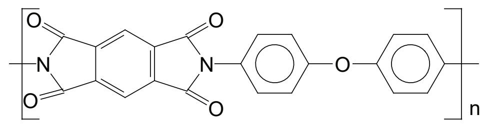
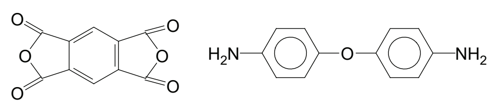
PI polyimide

PARAMETER	UNIT	VALUE	REFERENCES
GENERAL			
Common name	-	polyimide; poly(pyromellitimide-1,4-diphenyl ether)	
CAS name	-	poly[(5,7-dihydro-1,3,5,7-tetraoxobenzo[1,2-c:4,5-c']dipyrrole-2,6(1H,3H)-diyl)-1,4-phenyleneoxy-1,4-phenylene] (25036-53-7); 1H,3H-benzo[1,2-c:4,5-c']difuran-1,3,5,7-tetrone, polymer with 4,4'-oxybis[benzenamine] (25038-81-7)	
Acronym	-	PI	
CAS number	-	25036-53-7; 25038-81-7	
Formula			
HISTORY			
Person to discover	-	Paul John Flory; Edwards, W M and Maxwell, R I	
Date	-	1951; 1955	
Details	-	Flory reported condensation of sebacyl chloride and potassium phthalimide (first polyimide) and Edwards and Maxwell patented for DuPont PI made from pyromellitic acid	Fink, J K, High Performance Polymers, William Andrew, 2008.
SYNTHESIS			
Monomer(s) structure	-		
Monomer(s) CAS number(s)	-	89-32-7; 101-80-4	
Monomer(s) molecular weight(s)	dalton, g/mol, amu	218.12; 200.24	
Monomer(s) expected purity(ies)	%	97-98; 98-99	
Monomer ratio	-	1.11:1	
Formulation example	-	monomers, solvent (e.g., N-methyl-2-pyrrolidone), xylene (for azeotropic distallation to remove water)	
Method of synthesis	-	several routes can be used to obtain polyimides, including reaction between polyamic acid and diamine, isocyanate route, aqueous route, transimidization, and chemical vapor deposition	Fink, J K, High Performance Polymers, William Andrew, 2008.
Temperature of polymerization	°C	100	
Yield	%	94-100	
Number average molecular weight, M_n	dalton, g/mol, amu	10,000-100,000	
Mass average molecular weight, M_w	dalton, g/mol, amu	10,000-210,000	
Polydispersity, M_w/M_n	-	1.2-2.6	
Polymerization degree (number of monomer units)	-	25-275	
Molar volume at 298K	$cm^3 mol^{-1}$	calc.=275.5; 247 (crystalline)	
Van der Waals volume	$cm^3 mol^{-1}$	188.02; 184.1 (crystalline)	

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PARAMETER	UNIT	VALUE	REFERENCES
STRUCTURE			
Crystallinity	%	44-60	
Cell type (lattice)	-	orthorhombic	
Cell dimensions	nm	a:b:c=0.635:0.405:3.26	
Unit cell angles	degree	α:β:γ=90:90:90	
Chain conformation	-	planar zig-zag	Chang, C-J; Chou, R-L; Lin, Y-C; Liang, B-J; Chen, J-J, Thin Solid Films, 519, 5013-16, 2011.
Entanglement molecular weight	dalton, g/mol, amu	1,894	
Lamellae thickness	nm	5-15	Verker, R; Grossman, E; Gouzman, I; Eliaz, N, Composites Sci. Technol., 69, 2178-84, 2009.
Crystallization temperature	°C	282; 220 (peak)	
Avrami constants, k/n	-	n=2.6	Chung, T S; Liu, S L; Oikawa, H; Yamaguchi, A, Antec, 1494-8, 1998.
COMMERCIAL POLYMERS			
Some manufacturers	-	BASF; DuPont; Ensinger; Sabic	
Trade names	-	Kerimid, Matrimid; Cirlex, Kapton, Vespel; Tecapei; Ultem 1000	
PHYSICAL PROPERTIES			
Density at 20°C	g cm^{-3}	1.31-1.43	
Color	-	light amber	
Refractive index, 20°C	-	calc.=1.5932-.16429; exp.=1.61-1.68	
Birefringence	-	0.011	Wang, Y-W; Chen, W-C, Composites Sci. Technol., 70, 769-75, 2010.
Odor	-	none	
Melting temperature, DSC	°C	340-408	
Decomposition temperature	°C	185-400; 370 (fibers)	
Thermal expansion coefficient, 23-80°C	$°C^{-1}$	2-5.4E-5	
Thermal conductivity, 23°C	W m^{-1} K^{-1}	0.12-0.35	
Glass transition temperature	°C	190-385 (some like Vespel do not have T_g)	
Specific heat capacity	J K^{-1} kg^{-1}	1,090-1,130	
Heat of fusion	J g^{-1}	139	Huo, P P; Cebe, P, Polymer, 34, 4, 696-704, 1993.
Maximum service temperature	°C	-269 to 400-500	Cousins, K, Polymers in Electronics. Market Report, Rapra, 2006.
Long term service temperature	°C	300	
Heat deflection temperature at 0.45 MPa	°C	260-263	
Heat deflection temperature at 1.8 MPa	°C	221-360	
Vicat temperature VST/A/50	°C	257	

