PU polyurethane

PARAMETER	UNIT	VALUE	REFERENCES
GENERAL			
Common name	-	polyurethane	
IUPAC name	-	e.g., polyurea: poly[ureylene(2-methyl-1,3-phenylene)ureylenehexane-1,6-diyl]; polyurethane: poly{oxycarbonylimino(4-methyl-1,3-phenylene)iminocarbonyl[poly(oxyethylene)]}	
Acronym	-	PU; PUR (IUPAC)	
CAS number	-	9009-54-5, 75701-44-9	
HISTORY			
Person to discover	-	Otto Bayer	
Date	-	1937; 1954	
Details	-	Otto Bayer discovered polyurethane reaction in IG Farben; commercial production begun in 1954	
SYNTHESIS			
Monomer(s) structure	-	diols, triol, tetrafunctional polyols; 1-3 functional isocyanates	
Curatives		for polyols, isocyanates or isocyanurates play a role of curatives; prepolymers are cured either by polyols (frequently multifunctional to obtain tridimensional networks) or by amines; considering that amines are very reactive with isocyanate groups, amines are frequently used in a blocked form of ketimines and aldomines which require moisture to hydrolyze them to free reactive amines and this slows curing process up to the extent that frequently catalytic systems have to be used to bring reaction to a required rate	
Monomer(s) CAS number(s)	-	too many used to make their listing practical	
Monomer(s) molecular weight(s)	dalton, g/mol, amu	400-8,400 (polyols)	
Monomer ratio	-	+-5% stoichiometric	
Formulation example	-	polyol, isocyanate, catalyst	
Hydroxyl number	mg/g KOH	14-865	
NCO content	%	23-48	
Method of synthesis	-	components of formulation are mixed and formed to shape as soon as possible; catalyst selection is part of design to achieve required rate of polycondensation; in many cases prepolymers are produced first (prepolymers are low molecular products containing most frequently one molecule of polyol and two or more molecules of isocyanate)	
Temperature of polymerization	°C	room	
Time of polymerization	s	60-1,500	
Pressure of polymerization	Pa	usually atmospheric	
Catalyst	-	tin catalysts are the most popular in the case of prepolymer synthesis (polyureas), and amines in the case of polycondesation of polyol and isocyanate (polyurethane)	Abdel Hakim, A A; Nassar, M; Emam, A; Sultan, M, Mater. Chem. Phys., 129, 301-7, 2011.
Yield	%	close to 100%	
Typical concentration of residual monomer	ppm	full conversion; if isocyanate would not react with polyol component or curative, it will react with water	Spirkova, M; Pavlicevic, J; Strachota, A; Poremba, R; Bera, O; Kapralkova, L; Baldrian, J; Slouf, M; Lazic, N; Budinski-Simendic, J, Eur. Polym. J., 47, 959-72, 2011.
Number average molecular weight, M_n	dalton, g/mol, amu		Filip, D; Macocinschi, D; Vlad, S, Composites, Part B, in press, 2011.
Polydispersity, M_w/M_n	-		Filip, D; Macocinschi, D; Vlad, S, Composites, Part B, in press, 2011.

