Testing Plastics: This is a multi-component standard consisting of over 200 separate test methods covering the Thermal, Electrical, Mechanical, Chemical, Optical, Rheological and Other Properties of Polymers.

- BS 4618 Recommendations for the Presentation of Plastics Design Data: This is another multi-component standard consisting of 27 sections and subsections covering the same range of properties as BS2782.
- BS 5214 Testing Machines for Rubbers and Plastics
- BS 7825 Calibration of Rubber and Plastics Test Equipment
- BS 7008 Acquisition and presentation of comparable data for basic properties of plastics

ADDRESSES OF STANDARDS INSTITUTIONS

American National Standards Institute
11 W. 42nd St., 13th Floor,
New York, NY 10036
USA

ASTM
100 Barr Harbor Drive
West Conshohocken
PA 19429
USA

British Standards Institution
British Standards House
2 Park Street, London W1Y 2BS
UK

International Organisation for Standards
ISO Central Secretariat
1 rue de Varembe
Case Postale 56
CH-1211 Geneve 20
Switzerland

Deutsches Institut für Normung
Burggrafenstrasse 6
10787 Berlin
Germany

47: Strain Rate Effects

G. M. Swallowe

The mechanical properties of most materials vary with the rate of loading and this effect is particularly evident in polymers. It is usual when considering rate of loading effects in a material, rather than a structure, to quantify the loading rate in terms of a strain rate $\dot{\epsilon}$ where the strain rate can conveniently be visualised as the number of times a sample will increase its own length in a second. Strain rates of interest vary from very low $\sim 10^{-5} \text{ s}^{-1}$ which represent the lowest rates achievable in standard compression/tensile test rigs (though even lower rates are involved in **creep** tests) to $\sim 10^4 \text{ s}^{-1}$ which represents the highest rates achievable in standard high rate test equipments (see **The Hopkinson bar**). Even higher rates are attainable using exploding wire and plate impact techniques. Increasing strain rate has the effect of increasing both the modulus and the yield stress and flow stress of a polymer. Reported increases in yield stress (and the flow stress at a given strain) are in the region of 1 to 6 MPa per decade of strain rate for rates from 10^{-3} to 10^3 s^{-1} and the increase is almost independent of strain upto strains of ~ 0.3 . Typical values for a selection of polymers are listed below in units of MPa per decade of strain rate increase.

Table 1: Strain rate sensitivities of some polymers in the region 10^{-3} to 10^2 s^{-1} .

Polymer	Sensitivity (MPa per decade of strain rate)
Polypropylene	4
High density polyethylene	2
Polyethyleneterephthalate	6
Nylon 6,6	5
Polycarbonate	4
Polyethersulphone	3
Polyetheretherketone	4
Nylon 6	5

Most flow stress data can be fitted with an Eyring model of plastic deformation (see **Yield and Plastic Deformation**) leading to an equation of the form

$$\frac{\sigma}{T} = \frac{R}{v} \left[\Delta H / RT + \log(2\dot{\epsilon} / \dot{\epsilon}_0) \right] \quad (1)$$

with σ the flow stress, T the temperature, R the gas constant, $\dot{\epsilon}$ the strain rate, $\dot{\epsilon}_0$ a material constant and v an activation volume. The value of v is usually found to be of the order of $1 - 10 \text{ nm}^3$ and it is identified with the volume of the polymer chain segments co-operatively involved in the local deformation. Equation 1 describes a single stage

process with one activation energy and one activation volume. In some cases it is necessary to invoke two Eyring processes with a second activation energy and volume to satisfactorily describe stress-strain data over a very wide strain rate range and most data up to strain rates of 10^3 s^{-1} can be satisfactorily fitted by at most two simultaneously active Eyring processes.

At strain rates greater than $\sim 10^3 \text{ s}^{-1}$ the situation becomes unclear with some workers reporting more rapid increases of flow stress with strain rate and others reporting no effect or even decreases. Inaccuracies in data due to instrumental effects are much more prevalent at these very high rates and there is therefore much debate at present in the interpretation of the very high ($\partial\epsilon/\partial t > 10^3 \text{ s}^{-1}$) results. Figure 1 shows a typical plot of flow stress/temperature versus Log strain rate. Agreement with equation 1 over five decades of strain rate is evident. Fig. 1 also shows the rapid increase in flow stress at strain rates $\sim 10^3 \text{ s}^{-1}$ and virtual constancy of the strain rate sensitivity over a wide temperature range. At temperatures close to and above the glass transition temperature T_g the strain rate sensitivity may drop and this is also evident from Fig 1.

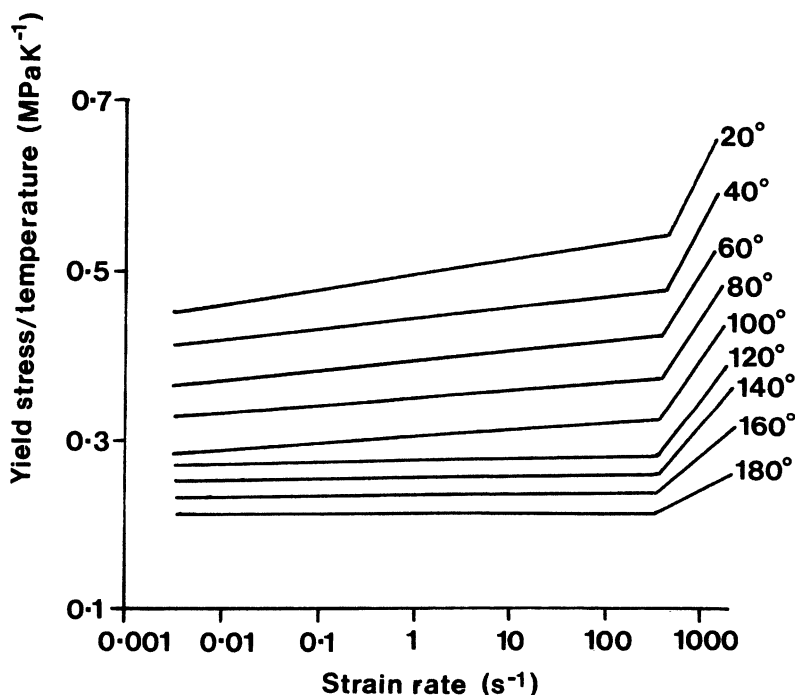


Figure 1: Yield stress/temperature versus log strain rate for PEEK at various temperatures. T_g for PEEK is 145°C .

TEMPERATURE RISES

During slow deformation the test is assumed to be isothermal with the sample remaining essentially at the same temperature throughout the test. The assumption is that any heating of the sample due to the plastic work being done during deformation is counterbalanced by heat transfer into the surrounding environment resulting in an effectively isothermal test (see **Adiabatic Shear Instability: Theory**). As the strain rate increases the rate of heat generation increases and this is exacerbated by the increase in flow stress with strain rate. Heat loss to the surroundings cannot then maintain the temperature at ambient and the sample will rise in temperature. At high rates deformation is adiabatic and the change from isothermal to adiabatic behaviour is generally accepted to occur at strain rates $\sim 1\text{s}^{-1}$ or less depending on sample size. However, the continuous temperature increase which occurs with increasing strain during an adiabatic test can cause the flow stress to fall. Thus two competing processes are occurring; an increase in flow stress due to strain rate effects and a decrease due to heating. The increase in flow stress with increasing strain rate can be less than the decrease due to thermal softening leading to a flow stress which decreases with strain at high strain rates (adiabatic) but increases at low rates (isothermal). Figure 2 illustrates this behaviour for a sample of PEEK. It can be seen that the the yield stress increases with strain rate but that the stress-strain curve at intrermediate strain rates falls below that of the low strain rate curve as the test proceeds and the sample temperature rises.

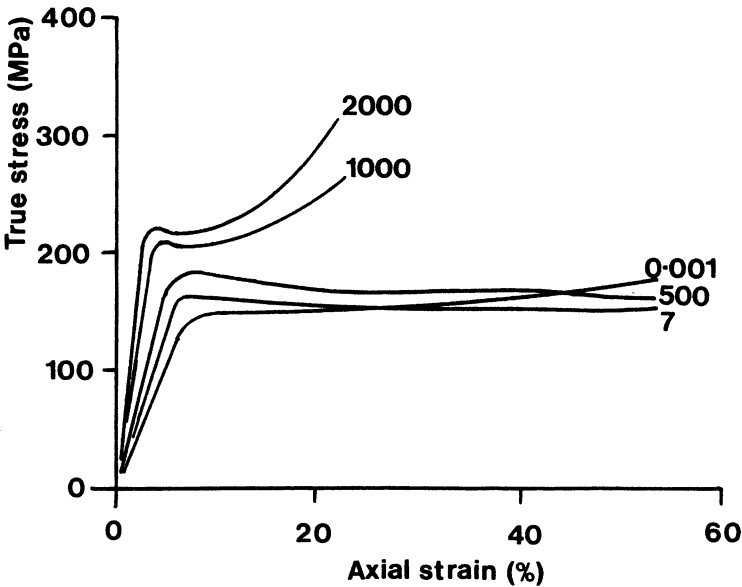


Figure 2: Flow stress versus strain for PEEK at various strain rates. Strain rates are in units of s^{-1} , all measurements at 20°C .

The temperature rise in the adiabatic region can reasonably accurately be estimated by using the expression

$$\Delta T = \int \sigma d\varepsilon / \rho C \quad (2)$$

where ΔT is the temperature rise, ρ the density, C the specific heat (assumed constant over the temperature range involved) and $\int \sigma d\varepsilon$ is the integral under the stress strain curve from the start of the test to the strain of interest. The assumption of constant specific heat is usually valid unless the test is close to T_g . A further assumption in the calculation of ΔT is that the deformation is uniform and that adiabatic shearing has not taken place.

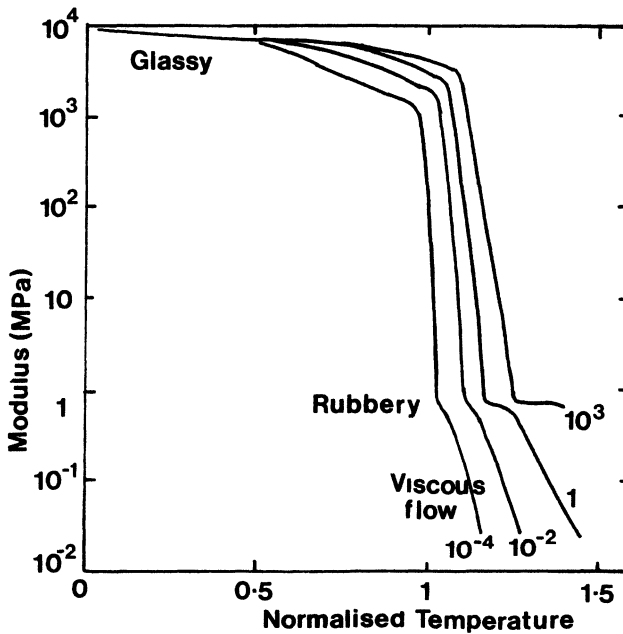


Figure 3: Schematic modulus versus normalised temperature (T/T_g) diagram for an amorphous polymer at various strain rates. Strain rate units are s^{-1} .

ELASTIC CONSTANTS

The behaviour of polymers is essentially described by non linear **viscoelasticity** so the elastic constants (Young's modulus, shear modulus, Poisson's ratio) are also sensitive to strain rate changes. The modulus normally quoted in the literature will be the slope of the stress-strain curve close to the origin and this can be seen in figure 2 to increase with strain rate. Typical changes (for measurements on the same batch of material) in the

value of E for HDPE are from 0.4 GPa to 2.6 GPa over the strain rate range 10^{-3} to 10^4 s^{-1} , 3.5 GPa to 5.5 GPa over the range 10^{-4} to 10^4 s^{-1} for PEEK and 2 to 5 GPa for Nylatron an MoS_2 filled Nylon. A reasonable estimation of the stress strain curve over a wide range of strain rates can be obtained by fitting test data using viscoelastic models such as the standard linear solid, the bi-linear elasto-plastic model or other **related** models of polymer behaviour. Different models tend to be more appropriate for different polymers but by choosing the best model for a particular polymer good predictions of stress-strain behaviour over a very wide range of strains and strain rates can be made. The parameters in these models are experimentally determined from a small number of stress strain tests (see **Polymer Models**).

The sensitivity of modulus to strain rate is greatest in the region of the glass transition as can be seen in the schematic diagram of Figure 3 which represents the change in modulus with strain rate for an amorphous material. This rate dependence is related to the polymer relaxation processes (see **Relaxations in Polymers**) and the inherent **viscoelastic behaviour of polymers**.

REFERENCES

1. Blazynski, T.Z. ed. (1987) *Materials at high rates of Strain* Elsevier Applied Science.
2. Walley, S.M. and Field, J.E. (1994) Strain rate sensitivity of Polymers in compression from low to high rates. *DYMAT Journal*, **1**, 211-227.

48: Stress and Strain

G.M Swallowe

The measurement of mechanical properties is basically the determination of the relationship between the two parameters stress and strain. Stress is simply defined as the force per unit area that the material is being subjected to and has units of kg m^{-2} also known as Pascals. Strain can be defined as the ratio of the change in dimension of the material measured along a particular direction to its original dimension, it is therefore a dimensionless unit. The conventional symbols for stress are the Greek letters σ and τ and the symbols used for strain are ϵ and γ .

The easiest way to visualise stress and strain is to consider a simple uniaxial test where a force F is applied to a length l_0 of material and the change in length Δl in the direction of the applied force is measured. Strain is determined as the ratio $\Delta l/l_0$ and the stress required to produce this strain is quoted as F/A_0 where A_0 is the original cross-sectional area of the test piece. When stress and strain are quoted in this way they are called engineering stress and engineering strain. There is however an alternative method of measuring stress. If the cross sectional area A is measured while the force is applied, rather than at the start of the test, the stress obtained, F/A , will be different from the first measurement, F/A_0 , and will be greater than the first measurement since A will be less than A_0 . When stress is quoted as F/A it is called true stress since it is a measure of the actual force per unit area being sustained by the material at a given strain. Similar considerations apply to the case of strain. The strain can be measured relative to the original pre-test length of the material l_0 or can be considered as the sum of a series of small incremental strains which arise during the application of the load and add together to produce a final strain. This leads to the definition of true strain as $\log_e (l/l_0)$ where l is the length of the test piece when the load is applied and $\log_e$ represents the natural logarithm.

The difference between these two methods of quoting strain is perhaps best envisaged by considering a sample which has a force F_1 applied to it producing a length change Δl_1 and which then has a second force F_2 added giving a total force $F = F_1 + F_2$ and another increment in strain Δl_2 . In this case the engineering strain will be quoted as $(\Delta l_1 + \Delta l_2)/l_0$ while the true strain can be envisaged as the sum of the two strains $\Delta l_1/l_0$ and $\Delta l_2/(l_0 + \Delta l_1)$. The true strain therefore represents the sum of a series of small strain increments measured by relating sample length increments to the actual length of the sample when the length increment is made, whereas engineering strain is a measure of the total length change related to the original length.

The relationship between the two methods of strain measurement, using the subscript e for engineering and t for true is

$$\epsilon_t = \log_e (1 + \epsilon_e) \quad (1)$$

Natural and engineering stress can be related by the relationship

$$\sigma_t = \sigma_e (1 + \epsilon_e) \quad (2)$$

The expression relating stresses is really only valid for plastic strains since the cross sectional area of the sample will depend on **Poisson's ratio** ν (the ratio of lateral strain to longitudinal strain) and the assumption that $\nu = 0.5$ which is used to derive this relationship is only true for plastic deformation. However, since plastic deformation normally commences at small strains and the differences between engineering and true values of stress and strain are very slight at small strains the above relationships may be considered sufficiently accurate for most purposes at all values of stress and strain.

There are several means by which a force could be applied to a sample of which uniaxial loading as described above is just one. If the force is applied along a plane it produces a shear stress τ which is also defined as the force per unit area and leads to a shear strain γ . Alternatively a uniform stress could be applied in all directions to the body, as would be the case if it had been immersed in a liquid, leading to a hydrostatic stress (or pressure) P , and a volume strain or dilatation Δ which is defined as $\Delta = \Delta V/V_0$ with ΔV the volume change and V_0 the original volume.

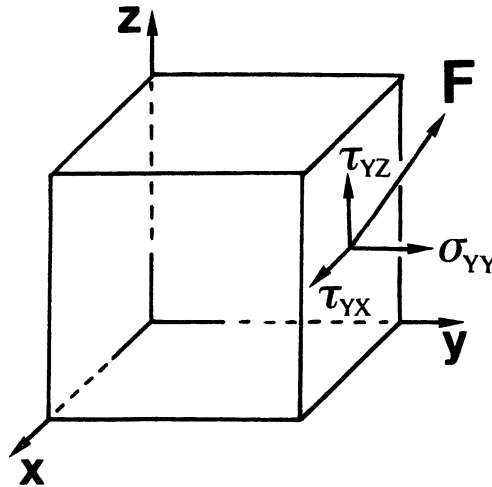


Figure 1: Force applied in an arbitrary direction to the face of a small cube in the interior of a material sample showing how it may be resolved into one normal (σ_{yy}) and two shear stresses (τ_{yx} and τ_{yz}).

GENERALISED STRESS

In general a stress applied in an arbitrary direction relative to a plane within the material will produce strain components in directions which are perpendicular and parallel to the plane (Fig 1). Since a single force can produce 3 stresses (one normal and two shear) a

double suffix notation is often used to describe the stresses where the first suffix denotes the direction of the perpendicular to the plane in question and the second suffix denotes the direction of the stress (Fig 1).

Consideration of a small cube within the body of a stressed material leads to the conclusion that there are a total of 9 stress components (Fig 2). These are often written as a 3 x 3 matrix.

$$\begin{matrix} \sigma_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_{zz} \end{matrix} \quad (3)$$

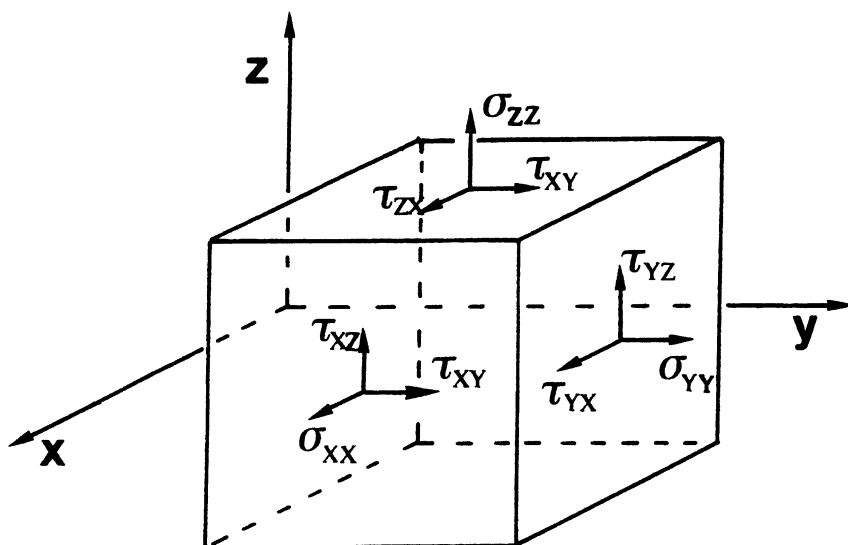


Figure 2: Generalising Figure 1 to a general stress state leads to the 9 stress components illustrated.

However if the material is in static equilibrium there must be a balance of stress components so that

$$\tau_{xz} = \tau_{yx} , \quad \tau_{yz} = \tau_{zy} , \quad \tau_{zx} = \tau_{xy} \quad (4)$$

and only six independent components of stress remain. Several special cases are of interest in mechanical testing.

These are *Uniaxial stress* - all components except σ_{zz} are zero leading to a stress matrix

$$\begin{matrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \sigma_{zz} \end{matrix} \quad (5)$$

Pure shear - all stresses except a 'pair' of shear stresses are zero leading to the stress matrix

$$\begin{matrix} 0 & \tau_{xy} & 0 \\ \tau_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{matrix} \quad (6)$$

Hydrostatic pressure- no shear stresses and all normal stresses equal leading to the matrix

$$\begin{matrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{matrix} \quad (7)$$

A further stress state commonly met in polymer processing and testing is *biaxial stress* in which a sample is subjected to stresses which act in a plane (σ_{xx} and σ_{yy}) with the third normal component (σ_{zz}) = 0.

GENERALISED STRAIN

Just as stress can be considered to consist of normal and shear components so too can strain and this is described by a generalised 3 x 3 strain matrix. The same matrix format is used to describe strain and using the symbol ϵ to represent axial strains and γ shear strains the matrix is written

$$\begin{matrix} \epsilon_{xx} & \gamma_{xy} & \gamma_{xz} \\ \gamma_{yx} & \epsilon_{yy} & \gamma_{yz} \\ \gamma_{zx} & \gamma_{zy} & \epsilon_{zz} \end{matrix} \quad (8)$$

As with stress the same special cases give rise to simplifications in the matrix. Following the same pattern as used for stress uniaxial strain leads to all components being equal to zero except for ϵ_{zz} , uniform expansion or compression would lead to non zero values only for ϵ_{xx} , ϵ_{yy} and ϵ_{zz} and pure shear to only one 'pair' of the γ components being non zero e.g. all nine components equal to zero except, for example, γ_{xy} and γ_{yx} .

STRESS-STRAIN RELATIONSHIPS

There are numerous textbooks which explain in detail the relationships between stress and strain and a selection of titles is given at the end of this article. However most materials response can be divided into two parts (1) Elastic response and (2) Plastic response. Elastic response represents deformation which is recovered when the load is

removed and plastic response the non recoverable permanent deformation.