PARAMETER	UNIT	VALUE	REFERENCES
Vicat temperature VST/B/50	°C	262-263	
Surface tension	mN m^{-1}	calc.=37.7-41.0	
Dielectric constant at 1000 Hz/1 MHz	-	2.74-3.6/3.55	Jacobs, J D; Arlen, M J; Wang, D H; Ounaies, Z; Berry, R; Tan, L-S; Garrett, P H; Vaia, R A, Polymer, 51, 3139-46, 2010.
Dielectric loss factor at 1 kHz	-	0.0033	
Dissipation factor at 1000 Hz		0.0014-0.003	
Dissipation factor at 1 MHz		0.0034	
Volume resistivity	ohm-m	1E13-1E16	
Surface resistivity	ohm	1E15-1E16	
Electric strength K20/P50, d=0.60.8 mm	kV mm^{-1}	22-506	
Arc resistance	s	165	
Coefficient of friction	-	0.29-0.48 (kinetic); 0.35-0.63 (static)	
Permeability to oxygen, 25°C	barrer	160	Cui, L; Qiu, W; Paul, D R, Koros, W J, Polymer, in press, 2011.
Diffusion coefficient of water	cm^2 s^{-1} $x10^9$	5.6-8.1	Musto, P; Ragosta, G; Mensitieri, G; Lavorgna, M, Macromolecules, 40, 9614-27, 2007.
Contact angle of water, 20°C	degree	71.5-79.9	
Surface free energy	mJ m^{-2}	43.8	
MECHANICAL & RHEOLOGICAL PROPERTIES			
Tensile strength	MPa	81-241	
Tensile modulus	MPa	1,200-3,800	
Tensile stress at yield	MPa	112-120	
Elongation	%	7-95	
Tensile yield strain	%	9	
Flexural strength	MPa	110-155	
Flexural modulus	MPa	2,900-3,520	
Elastic modulus	MPa		
Compressive strength	MPa	150-234	
Young's modulus	MPa	2,500	
Charpy impact strength, notched, 23°C	kJ m^{-2}	20-22	
Izod impact strength, unnotched, 23°C	J m^{-1}	NB to 750	
Izod impact strength, notched, 23°C	J m^{-1}	43-110	
Shear strength	MPa	55-90	
Poisson's ratio	-	0.15-0.42	
Rockwell hardness	-	M112	
Shrinkage	%	0.004-1.3 (molding); 0.03-0.17 (30 min/150°C); 1.25 (120 min/400°C)	
Intrinsic viscosity, 25°C	dl g^{-1}	0.75-2.18	
Melt index, 400°C/6.6 kg	g/10 min	10	

PARAMETER	UNIT	VALUE	REFERENCES
Water absorption, equilibrium in water at 23°C	%	0.39-2.9 (24 h)	
Moisture absorption, equilibrium 23°C/50% RH	%	1-1.8	
CHEMICAL RESISTANCE			
Acid dilute/concentrated	-	non-resistant	
Alcohols	-	resistant	
Alkalis	-	non-resistant	
Aliphatic hydrocarbons	-	resistant	
Aromatic hydrocarbons	-	resistant	
Esters	-	resistant	
Greases & oils	-	resistant	
Halogenated hydrocarbons	-	resistant	
Ketones	-	resistant	
Good solvent	-	hot p-chlorophenol and m-cresol	Wu, Z; Yoon, Y; Harris, F W; Cheng, Z D; Chuang, K C, Antec, 3038-42, 1996.
FLAMMABILITY			
Ignition temperature	°C	>540; chars but does not burn in air	
Autoignition temperature	°C	>540	
Limiting oxygen index	% O_2	37-53	
Heat release	kW m^{-2}	21	
NBS smoke chamber	DM	<1	
Burning rate (Flame spread rate)	mm min^{-1}		
Char at 500°C	%	51.957	Lyon, R E; Walters, R N, J. Anal. Appl. Pyrolysis, 71, 27-46, 2004.
Heat of combustion	J g^{-1}	26,030	Walters, R N; Hacket, S M; Lyon, R E, Fire Mater., 24, 5, 245-52, 2000.
Volatile products of combustion	-	CO, CO_2, H_2O	Pramoda, K P; Chung, T S; Liu, S L; Oikawa, H; Yamaguchi, A, Polym. Deg. Stab., 67, 2, 365-74, 2000.
UL 94rating	-	V-0	
WEATHER STABILITY			
Spectral sensitivity	nm	<500; vacuum ultraviolet (e.g., 172; it also has synergistic action with atomic oxygen)	Yokota, K; Ohmae, N; Tagawa, M, High Performance Polym., 16, 221-34, 2004.
Excitation wavelengths	nm	380, 450	
Emission wavelengths	nm	505, 508, 566	
Depth of UV penetration	μm	0.5; limited to surface because of strong intrinsic absorption	
Products of degradation	-	only surface erosion	
Stabilizers	-	resistance to γ-radiation, atomic oxygen, and Lyman emission	
Results of exposure	Florida	1300 h to reduce elongation by 50%	