PARAMETER	UNIT	VALUE	REFERENCES
Crosslink density	g mol cm^{-3} x 10^4	1.5-4	Amrollahi, M; Sadeghi, M M; Kashcooli, Y, Mater. Design, 32, 3933-41, 2011.
Molecular weight between crosslinks	g mol^{-1}	3,200-6,800	Amrollahi, M; Sadeghi, M M; Kashcooli, Y, Mater. Design, 32, 3933-41, 2011.
Radius of gyration	nm	1.2	Yang, H; Li, Z-s; Lu, Z-y; Sun, C-c, Polymer, 45, 6753-59, 2004.
STRUCTURE			
Crystallinity	%	0-13	Spirkova, M; Pavlicevic, J; Strachota, A; Poremba, R; Bera, O; Kapralkova, L; Baldrian, J; Slouf, M; Lazic, N; Budinski-Simendic, J, Eur. Polym. J., 47, 959-72, 2011.
Cell type (lattice)	-	triclinic	Petrovic, Z S; Ferguson, J, Prog. Polym. Sci., 16, 695-836, 1991.
Cell dimensions	nm	a:b:c=0.492:0.566:3.835 (MDI/BD) (III); a:b:c=0.96:0.56:3.68 (12-PUR)	Petrovic, Z S; Ferguson, J, Prog. Polym. Sci., 16, 695-836, 1991; Fernandez, C E; Bermudez, M; Versteegen, R M; Meijer, E W; Vancso, G J; Munoz-Guerra, S, Eur. Polym. J., 46, 2089-98, 2010.
Unit cell angles	degree	$\alpha:\beta:\gamma$=124:104.5:86 (MDI/BD) (III); $\alpha:\beta:\gamma$= 47.3:90:70.9	Petrovic, Z S; Ferguson, J, Prog. Polym. Sci., 16, 695-836, 1991; Fernandez, C E; Bermudez, M; Versteegen, R M; Meijer, E W; Vancso, G J; Munoz-Guerra, S, Eur. Polym. J., 46, 2089-98, 2010.
Number of chains per unit cell	-	2	
Polymorphs	-	I (quiescent crystallization), II (quiescent crystallization), III (orientation)	
Lamellae thickness	nm	21.9; 8-9	Yang, H; Li, Z-s; Lu, Z-y; Sun, C-c, Polymer, 45, 6753-59, 2004; Fernandez, C E; Bermudez, M; Versteegen, R M; Meijer, E W; Vancso, G J; Munoz-Guerra, S, Eur. Polym. J., 46, 2089-98, 2010.
Avrami constants, k/n	-	n=3.4-3.9	Fernandez, C E; Bermudez, M; Versteegen, R M; Meijer, E W; Vancso, G J; Munoz-Guerra, S, Eur. Polym. J., 46, 2089-98, 2010.
COMMERCIAL POLYMERS			
Some manufacturers	-	Bayer; DOW	
Trade names of polyols	-	Acclaim, Arcol, Baycoll, Desmophen, Hyperlite, Ultracel; Diorex	
Trade names of isocyanates	-	Baymidur, Desmodur; Papi	
Trade names of prepolymers		Desmocap, Desmoseal, Desmotherm; Echelon	
PHYSICAL PROPERTIES			
Density at 20°C	g cm^{-3}	1.10-1.25; 1.322 (fully crystalline)	
Color	-	off white to yellow	
Odor	-	none	
Melting temperature, DSC	°C	141-157	Fernandez, C E; Bermudez, M; Versteegen, R M; Meijer, E W; Vancso, G J; Munoz-Guerra, S, Eur. Polym. J., 46, 2089-98, 2010.
Decomposition temperature	°C	120-126	

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PARAMETER	UNIT	VALUE	REFERENCES
Thermal expansion coefficient, 23-80°C	10^{-4} °C^{-1}	1.8	
Thermal conductivity, melt	W m^{-1} K^{-1}	0.13	
Glass transition temperature	°C	-60.3 to -19	Sadeghi, M; Semsarzadeh, M A; Barikani, M; Chenar, M P, J. Membrane, Sci., 376, 188-95, 2011.
Maximum service temperature	°C	80-82	
Heat deflection temperature at 0.45 MPa	°C	136-252	
Heat deflection temperature at 1.8 MPa	°C	123-232	
Start of thermal degradation	°C		Fernandez, C E; Bermudez, M; Versteegen, R M; Meijer, E W; Vancso, G J; Munoz-Guerra, S, Eur. Polym. J., 46, 2089-98, 2010.
Enthalpy of crystallization	J g^{-1}	32.9-72.5	
Hansen solubility parameters, δ_D, δ_P, δ_H	$MPa^{0.5}$	18.8, 10.0, 8.2	
Interaction radius		9.8	
Hildebrand solubility parameter	$MPa^{0.5}$	22.8	
Surface tension	mN m^{-1}	calc.=36.3-39.0	
Dielectric constant at 100 Hz/1 MHz	-	7.8-9.4	
Dissipation factor at 100 Hz	E-4	59-95	
Volume resistivity	ohm-m	4.8E9	
Permeability to nitrogen, 25°C	barrer	8.7	Sadeghi, M; Semsarzadeh, M A; Barikani, M; Chenar, M P, J. Membrane, Sci., 376, 188-95, 2011.
Permeability to oxygen, 25°C	barrer	20	Sadeghi, M; Semsarzadeh, M A; Barikani, M; Chenar, M P, J. Membrane, Sci., 376, 188-95, 2011.
Contact angle of water, 20°C	degree	77.5-83.1	
Surface free energy	mJ m^{-2}	37.5	
MECHANICAL & RHEOLOGICAL PROPERTIES			
Tensile strength	MPa	7.6-66	
Tensile stress at yield	MPa	31-57.2	
Elongation	%	350-1,200	
Flexural strength	MPa	20-120	
Flexural modulus	MPa	540-3,000	
Tear strength	kN m^{-1}	24-119	
Compression set, 24h 70°C	%	27-40	
Shore A hardness	-	60-95	
Shore D hardness	-	36-91	
Shrinkage	%	1.2-2.5	
Brittleness temperature (ASTM D746)	°C	-70	