Elastic Response

For small strains (upto about 1%) stress is linearly related to strain by simple Hookean proportionality

$$\sigma = E\varepsilon \quad (9)$$

$$\tau = G\gamma \quad (10)$$

$$P = K\Delta \quad (11)$$

with E Young's modulus, G the shear modulus and K the Bulk modulus (compressibility) and Δ the volume strain (dilatation). These three together with **Poisson's ratio** ν constitute the commonly quoted elastic constants. For an anisotropic material the values of the constants will vary with direction and in most practical cases polymers will show at least some anisotropy, however the assumption of isotropy leads to the simple relationships below which give a good first estimate of the relationship between elastic stress and strain

$$\varepsilon_{xx} = \sigma_{xx}/E - \nu(\sigma_{yy} + \sigma_{zz})/E \quad (12)$$

$$\varepsilon_{yy} = \sigma_{yy}/E - \nu(\sigma_{xx} + \sigma_{zz})/E \quad (13)$$

$$\varepsilon_{zz} = \sigma_{zz}/E - \nu(\sigma_{yy} + \sigma_{xx})/E \quad (14)$$

$$\gamma_{xz} = \tau_{xz}/G \quad (15)$$

$$\gamma_{yz} = \tau_{yz}/G \quad (16)$$

$$\gamma_{xy} = \tau_{xy}/G \quad (17)$$

It can be shown that for an isotropic material only two elastic constants are needed to describe the stress - strain relationships. A further elastic constant called Lamé's constant, which is usually given the symbol λ , is also defined and used mainly in theoretical work. Since in an isotropic material only two constants are needed to describe the (elastic) mechanical properties the elastic constants are related by many equations some of the more useful of which are

$$\lambda = E\nu/(1 + \nu)(1 - 2\nu) \quad (18)$$

$$G = E/[2(1 + \nu)] \quad (19)$$

$$K = E/[3(1 - 2\nu)] \quad (20)$$

$$\nu = E/(2G) - 1 \quad (21)$$

$$\nu = \lambda/2(\lambda + G) \quad (22)$$

$$K = (\lambda + 2G/3) \quad (23)$$

$$\lambda = 2\nu G/(1 - 2\nu) \quad (24)$$

$$E = 9KG/(3K + G) \quad (25)$$

A complication of terminology is the use of the symbol λ to also represent the draw

ratio l/l_0 when a polymer is deformed in tension to a large strain. In this case λ is normally given a subscript which represents the direction of drawing and the convention is λ_1 represents drawing in the x direction, λ_2 the y direction and λ_3 the z direction. For small strains $\lambda_1 = 1 + \epsilon_{xx}$, $\lambda_2 = 1 + \epsilon_{yy}$ and $\lambda_3 = 1 + \epsilon_{zz}$. The relationships for large strain and anisotropic systems are much more complicated than those given above and the reader is referred to the volumes listed below for further information.

PLANE STRESS AND PLANE STRAIN

In reports of tests, particularly those involving fracture (see **Fast Fracture**), reference is frequently made to plane stress or plane strain conditions and the equations used for such factors as the stress intensity factor will depend on whether plane stress or plane strain conditions apply. Plane strain occurs when all displacements take place parallel to one plane and all dimensions perpendicular to that plane remain unchanged. Plane strain is also called biaxial strain and can be summarised by the conditions $\epsilon_x \neq 0, \epsilon_y \neq 0, \epsilon_z = 0$. In the case of plane strain there will be stress components in the x, y, and z directions. Plane strain conditions occur at crack tips in thick plates. Plane stress, also called biaxial stress is defined by the expressions $\sigma_x \neq 0, \sigma_y \neq 0, \sigma_z = 0$. It is clear that this is the stress state in thin sheets since the material/air (z direction) interface cannot support a stress and thus there will be a ϵ_z induced by Poisson's ratio effects as well as ϵ_x , and ϵ_y strains.

REFERENCES

1. Jaeger, J.C., (1969) Elasticity, Fracture and Flow 3rd ed., Methuen
2. Kelly, A. and MacMillan, N.H. (1986) Strong Solids 3rd ed., Oxford Science Publications
3. Nye, J.F. (1957) Physical Properties of Crystals, Clarendon Press Oxford

49: Structure-Property Relationships - Glassy Polymers

P J LUDOVICE

INTRODUCTION

Any predictive method for polymer properties is complicated by effects absent from most small molecule systems such as molecular weight, thermal history and non ideal structure. Therefore most predictive methods for polymer properties limit the problem by assuming a reference for these effects and focusing on the fundamental effect of polymer structure. Typically these methods assume a well annealed monodisperse infinite molecular weight system, with no branching or structural variation. However, since the models are derived from experimental measurements that qualitatively approach these limits they do contain some inherent error due to these effects.

Four basic methods can be used to estimate mechanical properties as a function of polymer structure:

- (i) Molecular Modeling
- (ii) Group Additivity Methods
- (iii) Basic Structural methods
- (iv) Graph Theory Methods.

Glassy polymers are simply polymer solids below the **glass transition** temperature (T_g). They are solids frozen in a state of amorphous or liquid-like order. This means that many of their thermodynamic properties can be modeled as a function of the average interactions of their various components. Therefore, the final three of the aforementioned methods, which are based on average contributions of local structure, are particularly effective. While molecular modeling (see also **Monte Carlo Techniques**) can provide insight into the connection between structure and properties it is often more time consuming than the experimental characterization of the polymer¹. Therefore the other three methods are more practical in the prediction of mechanical properties in amorphous polymers.

Mechanical properties characterize the connection between the stress, or force per unit area, applied to a polymer sample (σ) and the relative deformation (ϵ) in the polymer sample. Most engineering applications of glassy polymers are concerned with small strain behavior. This behavior can be described by a simple linear model in which a proportionality constant, called a modulus, is used to describe the ratio of the stress to the strain (see **Stress and Strain**). We will concentrate on the prediction of these moduli. No accurate structure-property relationships currently exist that account for the time dependence of this relationship, and the large strain behavior is addressed in the article **Structure-Property Relationships: Large Strain Behavior**. The stress may be applied in a uniaxial, isotropic or shearing mode and is related to strain by the Young's

(E), Bulk (B), or Shear (G) modulus respectively as seen in Figure 1. One additional parameter is the **Poisson's ratio** (ν), which is the relative contraction of the sample in the normal directions in response to uniaxial deformation. Poisson's ratio typically varies between 0.3 and 0.4 for glassy polymers, and is slightly below the constant volume limit of 0.5 for rubbery polymers. In the limit of amorphous structure the mechanical properties of a glassy polymer can be completely described by two of these four parameters. These parameters are related by

$$E=3B(1-2\nu)=2G(1+\nu). \quad (1)$$

Which means that any predictive structure-property method must only predict two of these four parameters to be useful for glassy polymers.

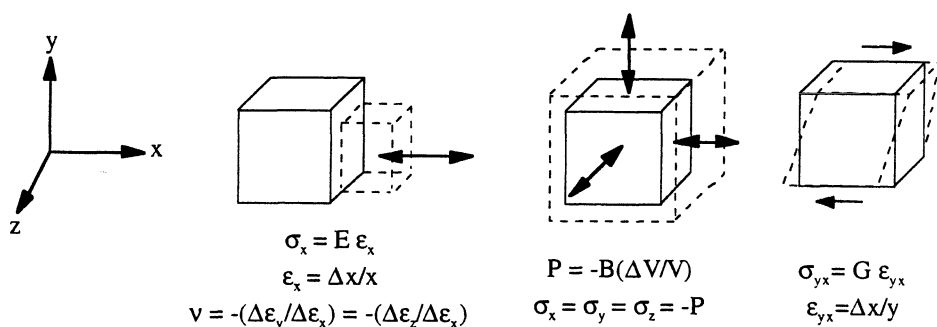


Figure 1: Various modes of elastic response

GROUP ADDITIVITY METHODS

These methods are based on the fundamental assumption that a property may be expressed as a sum of individual molar contributions for each structural group contained in the polymer repeat unit. This assumes that these contributions are relatively independent of each other. Unfortunately not all polymer properties possess this characteristic of molar additivity, and these properties must be derived using fundamental or empirical relationships from those properties that do. The most comprehensive work on these methods is that of Van Krevelen². Although mechanical moduli do not appear to possess molar additivity, Van Krevelen has deduced that the product of the molar volume and the cube root of the velocity of sound through a material does. Group additivity contributions for this quantity called the Rao function or molar sound velocity function (U_R) were tabulated for a number of organic structural groups by Van Krevelen (reference 2, chapter 14). Given the proportionality of the

sound velocity to the square root of the modulus of a material moduli should scale with U_R^6 . The following relationship can be used to calculate the bulk modulus of a polymer glass

$$B(T) = \rho(T) \left[\frac{U_R}{V(T)} \right]^6 \quad (2)$$

where $\rho(T)$ and $V(T)$ are the mass density and molar volume as a function of temperature T (reference 2, chapter 13). A similar approach is also taken for the shear modulus (G) using an alternative additive quantity develop by Hartmann and Lee³ called the molar Hartmann function (U_H) where

$$G(T) = \rho(T) \left[\frac{U_H}{V(T)} \right]^6 \quad (3)$$

can be used to calculate the shear modulus. Van Krevelen has provided some approximate values of U_H (reference 2, chapter 13). These two moduli can then be used with the general relations above to calculate the remaining elastic constants. Although the group additivity approach is quite effective, it requires a library of group additivity contributions for various molecular structural components. This limitation can be circumvented by correlating properties with structural elements or descriptors that can be calculated directly.

BASIC STRUCTURAL METHOD

Using basic thermodynamic relationships and empirical correlations Seitz has derived relationships between various properties and simple structural descriptors⁴. Using data from 15 polymers that span a broad range of polymer structures, Seitz has produced the following empirical relationship for the Poisson ratio at room temperature (298K):

$$\nu = 0.513 - 3.054 \times 10^{-6} \sqrt{\frac{V_w}{l_m}} \quad (4)$$

where V_w and l_m are the molar van der Waals volume and the fully extended length of the repeat unit. Here the van der Waals volume is the space occupied by a repeat unit that is impenetrable to other molecules. This can be easily calculated by summing the van der Waals volumes for each atom in the repeat unit less the volume overlap of the atoms bonded to it. This can be calculated using the following relations:

$$V_w = \sum_{k=1}^{\text{total atoms}} V_w^k$$

$$V_w^k = N_A \left[\frac{4}{3} \pi R_k^3 - \sum_{\substack{\text{bonded} \\ \text{atoms} \\ i}} \pi h_i \left(R - \frac{h_i}{3} \right) \right] \quad (5)$$

$$h_i = R - \frac{l_i}{2} - \frac{R^2 - r_i^2}{2l_i}$$

where N_A is Avogadro's number, R and r_i are the van der Waals radii of the atom k and atom i bonded to the atom k , and l_i is the bond distance between the atom k and atom i . Van der Waals radii are available from numerous references, or various group additivity methods for the V_w have been summarized by Van Krevelen [ref. 2, chapter 4]. The l_m parameter can be estimated using basic geometry and primary bond lengths and angles available in most organic or physical chemistry texts. Alternatively, many modern molecular modeling packages can estimate these parameters using generic force fields⁵. Although various parameters differ among commonly used force fields, van der Waals radii and bond lengths and angles remain fairly consistent.

Using the glass transition temperature (T_g), Seitz developed the following empirical expression for v as a function of temperature:

$$v(T) = v(298K) - \frac{1490}{T_g} \left\{ 0.00163 + \exp[0.459(285 - T_g)] \right\} \\ + \frac{50T}{T_g} \left\{ 0.00163 + \exp[0.459(T - T_g)] \right\} \quad (6)$$

Seitz also produced the following expression for the bulk modulus:

$$B(T) = 8.23333 E_{coh} \left[\frac{(5V(0K))^4}{V(T)^5} - \frac{(3V(0K))^2}{V(T)^3} \right]^6 \quad (7)$$

where E_{coh} is the cohesive energy or the decrease in internal energy per mole material due to the presence of its intermolecular forces. The Hildebrandt solubility parameter is simply the square root of the cohesive energy divided by the molar volume

$$\delta = \sqrt{\frac{E_{coh}}{V}} \quad (8)$$

Therefore the cohesive energy may be derived from experimentally measured solubility parameters. In the absence of such parameters, Bicerano has developed a predictive method based on chemical graph theory below⁶. Seitz provides the following correlation

between the molar volume of a glassy polymer $V(T)$ and the V_w .

$$V(T) = \left(0.15 \frac{T}{T_g} + 1.42 \right) V_w \quad (9)$$

Given the relative insensitivity of the relation above to temperature (T is in K) a reasonable estimate of T_g can produce a good estimate of the molar volume.

MOLECULAR GRAPH THEORY METHOD

Bicerano has recently derived a more general method to predict polymer properties, based on chemical graph theory of monomeric units, that requires neither group additivity contributions or thermodynamic properties such as T_g ⁶. Chemical graph theory describes molecular structures in terms of their topology and atomic connectivity⁷. The basic parameter used therein is that of the molecular connectivity index. The connectivity indices for a particular molecule are derived from a graph (diagram of the topology) of a molecule without hydrogen atoms (hydrogen suppressed graph). The connectivity indices are based on the sums of the reciprocals of two atomic indices. The atomic connectivity index is simply the number of non-hydrogen atoms bonded to a particular atom (δ), and, with limited exception, the valence index (δ^v) is given by the following formula:

$$\delta^v = \frac{(Z^v - N_H)}{(Z - Z^v - 1)} \quad (10)$$

where Z is the atomic number of the atom, Z^v is the number of valence electrons, and N_H is the number of hydrogen atoms bonded to the atom. The valence index is an indication of the valence level electronic interaction with the neighboring non-hydrogen atoms. Table 1 contains some basic values of these atomic connectivity indices calculated using the formula above.

Four descriptors are constructed from the atomic indices and the hydrogen suppressed graph of the molecule. The zero order connectivity index (${}^0\chi$) is simply the sum of the reciprocal of the connectivity indices for all the atoms in the molecule. Similarly the zero order valence index (${}^0\chi^v$) is the sum of the reciprocal of the atomic valence indices from the table above. While the zero order indices are sums over the atoms (or vertices in graph theory), the first order molecular indices are sums over the bonds (or edges in graph theory). The bond or edge indices (β and β^v) are simply the product of the connectivity or valence indices of the atoms connected by that bond. The first order molecular connectivity index (${}^1\chi$) is the sum of the reciprocal of the bond connectivity indices (β) for all the bonds in the molecule to atoms other than hydrogen, or all the edges in the hydrogen suppressed graph. Likewise the first order molecular valence

index is the sum of the reciprocal of the bond valence indices (β^v) for all the edges in the hydrogen suppressed graph. The example below for styrene monomer illustrates the calculation of these four descriptors.

Table 1: Atomic Connectivity Indices for some basic atoms

Atom	hybridization	N_H	δ	δ^v
C	sp^3	3	1	1
		2	2	2
		1	3	3
		0	4	4
	sp^2	2	1	2
		1	2	3
		0	3	4
	sp	1	1	3
		0	2	4
N	sp^3	2	1	3
		1	2	4
		0	3	5
	sp^2	1	1	4
		0	2	5
	sp	0	1	5
		0	2	6
O	sp^3	1	1	5
		0	2	6
	sp^{20}	0	1	6
F	---	0	1	7
Cl	---	0	1	7/9
Br	---	0	1	7/27

The connectivity and valence indices are labeled on the molecular graph of poly(vinyl chloride) in Figure 2 for both the atoms (vertices) and bonds (edges). These can be used to calculate the zero and first order molecular connectivity indices as seen below.

$${}^0\chi = \sum_i \frac{1}{\sqrt{\delta_i}} = \frac{1}{\sqrt{2}} + \frac{1}{\sqrt{3}} + \frac{1}{\sqrt{1}} = 2.2845$$
$${}^0\chi^v = \sum_i \frac{1}{\sqrt{\delta_i^v}} = \frac{1}{\sqrt{2}} + \frac{1}{\sqrt{3}} + \sqrt{\frac{9}{7}} = 2.4184$$
$${}^1\chi = \sum_i \frac{1}{\sqrt{\beta_i}} = \frac{1}{\sqrt{6}} + \frac{1}{\sqrt{6}} + \frac{1}{\sqrt{3}} = 1.3938$$
$${}^1\chi^v = \sum_i \frac{1}{\sqrt{\beta_i^v}} = \frac{1}{\sqrt{6}} + \frac{1}{\sqrt{6}} + \sqrt{\frac{9}{21}} = 1.4712$$

(11)

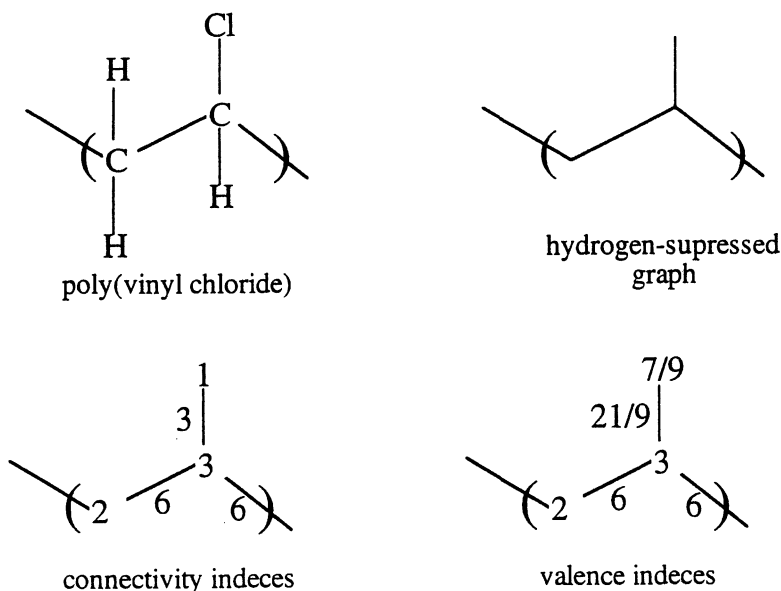


Figure 2: Structure and graphs of poly(vinylchloride)

The advantage of using these connectivity indices as descriptors is that they can be calculated for any polymer and do not require any additional data our group additivity parameters. Bicerano has formulated the following correlation for the Molar Rao function calculated using Van Krevelen's group additivity contributions.

$$U_R = 441.30 \chi^0 + 540.62 \chi^1 + 154.69 N_H + 105.91 N_{UR} \quad (12)$$

where N_H is the total number of hydrogen atoms in the repeat unit and N_{ur} is a linear function of the presence of various organic groups and is given by:

$$N_{UR} = 2N_{Cl} - N_F - 2N_{(-S-)} - 2N_{OH} + N_{cyanide} - 3N_{cyc} + 4N_{(6 \text{ member aromatic rings})} + N_{Si} \quad (13)$$

This correlation accounts for 99.94% of the variation in a sample of 129 polymers. Note that this correlation assumes that the valence indices of carbon are used for all silicon atoms. A correlation for the Molar Hartmann function (U_H) as a function of the Molar Rao function (U_R) was obtained by Bicerano:

$$U_H = 0.7931 U_R + 24.7545 N_{UH} \quad (14)$$

where

$$N_{UR} = +14N_{(\alpha\text{-substituted acrylate})} + 5N_{cyanide} + 3N_{Cl} + 5N_{C\equiv C} + 5N_{sulfone} - 4N_{(backbone \text{ ester})} \quad (15)$$

Similarly the valence indices for carbon were also used in the correlation above. Some caution should be used in employing the above correlation because the values of the U_H on which it is based are only estimates. The bulk and shear moduli can then be calculated using the equations above.

REFERENCES

1. Galiatsatos, V. (1995) *Comput. Chem.* **6**, 149-208
2. Van Krevelen, D.W. (1990) *Properties of Polymers: Their Correlation with Chemical Structure: Their Numerical Estimation and Prediction from Additive Group Contributions*, 3rd Ed. Elsevier, Amsterdam.
3. Hartmann, B. and Lee, G.F. (1982) *J. Polym. Sci., Polym. Phys. Ed.* **20**, 1269
4. Seitz, J. (1993) *J. Appl. Polym. Sci.* **49**, 1331-1351
5. See for example the Insight-Discover, CERIUS, QSPR and other programs available from Molecular Simulations Inc., San Diego CA, U.S.A. (www.msi.com).
6. Bicerano, J. (1996) *Prediction of Polymer Properties*, 2nd Ed., Marcel Dekker, New York.
7. Trinajstić, N. (1992) *Chemical Graph Theory*, 2nd Ed., CRC Press, Boca Raton

50: Structure-Property Relationships - Large Strain

P J LUDOVICE

INTRODUCTION

Mechanical Properties of glasses and rubbers are discussed in terms of moduli. Moduli are the proportionality constants between stress and strain, and represent the initial slope of the curves in Figure 1 which illustrate typical modes of polymer failure. Large strain is a relative term depending on the polymer and the temperature. For the purposes of this discussion, large strain refers to any strain outside the linear elastic regime that is approaching the failure point of the specimen. These moduli are relatively constant at low strains, but change at high strains because the conformation of the polymer changes at high strain. Exactly how the moduli changes at high strain is difficult to estimate because it is very sensitive to the thermal and mechanical history of the polymer as well as the time dependence of the applied stress. However, the point at which the polymer fails is of great importance because it determines the limits of the applied stress for this polymer.

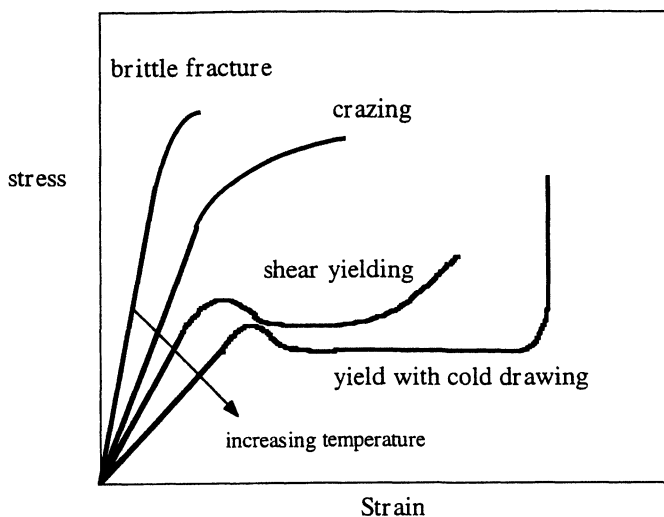


Figure 1: Schematic of some failure modes of glassy polymers.

The various failure modes in Figure 1 are not drawn to scale. Not all polymers have all these failure modes, but most have 2 or more depending on the temperature. For

example only brittle fracture and **crazing** are observed in atactic polystyrene below T_g . It is also important to note that some polymers may have different failure modes for different modes of deformation. In general all polymers at temperatures significantly below their glass transition temperatures ($T_g - T > 100^\circ\text{C}$) undergo brittle fracture. This failure mode is best illustrated in the shattering of metal oxide glasses such as window glass at room temperature (see **Fast fracture in Polymers**). In the region above the brittle fracture regime, but below T_g polymers usually yield and undergo irreversible (plastic) deformation as the modulus decreases. This is illustrated in the bump that occurs in the stress strain curves in Figure 1. After a sufficient amount of strain the polymer chains begin to align in the strain direction and the modulus increases until the plastically deformed sample eventually breaks. Deformation after the yield point can have various forms, depending on the structure and the mechanical and thermal history of the sample, such as shear yielding and cold drawing pictured in Figure 1. At an intermediate temperature between the regimes of brittle fracture and **plastic deformation**, many polymers undergo a non-catastrophic failure called **crazing**. This failure mechanism is characterized by cracks that are filled with both plastically deformed polymer fibrils and voids. Crazes are seen as the white film that appears when many plastic parts are bent at a sharp angle.

Crazing requires more chain mobility than brittle fracture, and likewise yielding requires even more chain mobility. At low temperatures the brittle fracture stress (σ_f) is lowest and brittle fracture dominates, but the theoretical crazing (σ_c) and yield (σ_y) stress decreases as the temperature increases (see **Ductile-Brittle Transition**). This typical behavior is qualitatively depicted in Figure 2 (the relationships are not necessarily linear).