PARAMETER	UNIT	VALUE	REFERENCES
Low earth orbit erosion yield	$cm^3\ atom^{-1} \times 10^{-24}$	2.81-3.0	Waters, D L; Banks, B A; De Groh, K K; Miller, S K R; Thorson, S D, High Performance Polym., 20, 512-22, 2008.
BIODEGRADATION			
Typical biodegradants	-	two steps are involved in degradation: an initial decline of resistance related to the partial ingress of water and ionic species into the polymer matrix. This is followed by further deterioration of the polymer by activity of the fungi, resulting in a large decrease in resistivity	
TOXICITY			
Carcinogenic effect	-	not listed by ACGIH, NIOSH, NTP	
TLV, ACGIH	$mg\ m^{-3}$	3 (respirable); 10 (total)	
OSHA	$mg\ m^{-3}$	5 (respirable); 15 (total)	
Oral rat, LD_{50}	$mg\ kg^{-1}$	15,600	
ENVIRONMENTAL IMPACT			
Aquatic toxicity, *Daphnia magna*, LC_{50}, 48 h	$mg\ l^{-1}$	16	
Aquatic toxicity, *Bluegill sunfish*, LC_{50}, 48 h	$mg\ l^{-1}$	380	
Aquatic toxicity, *Rainbow trout*, LC_{50}, 48 h	$mg\ l^{-1}$	340	
PROCESSING			
Typical processing methods	-	casting, compression molding, drawing of oriented films, extrusion, injection molding, sintering, spin coating, spinning, vapor phase deposition	
Preprocess drying: temperature/time/residual moisture	°C/h/%	175/4-6/0.02	
Processing temperature	°C	380-430	
Processing pressure	MPa	0.3-0.7 (back)	
Additives used in final products	-	Fillers: aluminum nitride, barium titanate, aluminum nitride, antimony trioxide, aramide fiber, attapulgite, carbon fiber, carbon nanofiber, carbon nanotubes, clay, glass fiber, graphite, molybdenum sulfide, montmorillonite, PTFE, silica, smectite, titanium oxide whisker; Plasticizers: diethylene glycol dibenzoate, dimethyl phthalate, triallyl phthalate, diethynyldiphenyl methane, phenylethynyldiphenyl methane, 4-hydroxybenzophenone; Antistatics: antimony-containing tin oxide, carbon black, carbon, nanotubes, indium oxide microspheres, polythiophene; Release: polyethylen wax, PTFE, silicone oil, zirconium chelate	
Applications	-	aerospace, composites, electronics (mostly films and coatings), foam composites, hollow fiber membranes, electronics, fibers, mechanical parts (bearings, piston rings, valve seats, washers), microprocessor chip carriers, non-lubricated applications, nuclear power plants, photosensitive materials for positive imaging, photovoltaic film, solar cells, space shuttle, structural adhesives, ultrafiltration membranes	
Outstanding properties	-	broad range of temperature resistance, low moisture uptake, excellent electric properties	

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PARAMETER	UNIT	VALUE	REFERENCES
BLENDS			
Suitable polymers	-	PEI, PBI, PEEK, PES, PTFE, TPU	
ANALYSIS			
FTIR (wavenumber-assignment)	cm^{-1}/-	imide absorption bands: C=O – 1780 and 725, C-N – 1380; carboxylic acid band of polyamic acid - 1700;	
Raman (wavenumber-assignment)	cm^{-1}/-	C-CO-C – 1788, 1728; C-N-C – 1394, 1124; aromatic dianhydride – 1614, 753	Samyn, P; De Baets, P; Van Craenenbroeck, J; Verpoort, F; Schoukens, Antec, 121-5; 2005.
NMR (chemical shifts)	ppm	C=O – 166.6-168.5	Powell, C E; Duthie, X J; Kentish, S E; Qiao, G G; Stevens, G W, J. Membrane Sci., 291, 199-209, 2007.
x-ray diffraction peaks	degree	5, 18	Goodwin, A A; Whittaker, A K; Jack, K S; Hay, J N; Forsythe, J, Polymer, 41, 7263-71, 2000.