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PARAMETER	UNIT	VALUE	REFERENCES
CHEMICAL RESISTANCE			
Acid dilute/concentrated	-	good	
Alcohols	-	good	
Alkalis	-	good	
Aliphatic hydrocarbons	-	very good	
Aromatic hydrocarbons	-	very good	
Esters	-	good	
Greases & oils	-	good	
Ketones	-	good	
Effect of EtOH sterilization (tensile strength retention)	%	103-109	Navarrete, L; Hermanson, N, Antec, 2807-18, 1996.
FLAMMABILITY			
Autoignition temperature	°C	340-560	
Limiting oxygen index	% O_2	25	
Heat release	kW m^{-2}	330-700	Kraemer, R H; Zammarano, M; Linteris, G T; Gedde, U W; Gilman, J W, Polym. Deg. Stab., 95, 1115-22, 2010.
Heat of combustion	J g^{-1}	24,000-28,000	Kraemer, R H; Zammarano, M; Linteris, G T; Gedde, U W; Gilman, J W, Polym. Deg. Stab., 95, 1115-22, 2010.
Volatile products of combustion	-	CO, CO_2, HCN, NO_x	
UL 94 rating	-	V-2	
WEATHER STABILITY			
Activation wavelengths	nm	313, 334, 365, 405, 435	
Excitation wavelengths	nm	320, 372	
Emission wavelengths	nm	420, 423, 455, 489	
Important initiators and accelerators	-	catalysts used in prepolymer synthesis, catalysts used in the curing process, heavy metals, peroxides in polyol, products of reaction of amine catalysts and polyols, nitrous oxide, acids and bases (hydrolysis), traces of solvents of types capable of producing hydroperoxides, products of thermooxidative degradation	
Products of degradation	-	photo-Fries rearrangement, yellowing, chains scission, hydroperoxides, carbonyls	

PARAMETER	UNIT	VALUE	REFERENCES
Stabilizers	-	UVA: 2,2'-dihydroxy-4-methoxybenzophenone; 2-(2H-benzotriazol-2-yl)-p-cresol; 2-benzotriazol-2-yl-4,6-di-tert-butylphenol; phenol, 2-(5-chloro-2H-benzotriazole-2-yl)-6-(1,1-dimethylethyl)-4-methyl-; 2-(2H-benzotriazole-2-yl)-4,6-di-tert-pentylphenol; 2-(2H-benzotriazole-2-yl)-4-(1,1,3,3-tetraethylbutyl)phenol; 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol; 2-(2H-benzotriazol-2-yl)-6-dodecyl-4-methylphenol, branched & linear; 2,4-di-tert-butyl-6-(5-chloro-2H-benzotriazole-2-yl)-phenol; 2-(3-sec-butyl-5-tert-butyl-2-hydroxyphenyl) benzotriazole; reaction product of methyl 3(3-(2H-benzotriazole-2-yl)-5-t-butyl-4-hydroxyphenyl propionate/PEG 300; ethyl-2-cyano-3,3-diphenylacrylate; (2-ethylhexyl)-2-cyano-3,3-diphenylacrylate; N-(2-ethoxyphenyl)-N'-(4-isododecylphenyl)oxamide; N-(2-ethoxyphenyl)-N'-(2-ethylphenyl)oxamide; benzoic acid, 4-[[(methylphenylamino) methylene]amino]-, ethyl ester; Screeners: carbon black; HAS: 1,3,5-triazine-2,4,6-triamine, N,N'''[1,2-ethanediyl-bis[[[4,6-bis[butyl(1,2,6,6-pentamethyl-4-piperidinyl) amino]-1,3,5-triazine-2-yl]imino]-3,1-propanediyl]bis[N',N''-dibutyl-N',N''-bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-; 2,4-bis[N-butyl-N-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)amino]-6-(2-hydroxyethylamine)-1,3,5-triazine; bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate and methyl 1,2,2,6,6-pentamethyl-4-piperidyl sebacate; bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate + methyl-1,2,2,6,6-pentamethyl-4-piperidyl sebacate; bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate; 2,2,6,6-tetramethyl-4-piperidinyl stearate; 2-dodecyl-N-(2,2,6,6-tetramethyl-4-piperidinyl)succinimide; poly[[(6-[1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl] [2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl[2,2,6,6-tetramethyl-4-piperidinyl)imino]]; butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol; alkenes, C20-24-.alpha.-, polymers with maleic anhydride, reaction products with 2,2,6,6-tetramethyl-4-piperidinamine; polymer of 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-dispiro [5.1.11.2]-heneicosan-21-on and epichlorohydrin; 1, 6-hexanediamine, N, N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-, polymers with 2,4-dichloro-6-(4-morpholinyl)-1,3,5-triazine; 1,6-hexanediamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-, polymers with morpholine-2,4,6-trichloro-1,3,5-triazine reaction products, methylated; Phenolic antioxidants: ethylene-bis(oxyethylene)-bis(3-(5-tert-butyl-4-hydroxy-m-tolyl)-propionate); pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate); octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate; N,N'-hexane-1,6-diylbis(3-(3,5-di-tert-butyl-4-hydroxyphenylpropionamide); benzopropanoic acid, 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-C7-C9 branched alkyl esters; 3,3',3',5,5',5'-hexa-tert-butyl-a,a',a'-(mesitylene-2,4,6-triyl) tri-p-cresol; 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione; 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)-2H-1-benzopyran-6-ol; isotridecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate; 2,2'-ethylidenebis (4,6-di-tert-butylphenol); 3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione; 3,5-bis(1,1-dimethyethyl)-4-hydroxy-benzenepropanoic acid, C13-15 alkyl esters; Phosphite: isodecyl diphenyl phosphite; Thiosynergist: 4,6-bis(dodecylthiomethyl)-o-cresol; 4,4'-thiobis(2-t-butyl-5-methylphenol); 2,2'-thiobis(6-tert-butyl-4-methylphenol); Amine: benzenamine, N-phenyl-, reaction products with 2,4,4-trimethylpentene; Optical brightener: 2,2'-(2,5-thiophenediyl)bis(5-tert-butylbenzoxazole)	