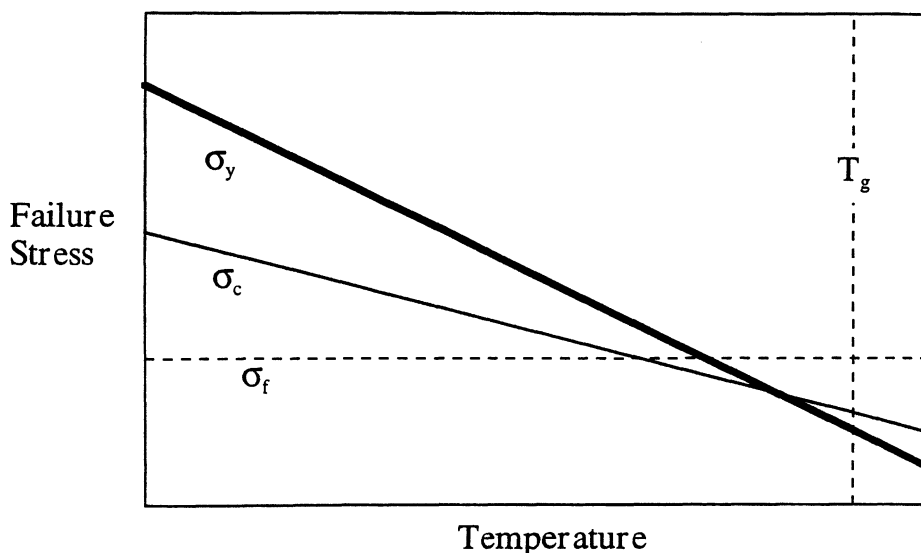


Figure 2: Qualitative variation of failure stress with temperature.

As in the case of rubbery polymers, the most useful method for the prediction of mechanical properties are basic structural methods (**Mechanical Structure Property Relationships - Rubbery Polymers**). To date, no significant group additivity or graph theory correlations have been formulated for these systems. Molecular modeling (see **Monte Carlo Techniques**) is relatively inefficient given the computational requirements for the large strain deformations. For a more detailed survey of these structural methods see Bicerano¹ and Van Krevelen².

BRITTLE FRACTURE STRESS

Van Krevelen points out that the theoretical fracture stress in uniaxial tension can be approximated by one tenth of the Young's modulus, but that the measured fracture strength σ_f is typically 10 to 100 times lower than the theoretical limit². This is simply a manifestation of the empirical observation that brittle materials typically fail between strains of 0.1 and 1% and can be used for order of magnitude estimates of σ_f (see **Fracture Mechanics**). Van Krevelen also showed that the fracture stress scales more closely with the Young's modulus to the 0.8 power.

Vincent first recognized the correlation of brittle fracture with the number of backbone bonds per unit area of the polymer sample and attempted to quantify this correlation³. Assuming a homogeneous distribution of polymer chains Seitz related the number of bonds to the fully extended length of monomer l_m divided by the molar volume⁴. He then obtained the following correlation by extending Vincent's original data set.

$$\sigma_f = 2.2884 \times 10^{11} \frac{l_m}{V(T)} \quad (1)$$

where the fracture stress (σ_f) is in MPa, l_m is in cm and the molar volume $V(T)$ is in cm³/mole. Seitz also showed that the fracture stress decreases with increasing number average molecular weight ($\overline{M}_n$)⁴. This dependence is described by the following relationship for $\overline{M}_n > 3.4 \overline{M}_n$

$$\sigma_f(\overline{M}_n) = \sigma_f(\infty) \left[1 - \frac{3.4 \overline{M}_e}{\overline{M}_n} \right] \quad (2)$$

where $\overline{M}_e$ is the effective entanglement length discussed in the section entitled **Mechanical Structure-Property Relationships - Rubbery Polymers**.

YIELD STRESS

As with the fracture stress, the yield stress in uniaxial tension can be related to the Young's modulus. Van Krevelen suggests that the yield stress scales as the Young's modulus to the 3/4 power². Seitz has correlated the yield stress with the Young's modulus to obtain the following linear relationship between the two parameters⁴

$$\sigma_y = 0.025E(T) . \quad (3)$$

Bicerano suggests that a proportionality constant of 0.28 be used in the above equation (1). Wu provides the following structure-property relationship for the yield stress

$$\log_{10} \left[\frac{\sigma_y(T)}{(T_g - T)\delta^2} \right] = -3.36 + \log_{10}(C_\infty) \quad (4)$$

where the yield stress is in MPa; δ and C_∞ are the solubility parameter in $(\text{MJ}/\text{m}^3)^{1/2}$ and the characteristic ratio respectively⁵. The temperature difference is in K. The aforementioned relationships may be used to determine the mode of failure by determining which stress (σ_f or σ_y) is lower at a given temperature as seen in Figure 2. However, given the mixed mode failure and crazing that often occurs at this transition, Bicerano suggests using the criterion $\sigma_f(T) > 1.2 \sigma_y(T)$ to determine the presence of shear yielding¹.

CRAZING STRESS

The complex and heterogeneous nature of crazing makes it difficult to develop simple yet accurate structure property relationships for this failure mechanism. Bicerano provides a brief review of some useful theories of crazing¹. In particular the growth of a craze which is heterogeneous and sensitive to the thermal history and chemical environment is difficult to characterize. However, some straightforward correlations do exist for the stress and strain at the inception of a craze (σ_{ci} and ϵ_{ci}) which is the point at which the crazing curve in Figure 1 begins to deviate from linear behavior. Kambour characterized the strain at the inception of a craze in terms of the Young's modulus, glass transition temperature, and solubility parameter with the following correlation⁶:

$$\epsilon_{ci} \propto \frac{\delta^2(T_g - T)}{E} . \quad (5)$$

Given the aforementioned linear relation between the yield stress and the Young's modulus, the yield stress may also replace the modulus in the above relationship. Wu has developed the following correlation for the stress at the inception of a craze

$$\log_{10}(\sigma_{ci}) \approx 1.83 + \frac{1}{2} \log_{10} \left(\frac{\rho}{M_e} \right) \quad (6)$$

where the craze inception stress (σ_{ci}) is in MPa and the entanglement density (ρ/M_e) is in millimole/cm³.

DEFORMATION OF ELASTOMERS

The theory of rubber elasticity treats polymer chains as entropic springs and leads to the following stress-strain relationship for uniaxial deformation⁷

$$\sigma = \frac{E_r}{3} \left(\lambda - \frac{1}{\lambda^2} \right) = G_r \left(\lambda - \frac{1}{\lambda^2} \right) \quad (7)$$

where λ is the extension ratio which is the ratio of the stretched to the unstretched dimension of the polymer sample. However, this expression is only useful at small deformations. Historically the stress-strain curves of elastomers have been described fairly well by the empirical relation known as the Mooney-Rivlen Equation⁸

$$\sigma = \left(C_1 + \frac{C_2}{\lambda} \right) \left(\lambda - \frac{1}{\lambda^2} \right) \quad (8)$$

where C_1 and C_2 are empirical constants. However, Van Krevelen points out that an approximation for of this equation can be written:

$$\sigma = G_r \left[1 - 0.4 \left(1 - \frac{1}{\lambda} \right) \right] \left(\lambda - \frac{1}{\lambda^2} \right) \quad (9)$$

REFERENCES

1. Bicerano, J. (1996) *Prediction of Polymer Properties*, 2nd Ed. Marcel Dekker, New York
2. Van Krevelen, D.W. (1990) *Properties of Polymers: Their Correlation with Chemical Structure: Their Numerical Estimation and Prediction from Additive Group Contributions*, 3rd Ed. Elsevier, Amsterdam
3. Vincent, P.I. (1972) *Polymer*, **13**, 558-560
4. Seitz, J. (1993) *J. Appl. Polym. Sci.* **49**, 1331-1351
5. Wu, S. (1990) *Polym. Eng. and Sci.*, **30**, 753-761
6. Kambour, R.P. (1983) *Polym. Comm.*, **24**, 292-296
7. Treloar, L.R.G. (1975) *The Physics of Rubber Elasticity*, 3rd Ed. Clarendon Press: Oxford
8. Mooney, N.J. *Appl. Phys.* **11**, 582 (1940); Rivlen, R.S. *Phil. Trans. Royal Soc. (London)*, **A240**, 459, 491, 509 (1948).

51: Structure-Property Relationships - Rubbery Polymers

P J LUDOVICE

INTRODUCTION

Like glassy polymers, rubbery polymers are also complicated by effects absent from most small molecule systems such as molecular weight, thermal history and non-ideal structure. Therefore most predictive methods for polymer properties limit the problem by assuming a reference of a monodisperse infinite molecular weight, with no branching or structural variation (see **Structure-Property Relationships: Glassy Polymers**). As with glassy polymers, we shall confine our discussion to low strains described by the “equilibrium” mechanical moduli. Rubbery polymers have the same amorphous structure as glassy polymers but this order is not frozen in as these polymers are above the **glass transition** temperature (T_g). Mechanical properties in rubbery polymers are characterized by the rubbery plateau seen Figure 1.

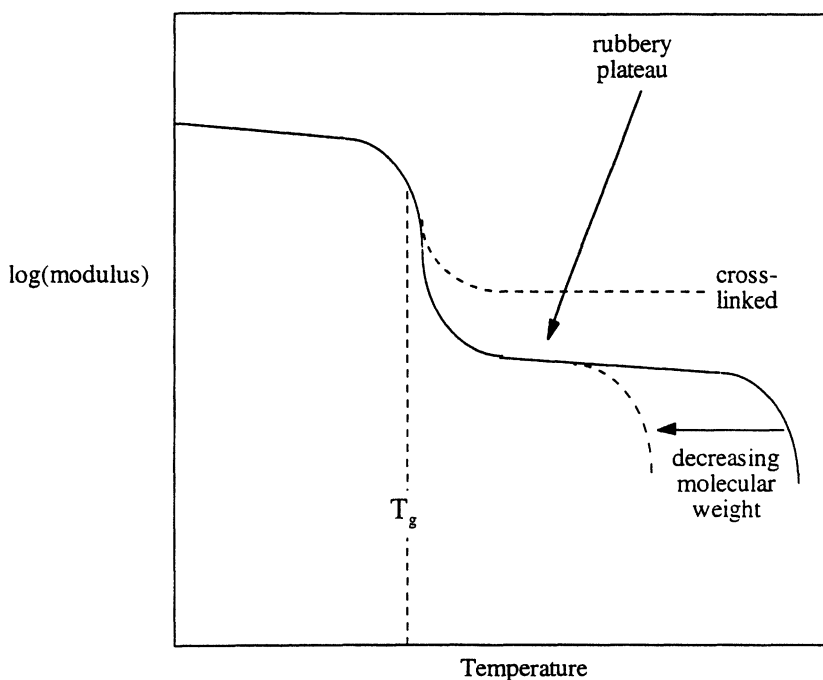


Figure 1: Mechanical moduli as a function of temperature.

This plateau region is characterized by a decrease in the mechanical moduli of several orders of magnitude from the values of the glassy state. In this region mechanical properties arise more from the entanglements between chains than the local energetics between chain segments that dominate mechanical properties in glassy polymers. The fact that general theories of rubber elasticity are based on entropy rather than these local energetics is a manifestation of this phenomenon. One should also note that the mechanical properties of glassy polymers can be related to the cohesive energy which is a measure of the local energetics (see **Structure-Property Relationships: Glassy Polymers**). For un-crosslinked or lightly crosslinked polymers, the rubbery plateau is also characterized by **viscoelastic** behavior to a larger degree than glassy polymers. However this time dependent phenomenon will not be discussed here.

STRUCTURE-PROPERTY RELATIONSHIPS

Of the four basic methods that can be used to estimate properties as a function of polymer structure: (i) molecular modeling, (ii) group additivity methods, (iii) basic structural methods (iv) graph theory methods, the third is most useful for rubbery polymers. The computational intensity of molecular modeling methods is not typically justified for rubbery polymers given the accuracy with which classic rubbery elasticity describes structure-property relationships. Molecular modeling is only justified when the details of specific energetic interactions are required. Rubbery elasticity theory works reasonably well by including mainly entropy. Similarly, group additivity and graph theory methods have not been used extensively to correlate structure and properties in rubbery polymers because their ability to describe specific structural interactions is not required here. This is in contrast to their use in predicting the cohesive energy which is important to the prediction of mechanical properties in glassy polymers (see **Structure-Property Relationships: Glassy Polymers**). The ability of basic structural methods to capture the local entropy of polymer chains makes them an efficient choice for predicting mechanical properties of rubbery polymers.

According to the theory of rubber elasticity¹ the equilibrium shear modulus for a crosslinked polymer (G_E°) is given by:

$$G_E^\circ(T) = \frac{\rho(T)RT}{M_c} \quad (1)$$

where $\rho(T)$, R and T are the density as a function of temperature, the ideal gas constant, and the temperature respectively. The average molecular weight of polymer segments between chemical crosslinks (M_c) is the principal factor in the determination of the modulus. By analogy, the equilibrium shear modulus of a non-crosslinked polymer (G_N°) is given by a similar expression:

$$G_N^0(T) = \frac{\rho(T)RT}{M_e} \quad (2)$$

except that now the effective molecular weight between physical entanglements (M_e) is employed. Bicerano suggests a simple estimation of M_e can be made from

$$M_e \approx \frac{M_{cr}}{2} \quad (3)$$

where M_{cr} is the “critical molecular weight” which is the molecular weight above which chain entanglements become significant². This point can be observed experimentally in a logarithmic plot of zero shear viscosity vs. molecular weight. For molecular weights below M_{cr} the shear viscosity is linearly related to the molecular weight, whereas above M_{cr} the viscosity scales with the molecular weight to the 3.4 power. The rubbery plateau pictured in Figure 1 above also vanishes at molecular weights near M_{cr} . If M_{cr} is not available to be used in the approximate relation above, a correlation developed by Seitz³ from a model developed by Edwards and Graessly⁴ may be used. This correlation approximates M_e (in grams/mole) as a function of easily calculated structural parameters:

$$M_e = 10.3 \frac{n_b M_o V_w}{N_A l_m^3} + 1120 \quad (4)$$

where M_o , V_w and l_m are the repeat unit molecular weight, the molar van der Waals volume of the repeat unit and the length of repeat unit in the fully extended conformation as defined in **Mechanical Structure-Property Relationships - Glassy Polymers**. N_A is Avagadro’s number and n_b is the number of rotatable bonds in the polymer backbone. A rotatable bond is one that can rotate a full 360° about its own axis without breaking a covalent bond. Bonds comprising rigid rings such as phenyl groups do not contribute to n_b . Since side chain bonds are not included, $n_b=2$ for vinyl polymers. Bicerano extended this correlation to include additional polymers and those that contain rings containing flexible single bonds. This correlation given below uses an alternate definition of n_b' .

$$M_e = 8.215 \frac{n_b' M_o V_w}{N_A l_m^3} + 1039.7 \quad (5)$$

where n_b' includes a contribution of +0.5 for each single bond contained in a flexible backbone ring such as those in a cyclohexane as opposed to a phenyl ring.

Like glassy polymers, rubbery polymers are amorphous in structure and hence their mechanical properties can be described by two independent quantities. Since rubbery polymers approximate a constant volume system, the **Poisson ratio** (ν) is very close to

1/2. This ratio varies between 0.49 and 0.49999 for most rubbery polymers. Using this estimate of 1/2 for ν , and substituting this into the general relationship between the shear modulus (G), the Young's or uniaxial modulus (E), the bulk modulus (B) and the Poisson ratio (ν)

$$E=3B(1-2\nu)=2G(1+\nu) \quad (6)$$

we find that the Young's modulus (E) can be approximated by three times the shear modulus (G). This approach works for the Young's modulus because it is fairly insensitive to the typical values of the Poisson ratio (ν). However the sensitivity of the bulk modulus (B) approaches infinity as ν approaches 1/2. This occurs because the limit of $\nu = 1/2$ represents a constant volume system which is completely incompressible, and the inverse of the bulk modulus is the compressibility so the bulk modulus (B) will become infinite. Therefore another method must be used to obtain B for rubbery polymers.

Arends has developed the following correlation from the analysis of a large amount of pressure-volume-temperature data⁵. The bulk modulus (B) in units of MPa is given as a function of the molar van der Waals volume (V_w) and the molar volume as a function of temperature $V(T)$:

$$B(T) = \frac{\frac{205V(T)}{V_w}}{\left[\frac{V(T)}{V_w} - 1.27\right]^2} - 2329 \left[\frac{V_w}{V(T)}\right]^2 \quad (7)$$

Bicerano recommends using the above correlation at temperatures that are at least 30°C above the glass transition temperature (T_g)². He suggests that the correlation above may be used for $T > T_g + 30^\circ\text{C}$, and the Seitz correlation for $T < T_g - 20$ (see **Mechanical Structure-Property Relationships - Glassy Polymers**) with linear interpolation between these two relationships being used to estimate the bulk modulus for range in between. This approach, as well as the correlations mentioned in this section, are incorporated into the polymer molecular modeling software available from Molecular Simulations Inc⁶.

REFERENCES

1. Treloar, L.R.G. (1975) *The Physics of Rubber Elasticity*, 3rd Ed. Clarendon Press: Oxford
2. Bicerano, J. (1996) *Prediction of Polymer Properties*, 2nd Ed., Marcel Dekker, New York
3. Seitz, J. (1993) *J. Appl. Polym. Sci.* **49**, 1331-1351
4. Graessly, W.W. and Edward, S.F. (1982) *Polymer*, **2**, 1329-1334
5. Arends, C.B. *J. Appl. Polym. Sci.* **49**, 1931-1938 (1993) and **51**, 711-719 (1994).
6. Molecular Simulations Inc., 9685 Scranton Road, San Diego, CA (www.msi.com).

52: Tensile and Compressive Testing

G M Swallowe

Tensile and compressive tests are the most common mechanical tests performed on materials. Tensile-Compression test machines normally consist of screw driven beams which can be moved at a range of operator chosen constant speeds. A load cell is mounted on the beam and, with the use of a pair of grips, a sample is fixed between the load cell and a fixed base plate. As the beam moves the force on the sample is recorded by the load cell and the strain measured using an extensometer. Test machines are available in a wide variety of sizes and from numerous manufacturers. Screw driven machines can operate in the strain rate range 10^{-5} to 1 s^{-1} . Higher strain rates can be achieved using hydraulically operated machines (up to 10 s^{-1}). Even higher rates (10^2 and above) require the use of specialised equipment such as **drop-weights** or **Hopkinson bars**.

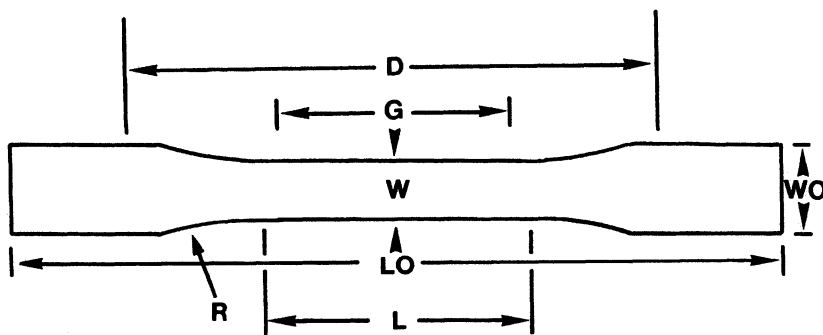


Figure 1: Standard tensile sample. See Table 1 for dimensions.

TENSILE TESTS

Tensile testing, in which a specimen is clamped between grips which are moved apart at a constant rate, is the most common deformation mode for polymer testing. However, the practice of using the constant separation speed of the grips to determine sample strain is prone to errors since the testing machine itself will deflect under the applied load and slippage of the sample within the grips is not uncommon. The use of an extensometer or other **transducer** to evaluate strain is therefore recommended. Slip in the grips can be reduced or prevented by the use of roughened faces on the grips. It is common practice to use a 'waisted' sample in order to confine the plastic deformation to a well defined region in the sample. Recommended sample dimensions are set out in ISO 527-1 which is equivalent to ASTM D638. The ASTM recommended shape for a sheet sample is illustrated in Figure 1. The exact dimensions depend on the thickness of

the sheet and a few representative examples are shown in Table 1. Recommend dimensions for rods and tubes are also given in the standards.

Table 1. Recommended tensile sample specimen dimensions for samples of the thicknesses indicated. All dimensions in mm.

	Thickness of sample			Tolerance
	7-14 mm	4-7 mm	<4 mm	
W	19	13	3.18	± 0.5
L	57	57	9.53	± 0.5
WO (min)	29	19	9.53	+ 6.4 (3.18 for <4 mm)
LO (min)	246	165	63.5	no max
G	50	50	7.62	± 0.25
D	115	115	25.4	± 5
R	76	76	12.7	± 1

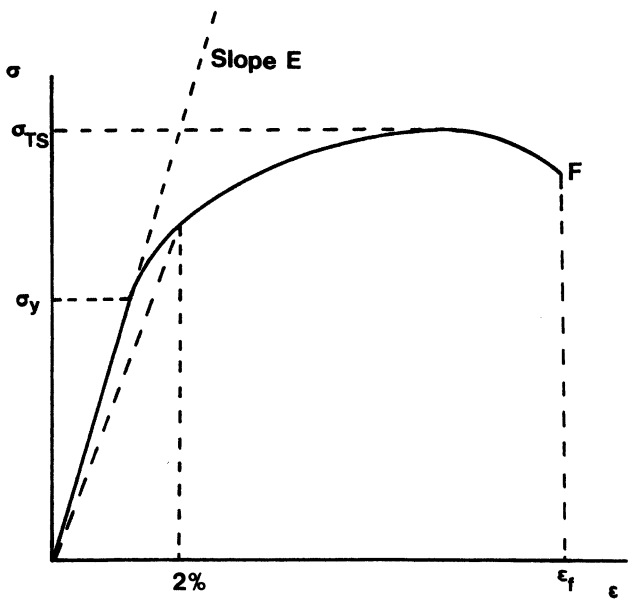


Figure 2: Schematic engineering stress (σ_e) engineering strain (ϵ_e) curve.

The results of tensile tests are used to determine a large number of specimen parameters. Figures 2 illustrates the types of data obtained. Strain is determined from the change in length of the gauge length G of the sample and can be expressed as engineering strain $\Delta G/G$ or true strain $\log_e (G/G_0)$ with G the gauge length at a given time and G_0 the initial gauge length (see **Stress and Strain**). The stress is expressed as

Engineering Stress, the force at a given time divided by the original cross sectional area of the gauge section of the sample, or True Stress, the force divided by the area at the time the force is measured. The fundamental material properties of the sample are described by a True Stress - True Strain curve and this is the type of data that must be provided for the production of constitutive models of the materials behaviour (see **The Finite Element Method**).

The tensile strength of a sample is defined as the engineering stress at the onset of necking, or at break if no necking occurs. Young's modulus is the slope of the initial (linear portion) of the stress strain curve. Frequently with polymers there is no linear portion to the curve and a tangent modulus (slope of a tangent to the stress strain curve) or a secant modulus in which the slope of a line drawn from the origin to a specified (often 2%) strain value on the stress strain curve is used to define a modulus. The yield stress is in principle the lowest stress which leads to permanent deformation on removal of the load. This is usually indicated by a rapid change of slope in the curve but can be difficult to determine. A flow stress at a particular strain, often the stress at 2% offset strain is then used to define a yield stress. % elongation to break is the breaking strain expressed as a percentage. Figure 2 illustrates these measurements. It is important to be aware of the units being used i.e. true or engineering (which is sometimes called nominal) in the stress strain curve.

The use of an extensometer (see **Transducers**) on the gauge length renders the measurement of strain fairly easy *until the onset of necking*. When necking begins the important strain is that in the neck and this is not so easily determined. Measurement of True Stress requires knowledge of the cross sectional area of the gauge area at all stages of the deformation. Since a constant value for **Poisson's Ratio** cannot be assumed the transverse dimension of the sample must be monitored with a second extensometer or micrometer. The use of a transverse extensometer does of course enable Poisson's ratio to be measured as a function of longitudinal strain.

Care must be exercised when using 'clip-on' extensometers since the stress required to ensure no slippage between the extensometer and sample during deformation can be sufficient to cause localised yielding in the sample in the region of the extensometer knife edges. Extensometers must of course have as low a mass as possible in order not to provide additional loading on the sample and introduce bending stresses. Non contact optical techniques are gaining increasing popularity as a way of avoiding these problems. Other potential inaccuracies such as bending stresses can be introduced due to misalignment of the clamps. The low modulus and yield stress of polymers also means that the frictional forces in the self aligning systems used in test machines can be sufficient to render the results inaccurate, particularly in the early stages of an experiment. Figure 3 illustrates the common result of a stress strain experiment which should ideally have the form of the schematics of Figure 2.

A problem, sometimes called the toe effect, which frequently occurs in tensile (and compressive) tests is illustrated in Figure 3. The region AB at the start of the test is not an accurate reflection of the sample material properties since it incorporates apparent strains due the take-up of slack and alignment in the system and to a lesser extent loads required to overcome friction in the linkages etc. ASTM D638 recommends procedures

to compensate for this effect by extrapolating the linear portion BC of the stress-strain curve back to the axis. However, other than for materials which have a linear portion of the stress strain curve where extrapolation back to zero stress can be used, any measurements of modulus made from a curve with a ‘toe’ must be treated with suspicion. Where strains are measured directly from a gauge length on the sample rather than from the displacement of the machine cross-head this problem is much reduced. An alternative method of measuring the modulus is to use an unloading curve DE since the displacements due to alignment etc. will not then not be such a major problem.

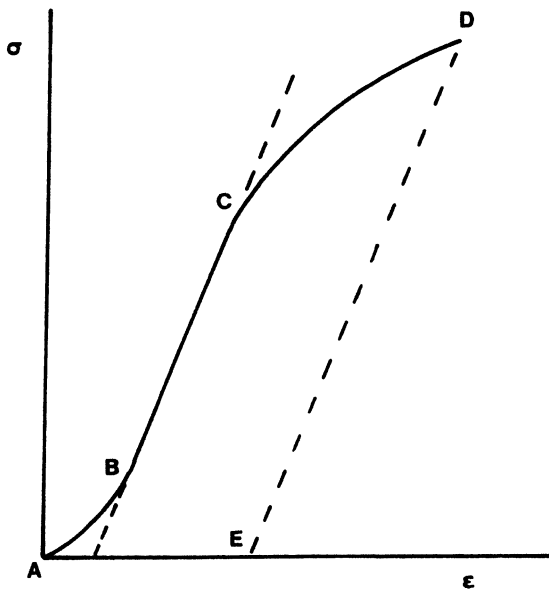


Figure 3: Stress-strain curve illustrating “toe effect”

COMPRESSIVE TESTING

Compressive testing is normally carried out using cylindrical samples compressed between flat hardened steel platens. The form of stress-strain curve obtained is similar to that of tensile tests and the same consideration of the “toe region” and stress and strain definitions apply. There are a number of problems associated with compressive testing that do not occur in tensile tests, these are buckling, barreling and friction. Buckling, rather than uniform compression, occurs if the aspect ratio (length/diameter) of the cylinder is large. The classical Euler Theory gives the Force required to cause buckling as $F = \pi^2 EI / l^2$ with l the cylinder length, E the modulus, and I the second moment of inertia. For a cylinder $I = \pi r^2 / 4$ giving

$$F = \pi^3 E r^2 / 4 l^2 \quad (1)$$

It can be seen that the tendency to buckle increases rapidly with aspect ratio and in order to avoid buckling ASTM D695 recommends an aspect ratio of 2:1.

Barreling, the type of deformation illustrated in figure 4, is caused by friction at the interface between the samples and platens. This problem can be greatly alleviated by the use of a lubricant at the interface. Smearing the sample with a thin layer of petroleum jelly greatly reduces the problem but as deformation continues the lubricant is expelled from the interface and the remaining lubricant spread over an ever increasing area and interfacial friction will again eventually lead to barreling. It is very difficult to produce compressive strains greater than $\sim 100\%$ without barreling. At higher strain rates sample inertia effects come into play¹ and it is generally accepted that an aspect ratio of ~ 0.5 to 1, rather than 2 (as recommended in the standards) gives a more reliable result.

Friction has also the effect of increasing the apparent compressive yield (or flow) stress. The apparent yield stress σ is given by

$$\sigma = \sigma_y \left(1 + \frac{2\mu r}{3l} \right) \quad (2)$$

with σ_y the true material yield stress and μ the coefficient of friction. Provided μ is small (i.e. a well lubricated system) $\sigma = \sigma_y$.

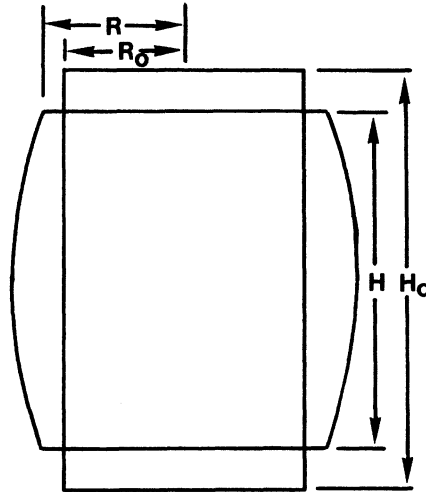


Figure 4: Illustration of barreling; R_0 and H_0 are the original sample radius and height, R and H the interface radius and overall height after compression.

Plane strain compressive testing in which the area of loading remains constant and thus the true stress calculation is made easier is carried out using the type of system illustrated in Figure 5. This is sometimes a preferred method if large strain data is

required but is not recommended for small strains since recovery of material extruded from between the die influences the results. Adequate lubrication is of course needed. In general for small strains a standard uniaxial compression stress is recommended and for large strains the plane strain test. Further information and description of compression and tensile testing is available in references 2, 3 and 4.

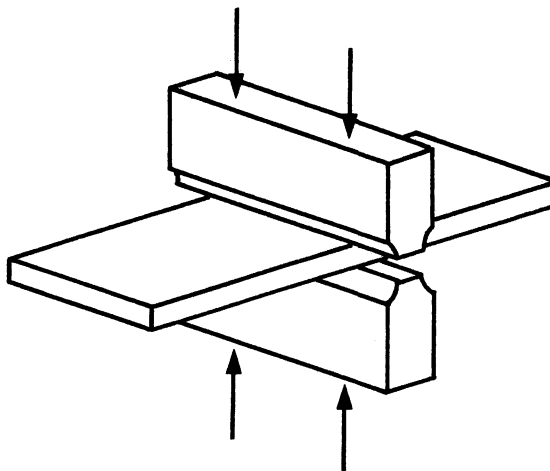


Figure 5: Plane strain compression test. Shaped platens are pressed into a sheet of sample material.

REFERENCES

1. Gorham, D.A. (1989) *J. Phys D.: appl. Phys.* **22**, 1888
2. Turner, S. (1983) *Mechanical Testing of Plastics* 2nd edition, George Godwin.
3. Brown, R.P. (1981) *Handbook of Plastics Test Methods* 2nd edition, George Godwin
4. Ives, G.C., Mead, J.A. and Riley, M.M. (1971) *Handbook of Plastics Test Methods*, Iliffe Books

53: Thermoplastics and Thermosets

A.R. Rennie

The terms thermoplastic and thermoset describe the processability of a material as the temperature is changed. A polymer that becomes plastic and flows on heating, either by reason of crystal melting or by exceeding the glass transition temperature T_g is thermoplastic. This process is reversible and so the material can be processed by, for example, moulding or extrusion after it has been prepared as a solid. A thermoset is a material that undergoes a chemical reaction on heating or curing that irreversibly sets the material to a given form.

It is common to think of thermoplastics as linear or branched polymers and thermosets as rigid resins with considerable cross-linking between molecules. However it is important to realise that mechanical properties can be extremely varied. A cross-linked or vulcanised rubber is a thermoset. On heating it will not flow to any arbitrary shape, it can be swollen but not truly dissolved in a solvent: the molecular network extends throughout a sample. Other thermoset resins such as epoxy adhesives or phenol/formaldehyde resins will be much more rigid. Some elastomers are thermoplastic being made from copolymers that provide thermally reversible 'cross-links' usually by segregation of one part of the molecules into glassy or crystalline solid domains. Common examples of thermoplastics are polystyrene and polyethylene.

There are a few polymers that cannot be categorised readily as either thermosets or thermoplastics. These contain no network of chemical cross-links but can not be processed as a melt. This usually occurs because the melting point of the crystals is so high that extensive chemical degradation is found at lower temperatures. An example of a material showing this behaviour is polytetrafluoroethylene (PTFE). Such solid materials have to be prepared by processes such as sintering or solvent casting or spinning.

REFERENCES

1. Ward, I.M. and Hadley, D. W. (1993) *An introduction to the Mechanical Properties of Solid Polymers*, Wiley
2. Cowie, J. M. G. (1973) *Polymers: Chemistry and Physics of Modern Materials*, Intertext Books

54: Time-Temperature Equivalence

G M Swallowe

Both the modulus and the compliance of viscoelastic materials are time dependent quantities and a complete characterisation of the modulus over a wide temperature and time range can be a very time consuming process (see **Viscoelasticity**). It is however possible, using the concept of time-temperature equivalence, to relate the compliance at one temperature to that at another temperature by a shift of the compliance-time curve along the time axis. This is illustrated in Figure 1.

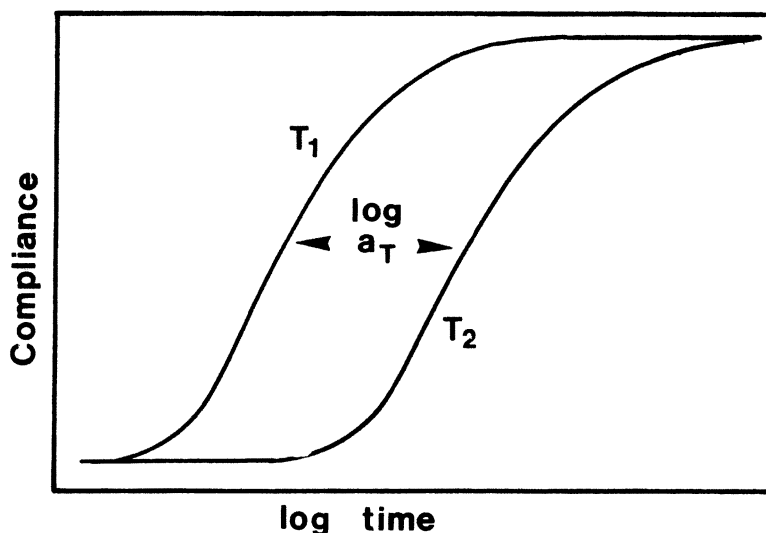


Figure 1: Diagram illustrating the basis of the time-temperature shift factor a_T . Schematic compliance versus log time curves are drawn for temperatures T_1 and T_2 with $T_1 > T_2$.

Figure 1 shows a plot of compliance as a function of log time at two temperatures T_1 and T_2 with $T_1 > T_2$. It can be seen that a simple shift along the time axis by an amount $\log a_T$ will superimpose one curve on the other. If the quantity a_T can be derived for a variety of temperatures then one set of compliance measurements made at a single temperature can be used to predict the compliance over a range of temperatures. On the assumption that the relaxation governing the viscoelastic process (see **Relaxations in Polymers**) has an Arrhenius dependence it can be shown that

$$a_T = \exp \left[\frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] \quad (1)$$

with ΔH the activation enthalpy of the relaxation and R the gas constant. The quantity a_T is called the shift factor. The same shift factor can be used to transpose plots of the loss factor $\tan\delta$ against log frequency.

The simple scheme outlined above is complicated by changes with temperature of the relaxed and unrelaxed compliances C_R and C_U as illustrated in Figure 2. At a higher temperature C_R and C_U will be greater and a simple vertical shift in order to move the reference curve to match the relaxed and unrelaxed compliances measured at the second temperature provides a reference to which the horizontal a_T shift can then be applied. Thus at least one measurement at the second temperature T_2 will be required to generate the compliance - time curve from the original measurements at T_1 .

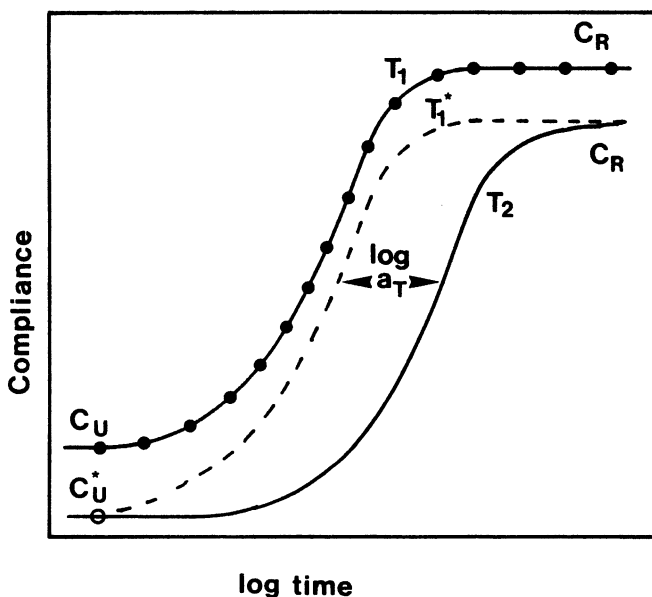


Figure 2: Schematic diagram showing the vertical adjustment in the reference curve required to allow for temperature variations in C_U and C_R . The measured curve (—) is shifted downwards so that $C_{U(T1)}$ matches the measured point at the extreme end of the lower temperature curve $C_{U(T2)}$ to produce a new reference curve (-----). This is then transposed using a_T to produce the T_2 compliance curve. Notional measured points are indicated by ● (the fully measured curve) and ○ (single point on T_2 curve).

In 1955 Williams, Landel and Ferry¹ adapted the theory of viscosity for low molecular weight liquids to the viscoelastic response of polymers and derived an equation, the WLF equation which gives the shift factor for a wide range of amorphous polymers over the temperature range T_g to $T_g + 100^\circ$. The equation can be expressed as

$$\log a_T = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \quad (2)$$

The WLF constants $C_1 = 17.44$ and $C_2 = 51.6^0$ are universal. However, if a temperature other than T_g is chosen as the reference temperature then the constants will change. The theoretical basis of the WLF equation is described in references 2 and 3.

Equations of the same form as the WLF equation can be used for semi-crystalline polymers but only over a much restricted time and temperature range. Further details can be found in reference 4.

REFERENCES

1. Williams, M.L., Landel, R.F., Ferry, J.D. (1955) *J. Am. Chem. Soc.* **77**, 3701.
2. Arridge, R.G.C. (1975) *Mechanics of Polymers* Clarendon Press, Oxford.
3. Ward, I.M. and Hadley D.W. (1993) *An Introduction to the Mechanical Properties of Solid Polymers*, Wiley.
4. Haddad, Y.M. (1995) *Viscoelasticity of Engineering Materials*, Chapman and Hall

55: Torsion and Bend Tests

G. M. Swallowe

TORSION TESTS

The most convenient method of measuring the shear modulus is via a torsion test (see **Stress and Strain**). The usual torsion test involves the use of a solid cylindrical specimen clamped rigidly at one end with a torque applied to the other end. This causes twisting of the sample as illustrated in figure 1 and results in pure shear of the sample. A convenient method of applying the torque is to use equal weights and a pulley system to provide the forces F illustrated in the figure. The same equipment can be used to study torsional creep as well as evaluate the shear stress-shear strain curve. Since the stresses at the clamped ends of the specimen will differ from those in the bulk a useful 'rule of thumb' is to make the specimen with a length of at least ten times its diameter. The time dependent shear modulus $G(t)$ is given by the expression

$$G(t) = \frac{2TL}{\pi R^4 \theta} \quad (1)$$

with T the torque ($= Fx$, with x the perpendicular distance between the forces), R the cylinder radius, θ the angle of twist and L the length of the cylinder. Alternative specimen forms are a hollow cylinder or a thin rectangular strip leading to the expression

$$G(t) = \frac{16TL}{wd^3 u \theta} \quad (2)$$

with w the strip width, d the thickness and u a parameter that depends on the w/d ratio. This system forms the basis for ASTM D1043 Standard test method for stiffness properties of plastics as a function of temperature. The values of u vary from 2.25 to 5.3 as w/d varies from 1.00 to 100.0 and are tabulated in ASTM D1043. In the case of a thin walled hollow cylinder of outer radius R and wall thickness n the expression becomes

$$G(t) = \frac{TL}{\pi R^3 n \theta} \quad (3)$$

Expression 2 is strictly true only for small angles of twist since a rectangular strip distorts when it is twisted about its longitudinal axis. However the correction factor is usually small leading to an error of $\sim 5\%$ for twist angles of $\sim 100^\circ$ and can usually be ignored. Twisting causes a force to be generated along the sample axis and therefore,

unless provision is made for the sample to contract in the longitudinal direction, a tensile force as well as a torque will be applied. Using a system that allows either the upper or lower clamp to move along the direction of the sample axis alleviates this problem.

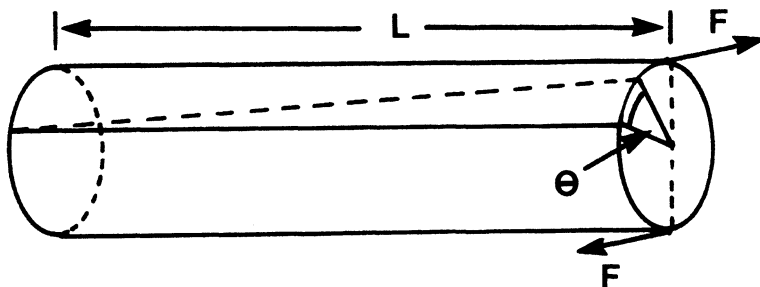


Figure 1: Torsion of a cylinder, Angle of twist θ is produced by equal forces F applied tangentially to the cylinder and perpendicular to its axis.

Shear stress - shear strain curves cannot be directly obtained from torsion tests since the shear stress will not vary directly with the radial position in the sample. Plots of twisting torque against shear strain are commonly produced and methods have been developed to transform these to shear stress - shear strain curves¹. The use of thin walled tubes rather than a solid cylinder greatly reduces the strengthening effect of inner sections restraining the yield of outer sections of the sample but can lead to problems caused by the buckling of the cylinder walls².

Torsional Pendulum

This is a modification of the torsional system described above which enables dynamic torsional measurements to be made. The basic system consists of a cylindrical sample suspended vertically and rigidly clamped at its upper end. A beam with adjustable weights (inertia bar) is clamped to the lower end of the specimen and can rotate freely in the horizontal plane see figure 2. The angle of rotation of the pendulum is conveniently measured by optical transducers. A problem with the basic design is that the sample is axially loaded in tension by the beam, however a modification to the system in which the sample is clamped at its lower end and the beam suspended by a torsion wire alleviates this problem.

Adjusting the weights and their position on the inertia bar changes the moment of inertia of the system and enables the oscillation frequency to be adjusted. For an elastic system the period of oscillation P is given by

$$P = 2\pi \sqrt{\frac{2I}{\pi G r^4}} \quad (4)$$

with r the sample radius, l the length of the sample and I the moment of inertia of the system. Damping of the oscillation occurs due to the viscoelastic nature of the polymer as well as air and frictional damping of the system. Assuming that other sources of damping can be made negligible in comparison to the viscoelastic damping and recognising that the modulus will be complex $G^* = G' + iG''$ (see **Viscoelasticity**) G in equation 4 can be replaced by G' . The log decrement (the natural logarithm of the ratio of successive oscillation amplitudes) can be used to obtain the loss tangent $\tan\delta$ using the relationships $(\log \text{ decrement}) = \pi \tan\delta$ and $G'' = G' \tan\delta$.

Torsional pendulums can generally be used over frequency ranges of sub Hertz to a maximum of about 100 Hz. **Dynamic Mechanical Analysis** systems include a forced oscillation form of torsional pendulum which enables much higher frequency tests to be carried out. The torsional pendulum method outlined above forms the basis of the standard test method EN ISO 6721-2 and is part of BS 2782 Part 3 (see **Standards for Polymer Testing**).

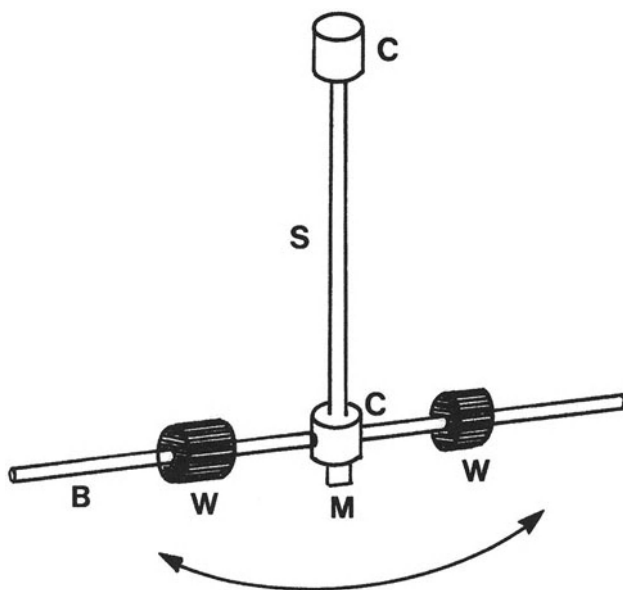


Figure 2: Basic Torsional pendulum, Cylindrical sample S is held in clamps C. A beam B carrying adjustable weights W is rotated and the released and the resulting oscillations monitored by the deflection of a light beam reflected by the mirror M.