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PARAMETER	UNIT	VALUE	REFERENCES
BIODEGRADATION			
Colonized products		catheters, coatings, fibrous membrane, microporous membranes, military components, paint	
Typical biodegradants	-	microbial degradation of polyester polyurethane is hypothesized to be mainly due to the hydrolysis of ester bonds by esterase enzymes	
Stabilizers	-	2,4-di-tert-butylphenol, 4,5,-dichloro-2-n-octyl-4-isothiazolone-3-one biocide, 2-n-octyl-4-isothiazolin-3-one, chitosan, gold nanoparticles, grafted 2,2,5,5-tetramethyl-imidozalidin-4-one, nonylphenol disulfide, silver nanoparticles	
TOXICITY			
Oral rat, LD_{50}	mg kg^{-1}	>5,000	
ENVIRONMENTAL IMPACT			
Aquatic toxicity, *Daphnia magna*, LC_{50}, 48 h	mg l^{-1}	3,500-4,900; 31,000-38,000 (EC_{50})	Lithner, D; Damberg, J; Dave, G; Larsson, A, Chemosphere, 74, 1195-1200, 2009; Lithner, Ph D Thesis, University of Gothenburg, 2011.
PROCESSING			
Typical processing methods	-	PU: chemical or moisture cure, coatings, compounding, electrospinning, mixing; TPU: blow molding, calendering coating, extrusion, injection molding, solution coating of fabrics	
Preprocess drying: temperature/ time/residual moisture	°C/h/%	85/3/0.01	
Processing temperature	°C	150-200	
Additives used in final products	-	Fillers: aluminum hydroxide, aluminum nitride, bentonites, calcium carbonate, calcium sulfate, fluoromica, graphite, kaolin, mica, montmorillonite, nanosilica, organic fibers, rubber particles, sand, sepiolite, silica; Plasticizers: adipates, azelates, benzoates, citrates, epoxidized soybean oil, phosphates, phthalates, sebacates; Antistatics: carbon black, carbon nanotubes, glycerol monostearate, graphite, polyaniline, polyethylene glycol, polypyrrole, silver-coated basalt particles, sulfonated polyol, tetraorganoboron, vanadium pentoxide; Antiblocking: diatomaceous earth, glass or ceramic spheres, natural silica, starch; Release: crosslinked silicone, fluorocarbon, isononylphenyl isocyanate, lecithin, silicone fluid, sodium myristate, sodium oleate, zinc stearate; Slip: ethylene bisstearamide, metal soap, montan ester wax, silicone oil	
Applications	-	PU: adhesives, coatings, foams, mortars, primers, sealants, and numerous other products; TPU: automotive, coatings, film and sheet, footwear, hose and tubes, wire and cable	
BLENDS			
Suitable polymers	-	CA, CHI, PCL, PDMS, PEG, SBS	
ANALYSIS			
FTIR (wavenumber-assignment)	cm^{-1}/-	N-N – 3330, 3430; hydrogen bonded carbonyl – 1703; free carbonyl – 1730	Amrollahi, M; Sadeghi, M M; Kashcooli, Y, Mater. Design, 32, 3933-41, 2011.

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PARAMETER	UNIT	VALUE	REFERENCES
x-ray diffraction peaks	degree	23; 13.64, 21.02	Spirkova, M; Pavlicevic, J; Strachota, A; Poremba, R; Bera, O; Kapralkova, L; Baldrian, J; Slouf, M; Lazic, N; Budinski-Simendic, J, Eur. Polym. J., 47, 959-72, 2011; Kumar, H; Siddaramaiah; Somashekar, R; Mahesh, S S, Mater. Sci. Eng, A447, 58-64, 2007.