BEND AND FLEXURE

The classical cantilever, three point and four point bend tests are particularly suitable for measurements of the modulus of brittle materials such as glassy polymers (see figure 3).

The modulus $E(t)$ as a function of loading time by a force F is given by the expressions

$$E(t) = FL^3 / 48al \quad (5)$$

$$E(t) = FL^3 / 3al \quad (6)$$

$$E(t) = L^2 Fx / 8al \quad (7)$$

with a the deflection, I the moment of inertia and L the distance illustrated in figure 3. Equation 5 refers to three point bending, equation 6 to a cantilever and 7 to four point bending. The cantilever method is however subject to end corrections which make it less accurate than the others. For rectangular beams of width w and depth d and circular rods of radius R or hollow cylinders of inner radius R_1 and outer radius R_2 , I is given by the expressions

$$I = wd^3 / 12 \quad (8)$$

$$I = \pi R^4 / 4 \quad (9)$$

$$I = \pi(R_2^4 - R_1^4) / 4 \quad (10)$$

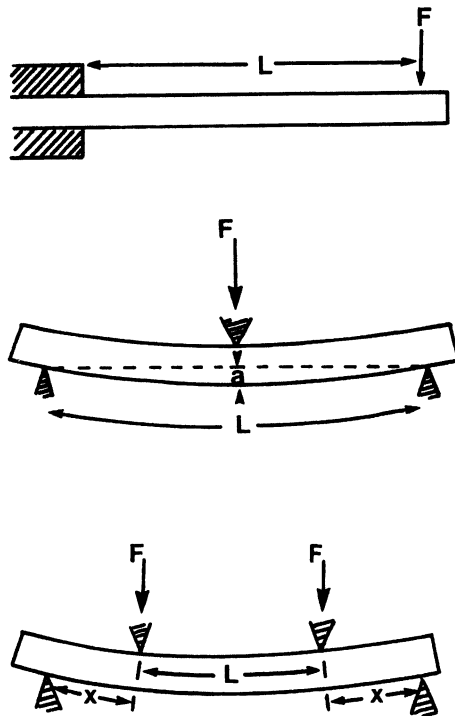


Figure 3: Flexural systems. Upper diagram cantilever, central diagram three point bending, lower diagram four point bending.

Since the dimensions of the beam appear to the fourth power in these expressions it is important that the beams are accurately uniform and accurately measured in order that reliable results may be obtained (see **Accuracy and Errors**). In general flexural measurements have an inherently lower accuracy than tensile tests since the stresses and strains vary across the thickness of the sample and cannot be as unambiguously defined as in a tensile test. A generally accepted accuracy is ~ 3-5% and this is adequate for most purposes. The simple flexural formulae apply only to the case of 'small' strain and this may be taken to mean a maximum strain in the beam of 5%. For a brittle material the fracture stress can be evaluated in a bend test by increasing the applied force in a three point bend test and noting the deflection at which fracture commences. The maximum (tensile) stress is given by

$$\sigma = 3fL / 2wd^2 \quad (11)$$

The initiation of fracture by three point bending forms the basis of the Charpy impact test (see **Impact Strength**). The flexural methods form the basis of ASTM standard tests D790 (Flexural Properties of Unreinforced and Reinforced Plastics), D747 (Apparent Bending Modulus of Plastics by Means of a Cantilever Beam) and D5934 (Determination of Modulus of Elasticity for Rigid and Semi-Rigid Plastic Specimens by Controlled Rate of Loading Using Three Point Bending).

The cantilever may be adapted to provide a dynamic method of determining E by setting the cantilever into oscillation and recording the frequencies at which resonance occurs. The oscillation can be conveniently induced without loading the beam by using a magnetic transducer connected to an oscillator and exciting the cantilever via a small piece of mumetal attached to the beam. Resonances occur at frequencies given by

$$\omega = (\beta L)^2 \sqrt{\frac{EI}{\rho L^4}} \quad (12)$$

with ω the resonance frequency (in radians/second), ρ the mass per unit length and $(\beta L)^2$ having values of 3.52 for the fundamental, 22.0 for the second mode and 61.7 for the third mode³. The reader is referred to the references below as well as to the ASTM and BS EN ISO standards for fuller information.

REFERENCES

1. *Testing of Polymers* (ed J. V. Schmitz) 1966 Volumes 1 and 2, Wiley Interscience
2. Timoshenko, S.P. and Gere, J.M. (1961) *Theory of elastic stability*, McGraw-Hill
3. Thompson, W.T. (1983) *Theory of Vibrations with Applications*, George Allen and Unwin
4. Ives, G.C., Mead, J.A. Riley M.M. (1971) *Handbook of Plastics test methods*, The Plastics Institute and Illfe Books.

56: Toughening

G. M. Swallowe

The process of increasing resistance to failure under mechanical stress is called toughening. Toughness is the energy absorbed by the material during deformation before failure. Depending on the type of application and the test involved are two ways of defining toughness. The first is the integral of the area under a true stress true strain curve up to the point of fracture (see **Stress and Strain**). Since stress is force/unit area and strain is length/length the units of the integral are force x length/area x length i.e. energy/volume. Toughness is therefore the energy absorbed by the material per unit volume during plastic deformation the units being Joules/m³. The second, and more usual in polymer science, way of considering toughness is to consider the amount of energy required to propagate a crack through the material. A brittle material will fail by crack propagation with little plastic deformation and the toughness of the material is then defined as the energy required for the crack to grow and create an increase in the surface area of cracked material, the units being Joules/m². This latter definition is the one relevant to impact processes (see **Impact Strength** and **Impact and Rapid Crack Propagation** and **Slow Crack Growth**).

The numerical value of toughness will vary with strain rate and temperature (see **Strain Rate Effects** and **Ductile-Brittle Transition**) with a decrease in toughness with decrease in temperature. The variation with strain rate is rather more complex but in general toughness increases with modest increases in strain rate before falling to a lower level during rapid crack propagation (see **Fast Fracture in Polymers**). The toughness of polymers, in terms of crack propagation, tend to lie in the range 1-10 kJ/m² and these are the values that are presented in tables of polymer properties. The energies dissipated per unit volume when the whole sample is plastically deformed are very much greater than this, of the order of tens or hundreds of Mega Joules /m³. However the relative ranking of polymers tends to be the same using either definition of toughness. The connection between the two values can be understood by considering that in crack propagation only a 'layer' of polymer microns thick on either face of the crack is deformed thus accounting for the $\sim 10^5$ factor between the two values.

TOUGHENING MECHANISMS

A mode of failure absorbing a large amount of energy will lead to a tougher material. Brittle fracture involving very little deformation of the material adjacent to the crack faces will absorb very little energy while **crazing** and multiple shear yielding which both involve extensive localised plastic deformation and hence energy absorption will produce a tough material. Toughness therefore depends on the amount and spatial extent

of plastic deformation in the region around a crack (see **Fracture Mechanics**). Toughening mechanisms are any means by which brittle failure may be suppressed and crazing and shearing promoted.

Crazing can be promoted by suitable changes to the polymer. The tendency to craze is increased by increasing the average length of the chain segments between entanglements. In general extensive crosslinking causes a reduction in toughness and although the effect is small at low crosslinking densities dramatic decreases in toughness occur when the number of repeat units between crosslinks falls below ~ 10 to 20. The toughness of linear polymers (such as polyethylene) is increased by a modest amount of crosslinking. In semicrystalline polymers toughness is increased by reducing the **crystallinity**. This can be accomplished by rapid cooling from the melt or the use of a larger molecular weight resin. The toughness increase is believed to be due to an increase in the number of 'tie molecules' which are molecules that are part of two crystallites or molecules that form entanglements in the amorphous regions between crystallites.

The most effective and widely used method of toughening is to introduce a second phase into the polymer. In its simplest form this will be a low molecular weight molecule which plasticises (see **plasticisers**) the polymer and inhibits brittle failure. However the use of a second polymer, a rubber or elastomer, which forms a multiphase structure is the most effective toughening mechanism for brittle materials (see **Alloys and Blends**).

The addition of rubbers to commercially available thermosets and thermoplastics was initiated with the production of High Impact Polystyrene in 1948. Rubber toughened grades of virtually all widely used polymers are now available with the exception of some soft polymers which already contain elastomeric regions within their structure. Between 5 and 20% of rubber is added to form a fine dispersion of rubber spheres within the matrix of the original polymer. Depending on the particular polymer/rubber combination the spheres form initiation sites for crazing, shear banding or multiple cracking and they also act to blunt crack tips. In order to be effective the rubber must be well bonded to the matrix polymer and be above its glass transition temperature. An even dispersion of small (100nm - 50 μ m) particles is more effective than a smaller number of large rubber particles. The exact particle size for most effective toughening depends on the particular matrix/rubber combination. It is now widely accepted that cavitation of the rubber particles under the action of the applied stress is the first stage of the toughening process with matrix shearing, crazing or fibrillation of the rubber particle comprising the following stage. References 1 and 2 include descriptions of the theory of toughening as well as descriptions of suitable polymer/rubber combinations and particle sizes.

A consequence of the toughening mechanisms is a reduction in the modulus. Indeed the limit on amount of toughening may well be an unacceptable reduction in modulus. The modulus of a rubber toughened polymer can be approximately calculated from a simple rule of mixtures calculation. The simple calculation leads to lower than observed values of modulus at low rubber concentrations and higher than observed values at high concentrations. This latter effect is believed to be due to the slight solubility of the

rubber in the matrix leading to a continuous network of rubber throughout the composite.

REFERENCES

1. *Polymer Toughening* (ed. C.B. Arends) (1996), Marcel Dekker
2. Collyer, A.A (1994) *Rubber Toughened Engineering Plastics*, Chapman and Hall.

57: Ultrasonic Techniques

G. M. Swallowe

Ultrasonic and other acoustic wave propagation techniques are used for two main purposes in polymer engineering. i) the evaluation of materials properties and ii) the detection of flaws in a component. For the evaluation of material properties the quantities of interest are the propagation speed and attenuation of the waves and in flaw detection the reflected (or transmitted) acoustic amplitude as a function of position in the sample.

Small amplitude sinusoidal waves are generated by attaching an appropriate oscillator to a piezo-electric transducer (see **Sensors and Transducers**) and launched into the sample. Other forms of wave generation such as electromagnetic acoustic transmitters (EMATs), magnetostrictive transducers and pulsed lasers¹ are also used but piezo-electric systems remain the most popular. In order to achieve a reasonable energy input into the sample the transducer must be coupled to the sample material. Essentially this requires minimising the reflection coefficient at the transducer/sample boundary. The amount of reflection at any boundary between two media is determined by the values of the characteristic acoustic impedances of the media where the acoustic impedance (Z) is given by the product of density (ρ) and wave speed (C). The power transmitted across a boundary is given by $Z_1 Z_2 / (Z_1 + Z_2)^2$ and the optimum impedance of a coupling layer is given by $Z^2 = Z_1 Z_2$. Table 1 lists representative wave speeds for a range of polymers and piezo-electric materials.

Bearing in mind that the density of most polymers can be taken as $\sim 1000 - 1500 \text{ kg/m}^3$ and that of lead zirconate titanate (PZT) and quartz, two of the most popular piezoelectric materials, are 7500 and 2600 kg/m^3 respectively it can be seen that there is a large impedance mismatch necessitating the use of a matching medium. This may be a solid but frequently oil, water or grease is used. Polyvinylidene fluoride (PVDF) is a relatively recently introduced piezoelectric polymer whose impedance is a close match to that of other polymers and would therefore be expected to be an ideal transducer material. However it is not widely used as the basis of a transmitting transducer since it requires an extremely high voltage to produce an acoustic wave of reasonable amplitude. Conversely it is an excellent detecting medium as a large output voltage is obtained from a small amplitude wave.

MATERIALS PROPERTIES

The methods employed fall into two groups a) pulsed and b) continuous wave. Pulsed methods involve either launching a short pulse of sound waves into the polymer and measuring the time taken for the pulse to travel to the other side of the sample where it is detected by another transducer or the time taken for it to be reflected and return to the

source which also acts as a receiver. Knowing the thickness of the sample and measuring the time involved to traverse it enables the wave speed to be measured and from this the elastic constants can be determined. The longitudinal wave speed is given by the expression

$$C_L = [(K + 4G/3) / \rho]^{1/2} \quad (1)$$

and the shear wave speed by

$$C_S = (G / \rho)^{1/2} \quad (2)$$

with G the shear modulus, K bulk modulus, and ρ the density (see **Stress and Strain**). Due allowance must of course be made for the transit time of the pulses through the transducer cover and the coupling medium. Because of the process of mode conversion, whereby the reflection of a longitudinal wave gives rise to both longitudinal and shear reflected waves, both types of wave can be produced with a single transducer and both wave speeds measured simultaneously when suitably shaped samples are used¹. An alternative to the direct contact technique where the transducers are attached directly to the sample is the immersion technique. Using this method a sample, often a large cube, is placed on a rotatable table in a water tank. Transducers are fixed in the tank close to the table and pulses launched in the usual way. The advantages are that angle between the sample/water interface relative to the direction of propagation of the ultrasonic pulse can be altered at will, and hence the amount of mode conversion adjusted, and also that anisotropic properties in the sample can be detected by differences in the wave speeds in different directions in the sample².

A further advantage of the immersion goniometer method is the possibility of determining wave speeds by the critical angle technique². In this method the angle between the incident pulses and the sample surface is varied and the reflected intensity monitored by a second transducer picking up specular reflections from the surface. Two maxima in the reflected peak intensities are observed at angles θ_L and θ_S corresponding to longitudinal and shear wave propagation in the sample. Knowing v_0 the sound speed in the immersion liquid the speeds in the sample v are determined from the expression

$$v/v_0 = 1/\sin \theta \quad (3)$$

Measurement of the attenuation of the pulses as a function of sample thickness gives an indication of defect density (crazes etc.) within the specimen since such defects scatter the ultrasonic waves and reduce the intensity reaching the other side of the sample. The measurement of the wave speed in polymers forms the basis of ASTM D4883 Test method for density of polyethylene by ultrasound technique.

Continuous wave measurements can be carried out at lower frequencies ($10^3 - 10^5$ Hz) with the sample in the form of a long rod or filament held under tension and simply driven by a loudspeaker cone. A piezo-electric sensor which can be moved along the sample is used to detect the amplitude and phase of the wave as a function of position

along the sample. This method requires that the diameter of the rod be small compared to the wavelength and works best with materials where the attenuation is high so that interference by reflections from the end of the sample is minimised. A plot of the phase angle θ (measured as the difference in phase between the sinusoidal wave at the input and measuring position) against position along the sample leads to a straight line, sometimes with superimposed damped oscillations, whose slope $k = \omega/C_L$ with ω the angular frequency of the wave ($= 2\pi \times \text{frequency}$) and C_L the longitudinal wave speed. The amplitude attenuation coefficient α can be obtained by comparing the amplitude of sensor response as a function of position along the sample. Knowing α , ω , C_L and the density ρ the real E^* and imaginary E^{**} parts of the complex modulus can be derived from the relationships

$$E^* = C_L^2 \rho \quad \text{and} \quad E^{**} = 2\alpha C_L^3 \rho / \omega \quad (4)$$

Resonance methods are a convenient method of determining wave speed C . A sample in the form of a disc or rod is excited by long pulses of narrow frequency band from a radio frequency oscillator and the amplitude of the oscillations in the sample recorded either on a receiving sensor on the other side of the sample or using the transmitting transducer. The transmitted frequency is slowly increased and the sample oscillation amplitude recorded as a function of frequency. Distinct peaks in output are observed when the frequency is such that standing wave resonances are excited in the sample. The resonance frequencies f are given by the expression

$$f = nC/2L \quad (5)$$

with L the sample length, C the sound speed and n an integer. In general the value of n will not be known but this is not important if several successive resonances are found since a plot of resonance frequencies f against the resonance numbers (n , $n+1$, $n+2$ etc. with n arbitrary) will yield a straight line whose slope is given by $C/2L$. The resonance method is one of the most accurate for the determination of C . An alternative and quicker, though less accurate, form of the method is to introduce a broad band input pulse and frequency analyse the received pulse to obtain the resonant frequencies.

Resonance methods in which a cantilever of the polymer is put into transverse vibration can be used to measure the Young's modulus E and loss factor $\tan \delta$ (see **Torsion and Bend Tests**). The measured resonance frequency determines E from the equation

$$\omega = (\beta L)^2 \sqrt{\frac{EI}{\rho L^4}} \quad (6)$$

with ω the resonance angular frequency, L the cantilever length, ρ the linear density (kgm^{-1}) and β a constant depending on the mode excited. The width of the resonance peak gives a measure of $\tan \delta$ where $\tan \delta = \Delta\omega/\omega_0$ with ω_0 the resonance frequency and $\Delta\omega$ the width of the resonance peak i.e. the range of frequencies where the amplitude is

greater than $1/\sqrt{2}$ of the maximum amplitude.

Table 1: Longitudinal wavespeeds in a selection of materials

Material	longitudinal wave speed ms^{-1}
PMMA	2700
polyethylene	2000
polystyrene	2350
PVC	2300
polyvinylidene chloride	2400
PZT	4800
Quartz	5720
oil	1400-1800
water	1500

FLAW DETECTION AND IMAGING

To carry out flaw detection thoroughly the surface of a sample is scanned by an ultrasonic transducer in a raster similar to that of a television screen. A plot of intensity of the reflected waves as a function of position of the transducer gives a map of the sample in which interior flaws show up clearly since the reflected wave amplitude from the impedance mismatch will be greater than that reflected from the back surface of the sample. Flaw detection is normally carried out with the sample and transducer immersed in a suitable liquid, often water, and with the transducer movement under automatic control. In some systems the transducer is fixed and the sample moved relative to the transducer. Care must of course be taken to maintain a constant distance between the transducer and the sample surface and to arrange that the raster pattern gives complete coverage of the sample. Transmission as well as reflection modes can be used in flaw detection and in this case it is the greater attenuation of the ultrasonic pulses due to reflection and scattering that indicates the presence of flaws and defects. Sophisticated modern systems make use of a fixed array of transducers and the scanning is performed electronically by means of time delays and phase shifts applied to the signals produced by the individual transducers.

Scanning acoustic microscopy³ is an extension of the scanning flaw detection technique which enables images of the interior of samples to be obtained at resolutions as low as tens of nm, although μm resolution is commonly used. Commercial scanning acoustic microscopy instruments are now available which form a very valuable adjunct to optical microscopes. Acoustic microscopy essentially images changes in elastic constants so that it can provide images where there is no optical contrast and an optical image could not be obtained without the use of staining techniques. Comprehensive descriptions of these techniques are given in references 1-3 and reference 4 is a journal

in which articles describing specific applications of ultrasonic techniques can be found.

REFERENCES

1. Blitz, J and Simpson, G. (1996) *Ultrasonic Methods of Non-destructive Testing*, Chapman and Hall
2. Szilard, J. (1982) *Ultrasonic Testing*, Wiley
3. Briggs, A. (1985) *An introduction to scanning acoustic microscopy*, Oxford University Press
4. *Ultrasonics*, Iliffe Industrial Publications

58: Viscoelasticity

G M Swallowe

INTRODUCTION

It is normal when considering the tensile behaviour of engineering materials to describe them in terms of an elastic modulus, which relates stress linearly to recoverable strain, and a yield stress, which quantifies the maximum stress that can be applied before plastic (permanent) deformation occurs. Alternatively a brittle fracture stress, when fracture occurs before plastic deformation commences (see **Stress and Strain**), may be quoted in addition to a modulus. There may be variations in these quantities with **strain rate** and temperature but the behaviour of most materials is adequately described in this simple manner. Exceptions do of course occur such as the creep of metals at elevated temperatures or the behaviour of glasses. The distinguishing feature of polymers is that at virtually all temperatures they do not conform to this simple model of material behaviour and **creep** is observed. Polymer creep is however different from creep in metals since metallic creep is not recoverable on removal of the load. Polymer behaviour can be modelled by the combination of linear elastic elements (springs) and viscous elements and hence is termed viscoelasticity (see **Polymer Models**).

The difference between viscoelastic and 'normal' response to an applied load is illustrated in Figure 1. Figure 1a illustrates the loading cycle. Figure 1b represents the response of a brittle elastic solid. Provided the load does not exceed the fracture stress the material 'instantaneously' strains to an amount given by $\epsilon_0 = \sigma/E$ where E is Young's modulus and immediately recovers on removal of the load. Should the strain be such that the fracture stress be exceeded during loading fracture will occur (point F). Figure 1c illustrates the case of a strain hardening elastic-plastic material. Application of the load leads to a strain consisting of the sum of an elastic deformation ϵ_e and a plastic deformation ϵ_p . Since the material hardens with increasing strain, plastic straining will stop when the applied stress equals the new (increased) yield stress. Figure 1d shows viscoelastic response. An initial rapid increase in strain (instantaneous elastic response) ϵ_e quickly gives rise to a strain-time curve with a slope which decreases with time but strain continues to increase continuously during the length of time the load is applied. This strain is composed of both a delayed elastic strain and a viscous flow component.

In a polymer the instantaneous strain is due to bond stretching and bending and the delayed elastic response to processes such as chain uncoiling. The viscous flow is attributed to chains slipping past each other. For most solid polymers the total strain tends to a limiting value ϵ_u and the slope of the curve eventually becomes zero. Unloading leads to a rapid recovery of the instantaneous elastic strain and slower recovery of the delayed strain. The viscous flow component will remain. In the case of solid polymers the viscosity is so high that, except for amorphous polymers above the **Glass Transition** temperature the viscous component can be neglected. The viscous

component can be neglected entirely for cross linked and highly crystalline polymers.

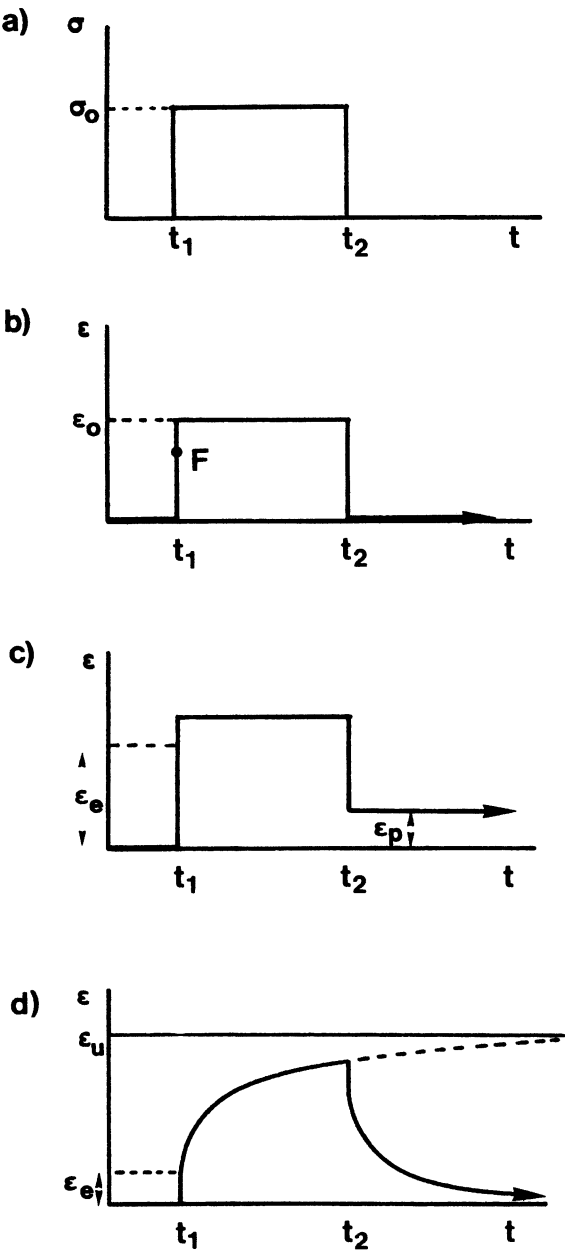


Figure 1: a) Stress σ_0 applied for a time t_1 to t_2 . b) Response of a brittle elastic solid. c) response of an elastic-plastic solid. d) Response of a viscoelastic solid.

LINEAR AND NON LINEAR VISCOELASTICITY

Because of their viscoelastic behaviour an elastic modulus has little meaning for a polymer except as a description of strain under short term loading. Instead it is usual to describe their behaviour in terms of a compliance $C(t, T)$ which is a function of time and temperature $C(t, T) = \epsilon(t)/\sigma$ (see **Creep and Measurement of Creep**). If a plot of stress against strain is constructed at a fixed temperature results similar to those illustrated in Figure 2 are obtained. Samples of elastic material loaded to a variety of stresses will produce the same strain no matter how long the load is applied for. A linear viscoelastic material will produce a linear stress strain curve provided that measurements of strain are made at precisely the same time after application of the load in each case. However measurements at a greater time will produce larger strains for the same load. A non linear viscoelastic material does not produce a linear stress strain curve for any fixed loading time. There are many models (**Polymer Models**) which can be used to accurately describe linear viscoelastic behaviour however non linear viscoelasticity is not easily treated and only in relatively recent years have theories emerged. In general polymers are linear viscoelastic materials for small strains and short times (up to $\sim 0.3\%$ strain and 100 seconds) and non linear at higher strains.

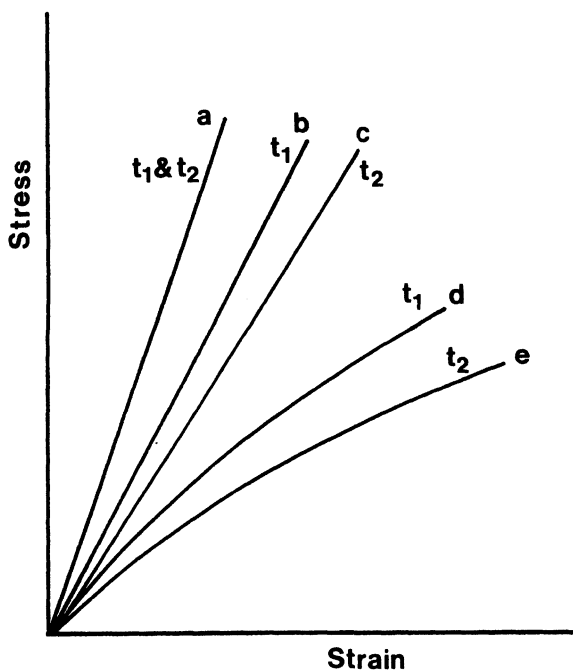


Figure 2: Stress strain behaviour of a) an elastic solid loaded for times t_1 and t_2 . b) and c) a linear viscoelastic solid loaded for times t_1 and t_2 . d) and e) a non linear viscoelastic solid loaded for times t_1 and t_2 . In all cases $t_2 > t_1$.

DYNAMIC ASPECTS

In a situation where the load is oscillating, such as might occur in a rotating shaft, the time dependence of strain will mean that the amount of strain reached during any loading part of the cycle will depend on the loading duration. With reference to Figure 1d it can be seen that a short loading time will elicit just the instantaneous elastic response while a long loading time will produce the full (recoverable) viscoelastic strain. Intermediate cyclic loading times (of the order half the time of loading of Figure 1d) will not be sufficient for recovery to occur before the next cycle begins. The compliance will therefore be frequency dependent and will change in value as the load cycling frequency passes through the relaxation time (see **Relaxations in Polymers**) of the visco elastic response (Figure 3). Viscous damping will also be greatest at this frequency leading to a maximum in energy absorption by the polymer i.e a maximum in the loss factor.

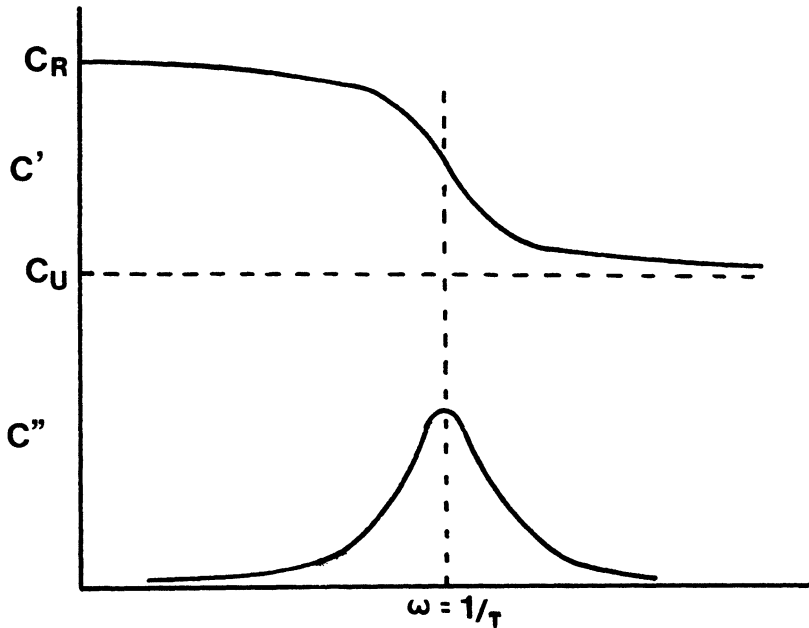


Figure 3: Values of, C' (upper trace), and C'' (lower trace), as a function of loading frequency ω .

Since the strain $\epsilon = \epsilon_0 \exp(i\omega t)$ will oscillate at the same angular frequency ω as the applied stress $\sigma = \sigma_0 \exp(i\omega t + \delta)$ but with a phase difference δ between stress and strain we can write the compliance as a complex number $C^* = C' - iC''$ where C' is the real or measured compliance and $i = \sqrt{-1}$. If we consider the high frequency case where only the instantaneous elastic response occurs then $C' = C_U$ the unrelaxed compliance whereas at low frequencies $C' = C_R$ the relaxed compliance. Using this terminology it can be shown that¹

$$C' = C_U + \frac{C_R - C_U}{1 + \omega^2 \tau^2} \quad (1)$$

$$C'' = \frac{(C_R - C_U)}{1 + \omega^2 \tau^2} \omega \tau \quad (2)$$

where τ is the relaxation time associated with the viscoelastic process.

It can be seen that for high frequencies $C' = C_U$ since $\omega^2 \tau^2$ will be large and at very low frequencies $C' = C_R$ since $\omega^2 \tau^2 \ll 1$. A plot of C'' against ω which represents the viscous loss reveals peaks in the region of $\omega = 1/\tau$.

Practical aspects of viscoelasticity are well treated in the texts by Crawford¹ and McCrum et al² and a good presentation of the present state of knowledge in the text by Haddad³.

REFERENCES

1. Arridge, R.G. (1975) *Mechanics of Polymers*, Clarendon Press, Oxford
2. Crawford, R.D. (1987) *Plastics Engineering 2nd edition*, Pergamon
3. McCrum, N.G., Buckley, C.P. and Bucknall, C.B. (1997) *Principles of Polymer Engineering 2nd edition*, Oxford University Press
4. Haddad, Y.M. (1995) *Viscoelasticity of Engineering Materials*, Chapman and Hall.

59: Wear

B. J. Briscoe and S. K. Sinha

Wear is the process of physical mass attrition from the surface of a material when in dynamic contact with another material; chemical attrition may also occur but this is usually termed corrosion. There can be two general types of wear situations; mild wear or slow mass attrition and catastrophic wear or scuffing. The wear of polymers, like all wear processes, is an extremely complex phenomena as a number of mechanisms operate during any surface interaction process¹. Here, we will discuss wear in simple sliding processes where a polymer surface interacts with a hard surface; wear may occur in rolling contacts due to subsurface fatigue. Because of the rather distinct surface and subsurface deformation mechanisms dominating the wear process for polymers the wear mechanisms in polymers is often separated into two classes; cohesive wear and interfacial wear. Cohesive wear results from surface and subsurface deformations caused by the harder asperities of the counterface. Abrasion and fatigue wear processes are termed as cohesive wear. In interfacial wear, mass removal takes place primarily at the surface. Adhesion is the process responsible for interfacial wear (see **Friction and Adhesion of Elastomers**). In the case of polymers there are (by most agreement) three principle types of wear processes: abrasive wear, fatigue wear and adhesive wear. In a process where the interfacial temperature rise is considerable, wear may take place by thermal melting and a chemical degradation of the polymer leading to seizure and catastrophic failure. Wear process for polymers, as indeed is the case for metals and ceramics, are very sensitive to the environmental conditions such as humidity and the chemical nature of the environment.

Friction produces heat and for polymeric systems this may be a major limitation upon the practicality of polymeric contacts. It is for this reason that is not advisable, as a matter of practice, to slide polymers on themselves and against substrates of low heat capacity and thermal conductivity. In some applications, for example brakes and clutches, the need for effective heat dissipation is the central concern.

ABRASIVE WEAR

Abrasive wear occurs when a polymer surface interacts with hard asperities of an another surface (metal or ceramic). Abrasion takes place by cutting or machining. For the abrasive wear of polymers, Ratner² proposed the following correlation:

$$\frac{V}{L} \propto \frac{\mu W}{H.S.e} \quad (1)$$

where V is the total volume of material removed L is the total sliding distance, μ is the coefficient of friction, W the normal load and H , S and e are the hardness, fracture

strength and elongation to fracture of the polymer respectively. V/L is considered as the wear rate of the material. The significance of the parameter $1/S.e$ has been described by Lancaster³.

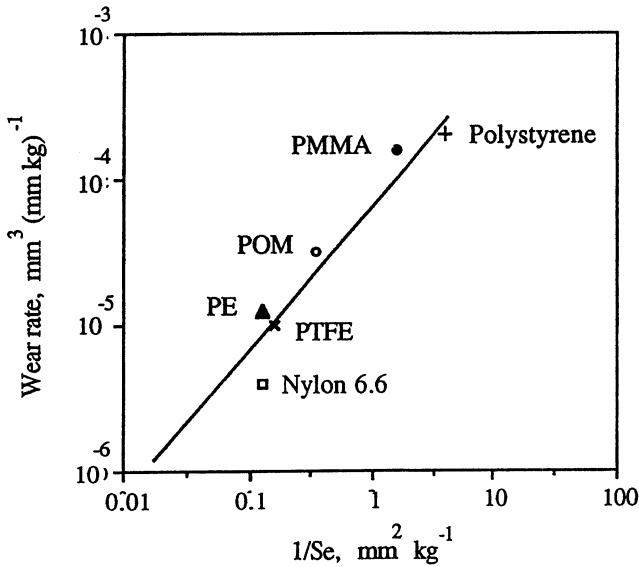


Figure 1: Correlation between wear rates of polymers and the reciprocal of the energy parameter $S.e$. The wear rates refer to single traversals over a rough steel surface (c.l.a. = 1.2 mm) and the results show that all the data lie close to a single curve.

Figure 1 shows variation of wear rate of polymers as a function of $1/S.e$. Lancaster suggested that the product $S.e$ is proportional to the work required to complete the process of producing a wear fragment although by common admission this is now regarded as a gross oversimplification; nevertheless the correlation is an effective means to ranking polymers for their abrasion resistance.

FATIGUE WEAR

Fatigue is an important polymer wear process. Although fatigue is the process of crack initiation and propagation, Ratner and Lura² have suggested that in the wear of polymers thermal softening and some other forms of weakening processes leading to failure may also be regarded as fatigue. Fatigue wear leads to the removal of the material in chunks or flakes and in many cases the cracks initiate from an inclusion in polymer such as particles and fibers. As a result of the stress and thermal effects the wear rate has been proposed to follow the relationship²

$$\text{Wear Rate (volume/unit distance)} \propto \exp (-[u_0 - kW] / RT) \quad (2)$$

where u_0 is an "activation" energy, W the normal load and k , R and T are Boltzman's constant, gas constant and absolute temperature respectively. The logical conclusion of equation (2) is that the wear rate of polymers is related to its resistance to thermal softening and degradation. A structural change in the polymer, due to the frictional thermal energy, which improves the parameter $1/S.e$ will increase the wear resistance of the material. Figure 2 shows variation of the wear rate as a function of temperature for some polymers. The data show that for a few polymers the wear rate decreases with initial temperature rise and subsequently the wear rate increases dramatically indicating a catastrophic failure due to melting or thermally induced chemical reaction (e.g. oxidation).

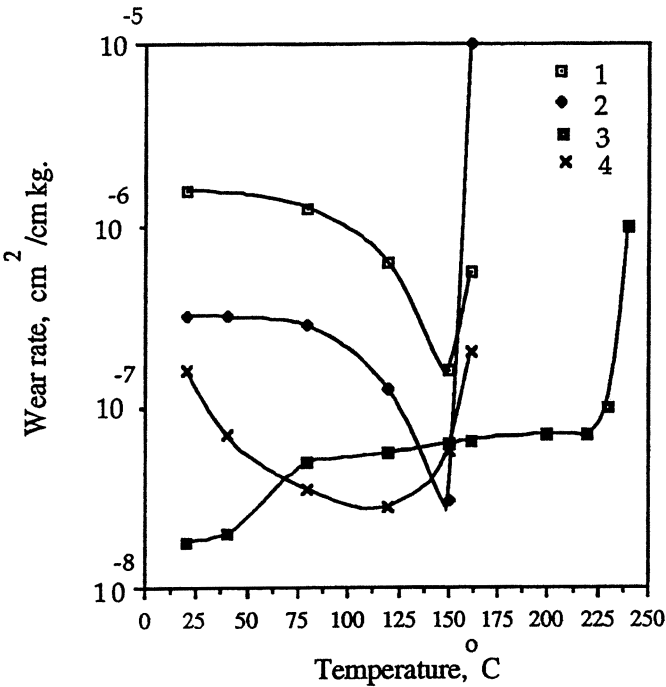


Figure 2: Temperature dependence of the wear rate for different polymers (after ref. 3). 1, PMMA; 2, polyformaldehyde; 3, Nylon 6.6; 4, polypropylene.

For elastomers wear takes place either due to abrasion by sharp needle like asperities on the counterface or by a process of crack initiation and propagation on the surface and subsurface. High friction leads to large tensile stresses on the surface of the elastomer and after repeated action of the tensile loading and unloading cracks nucleate at the surface and subsurface regions. Large hysteresis loss processes in elastomers is also a cause of wear due to heating and softening effects.

ADHESIVE WEAR

Adhesive wear is enhanced in a polymer when the interfacial strength between the polymer and the counterface is stronger than the shear strength of the bulk of the polymer. Under such situation lumps of polymer are transferred to the counterface resulting in heavy wear. Adhesive wear takes place only when the hard counterface is rather smooth (centre line average less than $0.05\text{ }\mu\text{m}$) giving high area of true contact between the two interacting surfaces. In such process a running-in period occurs before a steady state situation of wear is achieved. The wear rate in the running-in period is usually higher than in the steady state. In some cases the wear rate depends linearly upon the normal load (as shown in Figure 3) which is consistent with the Archard equation; $Q=KW/H$, where Q is the wear volume per unit sliding distance, W is the applied normal load, H is the hardness of the softer material and K is called the wear coefficient. The adhesive wear is greatly influenced by the rise in temperature of the polymer above the glass transition temperature (Figure 4).

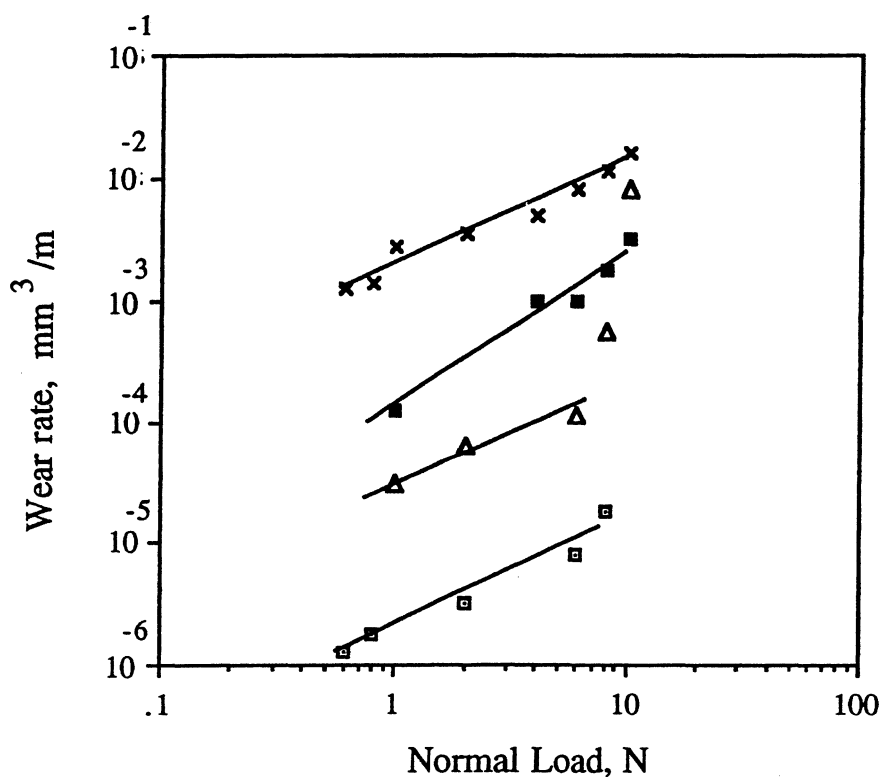


Figure 3: Wear rate as a function of normal load for selected load range (after ref.4). The wear rate varies linearly with the normal load in this load range. X PTFE, ■ PMMA, Δ Nylon 6, □ LDPE.

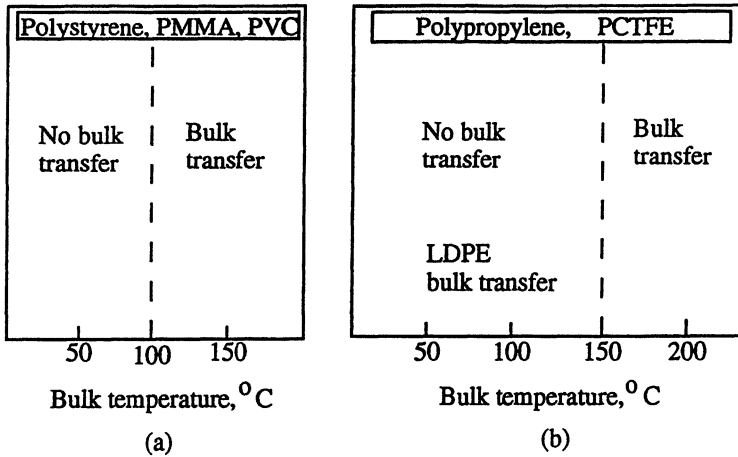


Figure 4: Slow-speed sliding of polymer over a clean, smooth glass surface. (a) amorphous polymers and (b) semicrystalline. Bulk transfer of the polymer at higher temperatures leads to adhesion and high wear rate.

EFFECTS OF TRANSFER FILM FORMATION

A large number of polymer interactions with metal surfaces result in the formation of transfer films on the counterface. This polymer film has a strong role to play in polymer friction and wear. There are primarily two phenomena occurring due to the formation of transfer films and they are changes in the roughness of the counterface (Figure 5) and the adhesive interaction of the polymer with the counterface. The transfer film may also significantly reduce the heat transfer properties of the interface; this is important in brake systems. Depending upon the type of polymer the formation of a transfer film can either increase or decrease the wear rate. Lancaster³ suggested that transfer films from polymers with high elongations, such as PTFE, polyamides, polyolefins etc. are beneficial and reduce the wear rate, whereas those from less ductile polymers, epoxies, polyesters, polystyrene, PMMA etc. are detrimental and increase wear. This action of the transfer film or 'third body' as it is sometimes termed in polymer tribology complicates any attempt to relate the bulk mechanical properties of polymers to the wear rate. The formation of transfer film facilitates in reducing the wear of polymer composites (particle or fiber filled). This is mainly because of the increased mechanical properties (stiffness, strength etc.) and thermal conductivity of the bulk of the polymer composite in comparison to the shear strength of the transfer film which is mainly the virgin polymer. Figure 6 shows a scanning electron micrograph of a polymer composite surface slid against a steel surface. The photograph shows a steady state situation when the polymer films on the counterface and the composite form and flow plastically giving rise to low friction and low wear rate.

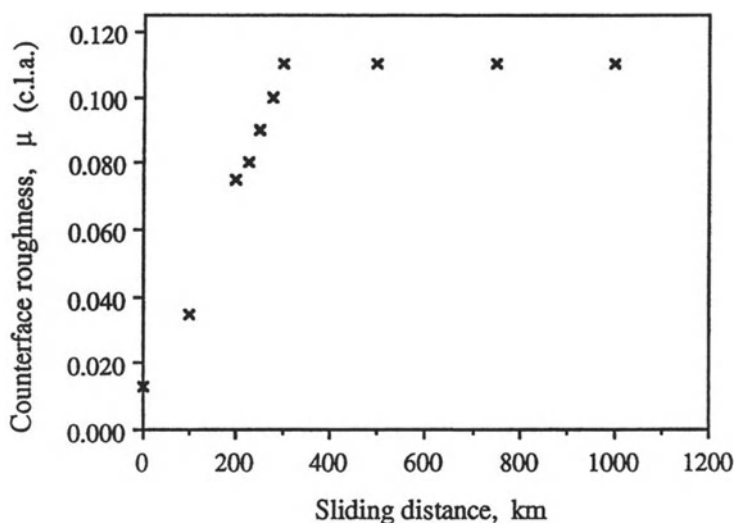


Figure 5: Countersurface roughness versus sliding distance for ultrahigh molecular weight polyethylene pin sliding against a dry stainless steel surface (after ref. 6). Normal load = 25 N, sliding velocity = 0.24 ms^{-1}

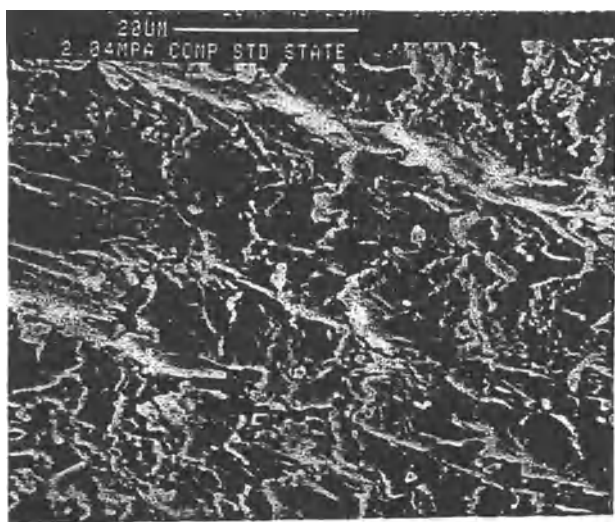


Figure 6: Scanning electron micrograph of phenolic resin - aramid fibre composite slid against steel. The figure shows the presence of a plastically deformed transfer film on the composite surface.

TESTING METHODS

Many different types of geometries have been adopted for sliding wear tests. Figure 7 shows some geometries which have been employed. By far the most common is the pin-on-disc configuration where a pin of one material (generally the test piece) is slid against the disc of another usually hard material. The friction force is measured by recording the force experienced by holding the pin stationary at one point while the disc is rotating. The wear rate of the pin can be measured either by monitoring the change in the length of the pin with sliding distance using a linear variable displacement transducer (LVDT) or by measuring the weight loss of the pin. It is also possible to measure the wear rate of the disc by plotting a profile of the wear track and assuming that same amount of the material has been removed all along the diameter of the track. In polymer friction and wear tests, it is a general practice to slide the polymer pin against a hard surface. For such cases, the disc does not generally wear and instead a polymer film is coated on the wear track of the disc as the sliding progresses. The choice of the geometry for friction and wear tests depends mostly upon the actual process which the test seeks to simulate. For example, to simulate the process of wear and friction for brake material for automobiles a pin on disc geometry is suitable whereas to simulate the action of bones in human femoral joints a reciprocating bob-in-cup or a reciprocating pin on plate geometry would be most appropriate.

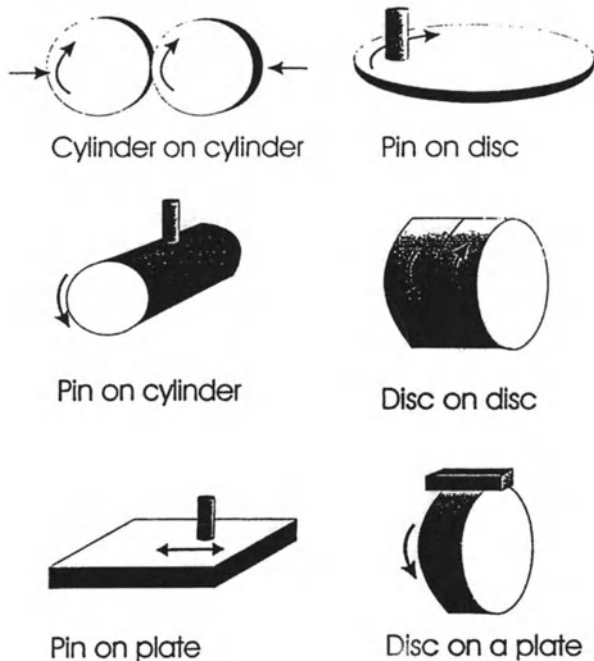


Figure 7: Sliding friction and wear test geometries.

REFERENCES

1. Briscoe, B.J., (1981) *Tribology International*, **14**, 231-243
2. Ratner, S.B. and Lure, E.G. (1966) *Dokl. Akad. Nauk. SSSR*, **166** (4), 909
3. Lancaster, J.K., (1969) *Wear*, **14**, 223
4. Evans, D.C. and Lancaster, J.K. (1979) in *Wear, Treatise on Materials Science and Technology*, Academic Press, **13**, 85-139
5. Briscoe, B.J. and Tabor, D. (1978) in *Surface properties of polymers* (eds. D. Clark and J. Feast), John Wiley
6. Atkinson, J.R., Brown, K.J. and Dowson, D. (1978) *Trans. ASME*, **100**, 208

60: X-Ray Scattering Methods in the study of Polymer Deformation

Athene M Donald

INTRODUCTION

Traditionally X-ray methods have been used to study deformation via *post mortem* studies, that is to say deformation has been allowed to proceed and subsequently the X-ray analysis is carried out. More recently the development of high intensity synchrotron sources, with X-ray fluxes several orders of magnitude greater than achievable with a conventional laboratory based X-ray source, have permitted the development of *in situ* techniques. In such experiments the X-ray scattering patterns are collected during the deformation, allowing a much closer examination of the correlation between changes in the scattering and the load-extension or **stress-strain** curves to be obtained.

X-ray scattering can be divided into two angular ranges. X-ray diffraction is associated with the wide-angle (WAXS) pattern. Because of the inverse relation between scattering angle and actual distance, this angular range corresponds to interatomic spacings. If the deformed polymer is **crystalline**, then the periodicities associated with the crystallinity will show up in the WAXS pattern. Conversely small angle X-ray scattering (SAXS) corresponds to larger distance scales. Typically the long range packing of lamellar structures will scatter into this angular range, as will any voids or crazes (see **Crazing**) that may form during deformation.

WIDE ANGLE X-RAY SCATTERING

Deformation may have several effects on the crystal structure and hence on the diffraction pattern, and exactly what is observed will clearly also depend on the initial polymer morphology (for instance whether polycrystalline, as for most commercial materials, or single crystal; whether isotropic or pre-oriented by some processing route). It may cause orientation of an initially isotropic material - in which case the isotropic rings visible in the starting diffraction pattern will change to arcs, whose extent is determined by the extent of orientation; it may change the orientation of an initially oriented material, depending on the relationship between the orientation axis and principle axes of deformation; finally it may change the morphology/crystal structure completely. Examples of this latter phenomenon may be found in the deformation of polyethylene which may both undergo a change in crystalline packing symmetry (from orthorhombic to monoclinic, as determined from the diffraction pattern) and/or form a fibrillar structure from an initially spherulitic texture. In the fibrillar structure all the

chains in the crystals are basically aligned. As an example of a careful analysis of how information can be extracted from WAXS experiments, the reader is referred to reference 1.

SMALL ANGLE X-RAY SCATTERING

Most crystalline polymers form lamellae. The long range periodicity associated with the lamellae (typically a few tens of nm, but it varies depending on processing conditions and in particular the temperature at which the crystals form), can be determined from the SAXS patterns. The lamellae are frequently disrupted during deformation, causing either changes in the lamellar spacing (if separation of the interlamellar amorphous material occurs for instance) or the loss of the peak associated with the spacing completely if the lamellae stacks are destroyed. Additionally, in tension but not in compression, voids frequently form as the lamellae separate completely. Such void scattering is very strong and will in general dominate the SAXS patterns.

For glassy polymers there is no initial scattering (other than from random heterogeneities), but upon tensile deformation a specific mode of deformation known as **crazing** may occur as a precursor to cracking. Crazes consist of a void-fibril network, with the fibrils being typically 6-10 nm wide and spaced about 25 nm apart. These dimensions mean that crazes will also scatter in the angular range of the SAXS pattern, and it is possible to quantify the extent of crazing from such scattering patterns². Since crazes grow perpendicular to the tensile axis (with the fibrils aligned along the tensile axis), such scattering will also be oriented perpendicular to the tensile direction. There will be a modulation in intensity along the scattering streak, from which the fibril dimensions can be determined. Additionally the sharp craze/undeformed polymer interface gives rise to a so-called anomalous scattering peak along the tensile axis, so that crazed samples give rise to a cross in the SAXS pattern.

SYNCHROTRON STUDIES

This rather new field of research has so far had only limited application in the area of polymer deformation. Its importance can be expected to grow, because of the power of being able to record scattering patterns simultaneously with load-extension curves. Both small and wide angle X-ray scattering may, at suitable sources and beamlines, be recorded simultaneously. The ability to correlate changes in the scattering with a particular part of the loading history will help to elucidate deformation mechanisms. Since the flux of X-rays is so high at a synchrotron source, even impact conditions can be followed in real time³. For instance, in the case of initially isotropic polyethylene, this approach has been able to demonstrate that the onset of the martensitic transformation i.e. when the monoclinic phase first appears in the WAXS pattern during tensile deformation can be associated with the yield point⁴. An additional advantage of this

approach is that, since the patterns are recorded whilst straining is occurring, there is no possibility that molecular or stress relaxation has occurred as may take place when only *post mortem* studies are carried out.

REFERENCES

1. Bartczak, Z., Argon, A.S. and Cohen, R.E. (1992) *Macromolecules*, **25**, 5036-5053.
2. Brown, H.R. and Kramer, E.J. (1981) *J. Macromol. Sci. Phys.*, **B19**, 487-522.
3. Bubeck, R.A., Buckley, D.J., Kramer, E.J. and Brown, H.R. (1991) *J. Mat. Sci.*, **26**, 6249-59.
4. Butler, M.F., Donald, A.M., Bras, W., Mant, G.R., Derbyshire, G.E. and Ryan, A.J. (1995) *Macromols.*, **28**, 6384-95.

Appendix 1: Further Reading - Selected Bibliography

BOOKS

There are numerous books which describe the properties of polymers and many of the articles in this volume refer to books that are particularly relevant to the article. Listed below is a selection of volumes of a more general nature covering all aspects of polymer mechanical properties and testing.

Allen, G., and Bevington J. C. eds. (1989) *Comprehensive Polymer Science*, Pergamon. Seven volume encyclopedic work by a large number of authors covering the synthesis, characterisation, reactions and applications of polymers.

Arridge, R. G. C. (1975) *Mechanics of Polymers*. Oxford University Press.
A mainly theoretical treatment linking the mechanical behaviour of polymers to their fundamental properties.

Bassett, D. C. (1981) *Principles of Polymer Morphology*, Cambridge University Press.
Good account of polymer morphology.

Brandrup, J., Immergut, E. H., Grulke, E. A., (1998) *Polymer Handbook 4th ed.*, Wiley
A comprehensive reference book containing tables of information on most aspects of polymer science.

Brown, R.P ed. (1981) *Handbook of Plastics Test Methods 2nd ed.*, George Godwin.
Contains a comprehensive and condensed description of a large range of tests covering all aspects of polymer properties together a full bibliography.

Brown, W. E. and Schmitz J. V. eds. (1965, 1966, 1967, 1969) *Testing of Polymers Volumes 1,2 3,4*. Interscience Publishers.
A four volume series with volumes containing a useful series of chapters covering most aspects of polymer testing.

Cowie, J. M. G. (1991) *Polymers: Chemistry and Physics of Modern Materials*, Blackie.
A good general introductory text covering both the chemical and physical properties of polymers.

Crawford, R. J. (1987) *Plastics Engineering*, Pergamon.
Undergraduate level text covering both the mechanical properties and processing of

polymers with many worked examples.

Haward, R. N. and Young R. J. eds. (1997) *The Physics of Glassy Polymers 2nd edition*, Chapman and Hall.

An advanced volume with chapters on aspects of the physics and mechanics of glassy polymers by a range of expert authors.

Ives, G. C., Mead, J. A. and Riley, M. M. (1971) *Handbook of Plastics Test Methods*, Butterworth.

A comprehensive description of a large range of plastics tests with references. Very similar to the volume edited by R. P. Brown (above).

Kinloch, A. J. and Young, R. J. (1983) *Fracture Behaviour of Polymers*, Applied Science.

Easy to read undergraduate level text.

Kroschwitz, J. I., Mark, H. F., Bikales, N. M., Overberger, C. G. and Menges, G. eds. (1985) *Encyclopedia of Polymer Science and Engineering*, Pergamon.

Eighteen volume (+ supplements) multi-authored encyclopedia covering all aspects of polymer science.

McCrum, N.G., Buckley, C. P. and Bucknall, C. B. (1997) *Principles of Polymer Engineering 2nd ed.* Oxford University Press.

An excellent and comprehensive undergraduate level text covering all aspects of polymer mechanical properties.

Treloar, L. R. G. (1975) *The Physics of Rubber Elasticity 3rd ed.*, Oxford University Press.

Classic and authoritative text on the mechanical behaviour of rubbers.

Turner S. (1983) *Mechanical Testing of Plastics 2nd ed.*, George Godwin.

Concentrates mainly on the theoretical aspects of testing methods and contains many useful critiques of test methods.

Thomas, E. L. (1993) *Materials Science and Technology Volume 12: Structure and Polymers of Polymers* (series editors Cahn, R.W., Haasen, P., Kramer, E.J.) VCH Publishers.

A readable graduate level text containing a wide range of contributions describing polymer structure-property relationships.

Ward, I. M. (1983) *Mechanical Properties of Solid Polymers 2nd ed.*, Wiley.

Excellent graduate level text with comprehensive coverage of mechanical properties.

Ward, I. M. and Hadley D. W. (1993) *An Introduction to the Mechanical Properties of Solid Polymers*, Wiley.

Essentially an updated but less advanced version of the volume by I. M. Ward.

Williams J. G. (1984) *Fracture Mechanics of Polymers*, Ellis Horwood.

An advanced but extremely useful volume with comprehensive coverage of the theoretical aspects of polymer fracture.

JOURNALS

There is a plethora of journals covering all aspects of polymer science. Those listed below are merely a personal selection of those to which I would first turn for recent work on polymer mechanical properties or testing methods. Articles relevant to polymer mechanical properties and testing appear in a much wider range of journals than those listed.

Advances in Polymer Science

Colloid and Polymer Science

European Polymer Journal

High Performance Polymers

International Journal of Adhesion and Adhesives

International Journal of Engineering Science

International Journal of Polymer Analysis and Characterization

Journal of the American Chemical Society

Journal of Applied Polymer Science

Journal of Macromolecular Science: Part B, Physics

Journal of Materials Science

Journal of the Mechanics and Physics of Solids

Journal of Polymer Science: Part B; Polymer Physics

Journal of Strain Analysis for Engineering Design

Macromolecules

Materials Science and Technology

Measurement Science and Technology

Philosophical Magazine A

Polymer

Polymer Engineering and Science

Polymer Testing

Proceedings of the Royal Society of London

Progress in Colloid and Polymer Science

Review of Scientific Instruments

Transactions of the ASME

Wear

The proceedings of the triennial International conferences on *Deformation Yield and Fracture of Polymers* published by The Institute of Materials are also a very good source of up to date material.

RAPRA Technology Ltd. produce a series of handbooks and reports on all aspects of polymer technology.

Appendix 2: Glossary

Affinity The extent of reactivity of a functional group with another reagent.

Anelasticity Time dependent elasticity in which strain lags behind applied stress.

Atactic Polymer in which side groups are arranged at random along the main carbon chain.

Bimodal Polymer in which the molecular weight distribution (number of molecules with a given molecular weight) peaks at two values of molecular weight.

Blending Mixing compatible polymers to produce a material with improved properties.

Calendering Process for producing plastic film and sheet by squeezing the material through two counter-rotating cylinders.

Centre line average Method of quantifying the roughness of a surface. It is a measure of the deviation from the centre line (average height) of the surface of the hills and valleys making up the roughness.

Characteristic Ratio A measure of the expansion of a polymer in dilute solutions.

Constitutive Equation Mathematical model of the flow stress of a material as a function of strain, strain rate, temperature etc. which enables its behaviour to be predicted.

Copolymers Polymers formed from the reaction of more than one type of monomer.

Crosslinks Bonds which join different polymer chains.

Daltons Unit used to express molecular weights, 1 Dalton = 1.66×10^{-24} grams.

Drawability A measure of the ability of a material to be extended in tension without fracture.

Draw Ratio The ratio of the 'drawn' or extended length to the original length.

Elution Washing a chromatography column with solvent to remove molecular species.

Elongation to fracture (break) The increase in the gauge length of a material just before fracture relative to the original gauge length. It is usually expressed as a %.

Elution Volume The volume of solvent passed through a chromatography column required to elute a particular molecular species.

Flory-Fox equation Relationship between the viscosity η of a polymer solution and the molecular weight M . In a theta solvent $\eta = KM^{0.5}$ with $K = \Phi(r^2/M)^{3/2}$, r the molecular radius and Φ a constant. The equation can be modified for use in non-ideal solvents.

Fractionation Separation of a polymer into fractions consisting of whole molecules of more similar structure (tacticity, molecular weight etc.) than the original sample.

Gel-Spinning Technique to produce highly oriented polymer films by using a solvent to swell the polymer and form a gel. The gel is then oriented by spinning and drawing.

Grafting Method of polymer synthesis in which a polymer backbone consisting of one type of monomer has side branches formed from another monomer.

Hertzian stress Elastic stress formed under an indenter calculated using the Hertz theory. Indenting a flat surface of modulus E_2 with a sphere of modulus E_1 and radius r using a load W leads to a contact area of diameter $2a$ with

$$a = 1.1 \left(\frac{Wr}{2} \left[\frac{1}{E_1} + \frac{1}{E_2} \right] \right)^{\frac{1}{2}}$$

The mean stress is given by $W/\pi a^2$.

Homopolymers Polymers containing only one type of repeat unit.

Isocratic elution Elution with a mixed solvent whose composition is kept constant during elution.

Isotactic Linear substituted polymer in which all the substituent groups lie on the same side of the carbon chain.

Lamellae Polymer crystals are in the form of lamellae, thin sheets of thickness $\sim$ nm but much larger lateral dimensions.

Mark Houwink equation For a given polymer/solvent system viscosity η and molecular weight M can be related by $\eta = K_v M^v$ where the constants K_v and v are determined by calibration.

Necking In a tensile test during plastic deformation the cross sectional area may reduce faster in a short region of the sample than in the rest of the length. This region is called a 'neck'.

Orthotropic material A particular type of anisotropic material which is symmetrical with respect to three perpendicular planes e.g. a laminate consisting of layers of cross-ply polymer fibres.

Pole figures Representation by projection onto a (2 dimensional) map of the orientations of the crystallographic planes in a sample. Random orientations gives rise to rings, highly oriented samples to spots.

Polydisperse A polymer composed of a range of molecular weights.

Polymer Radius of Gyration Parameter characterising the size of a polymer random coil.

$$R_G = \frac{\sum m_i s_i^2}{\sum m_i} = \sum_i \frac{s_i^2}{n}$$

where the chain has n segments each of mass m located a distance s from the centre of gravity of the coil.

Reptation Snake like sliding motion of a polymer chain that enables it to undergo long range conformational changes.

Retention Calibration Calibration of elution volume in chromatography.

Solubility Parameter Symbol δ , a guide to the miscibility of polymers. Similar values of δ indicate good miscibility and compatibility.

Spherulites Ordered aggregations of sub-microscopic polymer crystals consisting of layers of crystalline lamellae. Spherulites have dimensions of the order of the wavelength of light.

Stereoregularity An alternative name for tacticity.

Stockmayer-Fixman equation Equation relating viscosity to molecular weight M and radius of gyration R.

$$\eta/M^{0.5} = k + 0.5BM^{0.5}\phi \text{ with } k, B \text{ and } \phi \text{ constants and } k = \phi 6^{1.5} (R^2/M)^{1.5}$$

Strain Rate Rate of deformation expressed in units of strain per second. Since strain is dimensionless (length/length) the units of strain rate are s^{-1} .

Syndiotactic Polymer in which substituent groups lie alternately on either side of the backbone chain.

Tacticity Describes the arrangement of units in the main chain of a polymer.

Telomers A polymer with typically 10-20 monomer repeat units which contains reactive groups as chain end groups. They can react to form block co-polymers.

Thermoplastic A polymer that can be softened on heating and molded to a desired shape. On repeated heating the polymer softens and can be remolded to a different shape.

Thermoset A polymer which becomes permanently hard when heated above the temperature at which crosslinks form. It cannot be melted on further heating

Theta solvent An ideal solvent in which polymer molecules are in their 'natural' unperturbed state.

Toughness A measure of the amount of work required to propagate a crack in a material.

Appendix 3: Table of Mechanical Properties

The data in the following table is drawn from a wide variety of sources including published literature, manufacturers data sheets, reference works as well as measurements made in the Loughborough Physics department. It therefore consists of representative room temperature values only and, for any specific application, readers are advised to consult manufacturers data sheets for the specific grade of the polymer of interest or to conduct measurements themselves. Numerical values of the properties obtained from different sources for nominally the same material may vary greatly and the data reproduced below attempts to cover the range of reported values while excluding extreme values that are not in line with those more generally reported.

Mechanical properties of selected polymers

Material	Density gcm^{-3}	Tensile Modulus GPa	Tensile Strength MPa	Elongation to Break %	Izod Impact Strength Jm^{-1}	Hardness Rockwell
Cellulose Acetate	1.23 - 1.34	1.0 - 4.0	12 - 110	6 - 70	100 - 450	R35 - R125
ABS	0.99 - 1.10	1.8 - 2.8	35 - 48	10 - 140	160 - 640	R90 - R110
Polyamide Nylon 6,6	1.14	1.8 - 3.3	80 - 84	60 - 300	40 - 110	R108 - 118
Polyamide Nylon 6,12	1.06	2.1	52 - 62	100 - 340	50 - 80	R95-R120
Polybutylen terephthal- ate	1.63	12	185	2	70	M93
Poly- carbonate	1.2	2.2 - 2.4	55 - 75	60 - 150	640 - 850	M80 - R125
Polyether- etherketone	1.26 - 1.32	3.7 - 4.0	70 - 100	40 - 50	60 - 85	M99 - R123
Polyether- sulphone	1.37	2.4 - 2.6	70 - 95	40-80	70 - 85	M68 - M88
High density poly- ethylene	0.94 - 0.97	0.5 - 1.4	15 - 40	15 - 800	20 - 210	~R65
Low density poly- ethylene	0.91 - 0.93	0.1 - 0.3	7 - 21	50 - 800	no break (>1000)	~R10

Material	Density gcm ⁻³	Tensile Modulus GPa	Tensile Strength MPa	Elongation to Break %	Izod Impact Strength Jm ⁻¹	Hardness Rockwell
Poly- ethylene tere- phthalate	1.3 - 1.4	2.0 - 10	40 - 150		13 - 80	M94 - R120
Polymethyl - meth- acrylate	1.17 - 1.20	2.4 - 3.3	50 - 80	2.5 - 5	15 - 32	M85 - R130
Poly- propylene	0.9	0.9 - 1.6	25 - 40	150 - 600	20 - 100	R80 - R110
Poly- styrene	1.04 - 1.11	2.3 - 4.1	30 - 90	1 - 4	10 - 25	M60 - M 90
Polytetra- fluoro- ethylene	2.1 - 2.2	0.3 - 0.8	10 - 41	250 - 600	130 - 210	D50 - D65 (Shore)
Polyvinyl- chloride	1.38 - 1.40	2.0 - 4.2	30 - 65	2 - 40	50 - 1000	R110 - R120
Polyvinyl- idene- chloride	1.63	0.3 - 0.55	19 - 100	~ 350	15 - 55	M60 - M 65
Epoxies	1.0 - 3.2	1.4 - 4.1	35 - 140	1.5 - 10	15 - 50	~M106
Polyesters unsaturated	1.1 - 1.4	2.0 - 10	40 - 150	1.3 - 3.3	30 - 500	M60 - M117

Index

- abrasive wear, 270
- accuracy, 1, 118
- adhesion, 5, 105
- adhesive wear, 273
- adiabatic shear, 10, 15
- adiabatic heating 15, 216
- affinity, 290
- alloys, 15, 20
- amorphous polymers, 17, 23, 25, 32, 34, 38, 45, 50, 53, 73, 78, 109, 119, 121, 146, 147, 163, 164, 179, 191, 194, 195, 205, 217, 225, 226, 238, 240, 250, 265, 274, 279
- anelastic deformation, 175, 178, 191, 194
- anelasticity, 290
- atactic, 290
- auxetic polymer, 135
- barreling, 246
- bending, 47, 48, 138, 209, 255, 256,
- biaxial stress, 27, 222, 224
- bimodal, 145, 290
- blends, 20, 111
- Brinell, 113, 115
- brittle-ductile transition, 40
- brittle fracture, 40, 41, 42, 71, 127, 204, 234, 235
- bulk modulus, 184, 227, 228, 241
- calendering, 290
- catastrophic failure, 13, 72, 76, 270, 272
- centre line average, 290
- chain branching, 154
- chain scission, 52, 53
- Charpy test, 59, 71
- compatibility, 20, 181, 211
- complex modulus, 43, 262
- compliance, 29, 30, 113, 116, 118, 137, 249, 267, 268
- compression, 43, 123, 167, 176, 177, 191, 222, 245, 246, 247, 279, 283
- compressive testing, 192, 245, 246
- Consider construction, 282
- constitutive equation, 85, 86, 290
- copolymers, 111, 144, 155, 248, 290
- corrosion, 53, 54
- Coulombic friction, 102
- crack extension force, 74, 96, 98, 205
- crack growth and propagation, 53, 71, 72, 73, 77, 78, 80, 130, 132, 133, 148, 204, 205, 206, 208, 209
- crack initiation, 72, 130, 271, 272
- crack opening displacement, 100
- crack resistance, 73, 145
- craze, 25, 26, 28, 53, 71, 73, 100, 148, 149, 150, 205, 206, 236, 258, 279
- crazing, 17, 25, 26, 27, 28, 149, 234, 236, 257, 258, 279
- creep, 29, 31, 47, 137, 138, 139, 187, 189, 265
- crosslinking, 41, 50, 109, 111, 165, 205, 258
- crosslinks, 290
- crystallinity, 32, 34, 35, 36, 37, 38, 55, 109, 120, 146, 147, 148, 149, 180, 258, 278
- crystallinity determination , 35
- crystallisation, 34, 37, 147
- daltons, 290
- degradation, 52, 53, 54, 55, 181, 270, 272
- density measurements, 36
- differential scanning calorimetry, 21, 36, 54, 88, 110
- diffusion, 5, 88, 148, 173
- double cantilever beam, 208, 209
- double torsion, 133, 208, 210
- draw ratio, 290
- drawability, 290

- drop test, 11, 57, 58, 66
- dropweight, 11, 12, 57, 61, 66
- ductile, 40, 71, 72, 146, 206
- Dugdale model, 100, 205
- dynamic mechanical analysis, 21, 43, 110
- elastic constants, 223
- elastomers, 5, 6, 8, 9, 114, 172, 237, 238, 248, 272
- electron microscopy, 49, 50, 51, 80
- elongation to fracture, 290
- elution, 290, 291
- energy to break, 58
- engineering strain, 141, 185, 219, 243
- engineering stress, 124, 219, 243, 244
- environmental effects, 52, 53, 181
- errors, 1, 2, 3, 37, 38, 47, 68, 86, 118
- extrusion, 88, 91
- Eyring theory, 40, 214, 215, 284
- falling weight test, 57, 58, 61, 66
- fast fracture, 71, 130
- fatigue, 75, 76, 77, 148, 271
- fatigue crack propagation, 77
- fatigue wear, 271
- fibrils, 25, 26, 28, 135, 279
- finite element, 81, 85, 86
- flaw detection, 260, 263
- flexure, 138
- Flory, 144
- Flory-Fox equation, 111, 291
- flow of molten polymers, 88
- flow stress, 14, 123, 126, 214, 215, 216, 290
- foams, 134
- force transducers, 202
- fractionation, 151, 291
- fracture, 40, 41, 42, 66, 71, 72, 73, 97, 98, 99, 100, 130, 132, 146, 204, 206, 208, 235, 256
- fracture mechanics, 59, 96, 97, 132, 148
- fracture resistance, 71, 72, 98, 128, 132, 206
- fracture toughness, 72, 97, 128, 132, 148, 205
- friction, 102, 103, 105, 179, 201, 245, 246, 270, 272, 274, 276, 283
- gel-spinning, 291
- glass transition, 21, 23, 45, 46, 109, 110, 111, 181, 196, 234, 238
- GPC, 151, 152, 153
- grafting, 291
- graph theory, 229
- group additivity, 226
- hardness, 113, 115, 116, 118, 119, 121, 270, 273
- hardness tests, 113, 115
- HDPE, 42, 146, 218, 294
- Hertzian stress, 291
- Hopkinson bar, 123, 124, 125
- hydrostatic pressure, 222
- impact, 10, 15, 66, 71, 123, 130, 257
- impact strength, 72, 127, 128, 130, 132, 147
- impact test, 10, 15, 57, 59, 61, 66, 68, 71, 127, 130, 132
- indentation, 113, 115, 119
- interfacial, 5, 6, 102, 103, 270, 273
- isothermal tests, 15
- Izod, 130, 131, 212, 294, 295
- Kelvin model, 188
- lamellae, 32, 279, 291
- LDPE, 42, 90, 273
- Mark Houwink equation, 291
- Maxwell model, 187
- melt elasticity, 90
- melt flow index, 91
- Metropolis algorithm, 156, 158, 163
- microhardness, 116, 119, 120
- miscibility, 6, 20
- models, 187
- modulus, 29, 34, 43, 44, 45, 109, 121, 139, 180, 185, 195, 196, 217, 223, 225, 227, 228, 236, 239, 241, 249, 255, 258, 261
- molecular modeling, 225
- molecular structure, 229

- molecular weight, 28, 41, 93, 143, 147, 151, 239, 240
- molecular weight distribution 143, 151
- Monte Carlo, 156, 157, 163
- necking, 282, 292
- neutron diffraction, 171
- neutron scattering, 171
- noise, 202, 203
- non elastic deformation, 174, 175, 191, 194
- nylon, 14, 38, 42, 119, 214, 218, 294
- Paris equation, 78
- PEEK, 34, 35, 119, 121, 215, 216, 218
- PET, 34, 35, 37, 42, 295
- plane strain, 12, 99, 224, 247
- plane stress, 12, 99, 224
- plastic deformation, 40, 174, 191, 214, 247, 282
- plasticisers, 179, 180, 181
- ploughing, 102, 103, 104
- PMMA, 12, 16, 34, 42, 72, 74, 107, 116, 117, 119, 121, 127, 132, 148, 175, 176, 177, 192, 193, 194, 204, 207, 209, 263, 272, 273, 274, 284
- Poisson's ratio, 134, 140, 183
- polycarbonate (PC), 14, 42, 45, 176, 294
- polydispersity, 151
- polyethylene, 30, 34, 38, 71, 90, 120, 143, 214, 263, 275, 294
- polymer melts, 88, 90
- polymethylmethacrylate (PMMA), 42, 107, 117, 119, 176, 177, 192, 193, 194, 204
- polypropylene, 30, 38, 119, 120, 121, 272, 295
- polystyrene (PS), 38, 148, 176, 263, 295
- postprocessing, 86
- preprocessing, 85
- process zone, 99
- processing, 88, 92, 93, 144
- PTFE, 42, 106, 135, 248, 273
- pure shear, 222, 283
- PVC, 42, 179, 263, 295
- random errors 1, 2
- rebound hardness, 113
- recovery, 191, 193, 265
- relaxation, 45, 187, 195, 196, 197, 268
- reptation, 292
- residual stress, 53, 54
- rheometers, 94
- Rockwell, 114, 115, 212, 294, 295
- rolling test, 107
- rubber elasticity, 237, 239
- scanning electron microscopy, 49
- semi-crystalline, 32, 34, 36, 46, 111, 147, 251
- sensors, 199, 200, 201
- sharkskin, 91
- shear bands and localisation, 10, 12, 15, 16, 18
- shear flow, 88, 91
- shear modulus, 139, 185, 223, 226, 227, 239, 252
- shear stress, 17, 91, 93, 220, 222, 252
- slow crack growth, 73, 204, 205, 206, 208, 209
- small angle scattering, 172, 279
- S-N curve, 76, 77
- solubility, 6, 181
- spherulites, 292
- standard linear solid, 188
- standards, 55, 113, 153, 211, 242
- Stockmayer-Fixman equation, 292
- strain hardening, 34, 167, 175, 265, 281
- strain rate, 15, 40, 41, 89, 214, 215, 216, 217, 257, 284, 292
- strain recovery, 191
- strain sensors, 200
- strength, 96
- stress analysis, 97
- stress intensity factor, 59, 78, 97, 205
- stress-strain, 13, 16, 89, 145, 174, 215, 216, 237, 245, 281
- structural method, 227

- structure-property relationships, 225, 233, 235, 238, 239, 240, 241
- syndiotactic, 292
- systematic errors, 1
- temperature sensors, 199
- tensile strength, 145, 146, 180
- tensile tests, 130, 242
- tension, 46, 137, 168, 235, 236, 242, 283
- thermal failure, 76
- thermal softening, 15, 16, 216, 271, 272
- thermoplastic, 25, 40, 205, 248
- thermosets, 206, 248
- time-temperature equivalence, 249
- time-to-failure, 209
- toe effect, 244, 245
- torsion, 44, 139, 208, 210, 252, 253
- torsional pendulum, 253
- toughening, 22, 128, 257, 258
- toughness, 45, 73, 96, 97, 99, 132, 148, 179, 208, 257, 258
- transducers, 199, 202, 203, 260, 263
- transfer film, 108, 274
- transmission electron microscopy, 50
- Tresca criterion, 283
- tribology, 102, 107, 274
- true strain, 124, 219, 243
- true stress, 124, 219
- Ultrasonic techniques, 260
- uniaxial test, 219, 282
- Vickers, 113, 115, 119
- viscoelasticity, 29, 30, 44, 88, 103, 185, 187, 195, 254, 265, 267, 281
- viscometer, 92, 94
- viscosity, 88, 89, 93, 144, 154, 181, 240, 291, 292
- viscous flow, 88, 92, 265
- von-Mises criterion, 283
- wear, 270, 271, 273
- wear tests, 276
- weathering, 52, 54, 55
- wide angle scattering, 172, 278
- WLF equation, 250, 251
- X-ray methods, 32, 35, 38, 278, 279
- yield criteria, 282
- yield stress, 34, 40, 120, 174, 214, 216, 236, 243, 246, 283, 284
- yielding, 26, 175, 281, 282

Polymer Science and Technology Series

1. G. Pritchard: *Plastics Additives*. An A-Z Reference. ISBN 0-412-72720-x
2. J. Karger-Kocsis: *Polypropylene*. An A-Z Reference. ISBN 0-412-80200-7
3. G.M. Swallowe (ed.): *Mechanical Properties and Testing of Polymers*. An A-Z Reference. ISBN 0-412-80170-1

61: Yield and Plastic Deformation

G. M. Swallowe

INTRODUCTION

Plastic deformation can be defined as a non-recoverable deformation which leads to a permanent 'set'. Conventionally yield occurs when a given stress, the yield point, is exceeded as illustrated in Figure 1. For most polymers the tensile yielding behaviour is better described by curve (B) in which yield is followed by a load drop in the nominal stress-strain curve and the formation of a neck which grows to fill the gauge volume at a nearly constant flow stress. This is followed by strain hardening, a rapid increase in flow stress with strain. In many cases the value of the yield point is not well defined and it is often common to quote a flow stress at a given strain. In the case of polymers, the 'permanent' deformation may decrease with time or even disappear completely if the material is heated close to T_g . This arises because of the viscoelastic nature of polymer deformation and the entropic forces which tend to relax extended chains if sufficient thermal energy is available. The resultant recovery that may take place after removal of a load is described in the article **Recovery Behaviour of Glassy Polymers**. (see also **Viscoelasticity, Stress and Strain**).

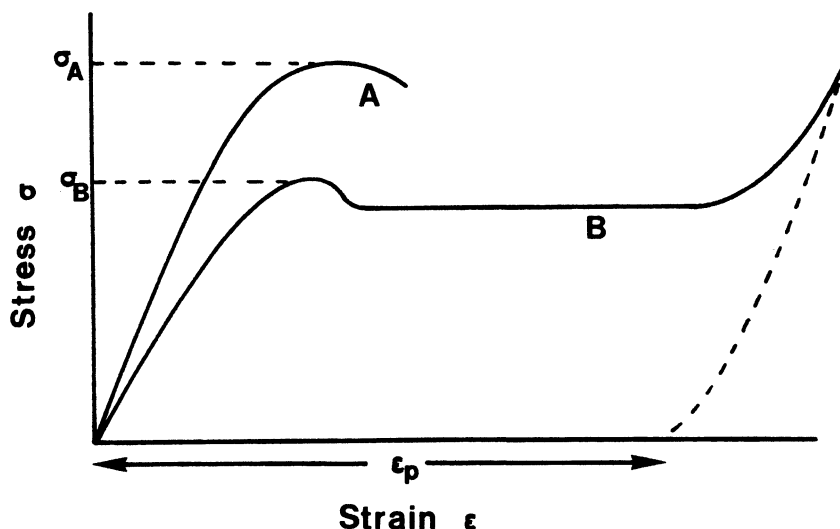


Figure 1: Schematic nominal stress - nominal strain curves for typical polymers. A: Polymer which necks but does not draw. B: Polymer which forms a stable neck and draws. Yield stresses are σ_A and σ_B , ϵ_p the plastic strain in polymer B and the dashed line the unloading curve of B.

Definition of the yield point is conventionally carried out with the assistance of Considère's construction. This involves plotting true tensile stress against nominal strain (ϵ_n) as illustrated in Figure 2. The tensile yield stress is defined by the first tangent made by a straight line drawn from $\epsilon_n = -1$ to the stress strain curve. Strain softening is said to occur if the slope of the stress strain curve becomes negative and strain hardening if the slope becomes positive after yield. Yield initiates at some point in the gauge length where the local stress is higher than in adjacent material, usually because of an imperfection or flaw leading to a slightly smaller cross sectional area and hence higher stress. Yielding will further decrease this area forming a neck. Thus in Figure 2 polymer A strain hardens but not sufficiently to form a stable neck. Necking continues and failure occurs with increasing stress. This behaviour is similar to that of ductile metals. Polymer B however has a second tangent in the Considère construction. At strains greater than that at which the second tangent touches the curve the material strain hardens at a rate greater than that required to sustain the load and therefore adjacent material to that which has already begun to neck will now yield and strain harden and the process continues along the gauge length leading to 'drawing'.

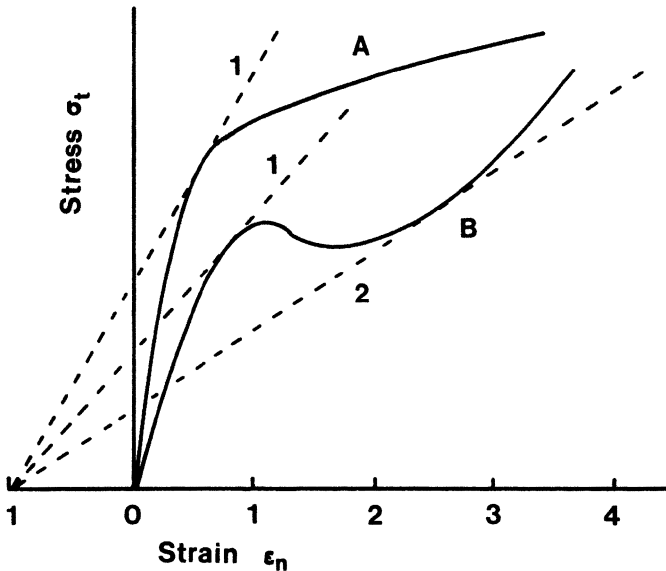


Figure 2: Considère's construction for the polymers of Figure 1. Tangents 1 indicate yield (necking stress) and Tangent 2 cold drawing.

YIELD CRITERIA

Yield criteria are designed to predict the stress conditions at which plastic deformation will commence. A uniaxial test produces a stress strain curve like the schematics of

Figure 1 and the yield criteria endeavour to make use of this information to predict when yield will occur in a multiaxial loading situation. A number of simple criteria have been developed, mainly with metals in mind, but they can, with some reservations be used for polymers.

Tresca yield criterion

The Tresca criterion simply states that yield will occur if the difference between the maximum and minimum principle stresses in the material exceeds a given value. Representing the three principle stresses as σ_1 , σ_2 and σ_3 the criterion can be expressed as

$$(\sigma_1 - \sigma_3) = 2\tau_y \quad (1)$$

where τ_y is the shear yield stress. It is evident from considering a simple tensile test in which σ_2 and $\sigma_3 = 0$ that equation 1 predicts that yield will occur when the applied tensile stress $\sigma_1 =$ the tensile yield stress $\sigma_t = 2\tau_y$.

Von Mises criterion

The Von Mises criterion is a more algebraically complex criterion that provides somewhat better predictions of yield stress than the Tresca criterion. It can be expressed as

$$[(\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3)^2]^{1/2} = \sqrt{2} \sigma_t \quad (2)$$

In the case of pure shear $\sigma_1 = -\sigma_2$ and $\sigma_3 = 0$ so $\sigma_1 = \sigma_t / \sqrt{3}$ and the yield stress in pure shear is equal to $1/\sqrt{3}$ of that in tension. A test of the criteria is their predictions of the comparative values of yield stress in tension (σ_t) and compression (σ_c). Tresca predicts that yield will occur at the same values of applied stress in tension and compression with $\sigma_t = \sigma_c = 2\tau_y$, whereas Von Mises, while again predicting that the tensile and compressive yield stresses will be the same, gives their value as $\sqrt{3} \tau_y$. For polymers it is found that the compressive yield stress is greater than the tensile yield stress and that the ratio of σ_t to τ_y is less than 2 and, in most cases, less than $\sqrt{3}$. The Von Mises criterion is therefore more useful than the simpler Tresca criterion but still does not adequately predict yield.

A further yield criterion, the Coulomb criterion, originally proposed for the slip of soils, states that slip will occur on a given plane when the shear stress τ exceeds a value given by $\tau_c - \mu\sigma_N$ with τ_c a 'cohesive' stress, μ the equivalent of a coefficient of friction and σ_N the normal stress on the plane under consideration. It can be seen that this expression will predict higher shear stresses yield stresses in compression (σ_N negative) than in tension and when combined with the Von Mises criterion can give an adequate

description of the yield process in polymers (e.g. polystyrene, PMMA). The Coulomb criterion can be rewritten as $\tau = \tau_c + \alpha P$ with P the applied pressure and α a coefficient of increase in shear stress with pressure. In fact it turns out that α is very close to μ , the coefficient of **friction** of the polymer sliding against itself. The pressure modified Von Mises criterion i.e. the Von Mises criterion in which the shear yield stress is written as $\tau_y = \tau_y^0 + \alpha P$ with τ_y^0 the normal tensile yield stress provides a good description of yield in many polymers.

$$(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 6(\tau_y^0 + \alpha P)^2 \quad (3)$$

The criteria outlined above are macroscopic continuum criteria, they provide a means to predict the stress state at which yield will occur, but do not take any account of the mechanisms by which yield occurs.

THE YIELD PROCESS

The most successful theories of yield in polymers are based on the Eyring equation in which the deformation of a polymer at a strain rate $\dot{\epsilon}$ is modeled as a thermally activated process which depends on both an activation energy ΔH and an activation volume v . It is envisaged that thermal energy enables chain segments to move within the material and that these random movements are, in the absence of stress, just as likely to occur in any direction in the material. When a stress σ is applied the movement of chain segments in the forward direction, i.e. the direction of stress, is assisted by a reduction of $v\sigma$ in the 'forward motion' activation energy and an increase of the same amount in the activation energy for chain motion in the reverse direction. This leads to the equation

$$\dot{\epsilon} = \dot{\epsilon}_0 e^{-\Delta H / RT} (e^{v\sigma / RT} - e^{-v\sigma / RT}) \quad (4)$$

where R is the gas constant and T the temperature. For high values of stress the equation can be re-written as

$$\frac{\sigma}{T} = \frac{R}{v} \left[\frac{\Delta H}{RT} + \log \frac{2\dot{\epsilon}}{\dot{\epsilon}_0} \right] \quad (5)$$

Equation 4 represents a process with only a single activation energy and activation volume. Nevertheless, either in the single activation energy form or in combination with a second Eyring type process it has been found to apply to a very wide range of polymers over a very wide range of strain rates from creep to rapid deformation (see **Strain Rate Effects**). Equation 4 leads to an expression for the variation of yield stress with temperature and strain rate

$$\sigma_y = \sigma_0 + \frac{RT}{v} \log \left(\frac{2\dot{\epsilon}}{\dot{\epsilon}_0} \right) \quad (6)$$

where σ_0 represents the yield stress at 0 K and is equal to $\Delta H/v$. Eyring type processes explain many of the features of yield in glassy polymers. The theory is grounded in the concept of viscous flow, which is not unreasonable for a glassy material. Extensions to the theory, notably the molecularly based re-working due to Argon¹ have introduced the concept of chain 'kinks' as the sources of strain. Fits of experimental data to the Argon model are generally excellent. Alternative models e.g. that of Robertson², also provide very good fits.

It is more difficult to provide a theory for yielding in semicrystalline polymers. This is because they are essentially a composite of crystalline and glassy material together with an interphase in which chains may wander from glassy to crystalline phase and back again. Adequate theories to explain yield behaviour have not been fully developed. For a reasonably up to date summary see the chapter by Crist³.

REFERENCES

1. Argon, A.S. (1975) in *Polymeric Materials* (eds E. Baer and V.S. Radcliffe) , Am. Soc. Met.
2. Robertson, R.E. (1966) *J. Chem. Phys.* **44**, 3950
3. Crist, B. (1993) Plastic Deformation of Polymers in *Materials Science and Technology Volume 12* (eds. R.W. Cahn, P. Haasen, E.J. Kramer) VCH Publishers