

# TPU thermoplastic polyurethane

PARAMETER	UNIT	VALUE	REFERENCES
<b>GENERAL</b>			
Common name	-	thermoplastic polyurethane	
Acronym	-	TPU	
<b>HISTORY</b>			
Person to discover	-	Charles Schollenberger	
Date	-	1959	
Details	-	after 10 years of experimental work Charles Schollenberger developed technology of thermoplastic polyurethane for BFGoodrich, which resulted in fully automatized production of Estane	
<b>SYNTHESIS</b>			
Monomer(s) structure	-	polyols and isocyanates (see PU)	
Monomer ratio	-	usually stoichiometric with as small excess of polyol; example: MDI (aromatic isocyanate) – 10%, aliphatic isocyanate – 32%, aliphatic diol – 58% (Irogram PS455-203)	Lavall, R L; Ferrari, S; Tomasi, C; Marzantowicz, M; Quartarone, E; Magistris, A; Mustarelli, P; Lazzaroni, S; Fagnoni, M, J. Power Sources, 195, 5761-67, 2010.
Method of synthesis	-	polyol(s) are dried by azeotropic distillation (e.g., with toluene), catalyst is added followed by addition of isocyanate	Ojha, U; Kulkarni, P; Faust, R, Polymer, 50, 3448-57, 2009.
Temperature of polymerization	°C	80	
Time of polymerization	h	6	
Catalyst	-	most frequent: tin derivatives and amines	
Number average molecular weight, $M_n$	dalton, g/mol, amu	83,000-163,000	Ojha, U; Kulkarni, P; Faust, R, Polymer, 50, 3448-57, 2009.
Mass average molecular weight, $M_w$	dalton, g/mol, amu	120,000	
Polydispersity, $M_w/M_n$	-	1.2-3.7	Ojha, U; Kulkarni, P; Faust, R, Polymer, 50, 3448-57, 2009.
<b>STRUCTURE</b>			
Crystallinity	%	45.7-47.8 (TSPU); 2.7-18.3 (TPU)	Chen, Y; Wang, R; Zhou, J; Fan, H; Shi, B, Polymer, 52, 1856-67, 2011; Buckley, C P; Priscariu, C; Martin, C, Polymer, 51, 3213-24, 2010.
<b>COMMERCIAL POLYMERS</b>			
Some manufacturers	-	Bayer; Huntsman; Lubrizol	
Trade names	-	Desmopan, Texin; Irogram; Estane	
<b>PHYSICAL PROPERTIES</b>			
Density at 20°C	g cm <sup>-3</sup>	1.02-1.12	
Melting temperature, DSC	°C	170-220	
Thermal expansion coefficient, 23-80°C	10 <sup>-4</sup> °C <sup>-1</sup>	0.86	
Glass transition temperature	°C	-44 to -66	Ojha, U; Kulkarni, P; Faust, R, Polymer, 50, 3448-57, 2009.
Vicat temperature VST/A/50	°C	60.6-71.1	
Dielectric constant at 60 Hz/1 MHz	-	3.7	

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Electric strength K20/P50, d=0.60.8 mm	kV mm <sup>-1</sup>	15	
Permeability to nitrogen, 25°C	cm <sup>3</sup> cm cm <sup>-2</sup> s <sup>-1</sup> cmHg <sup>-1</sup> x 10 <sup>10</sup>	1.4	Chen, Y; Wang, R; Zhou, J; Fan, H; Shi, B, Polymer, 52, 1856-67, 2011.
Permeability to oxygen, 25°C	cm <sup>3</sup> cm cm <sup>-2</sup> s <sup>-1</sup> cmHg <sup>-1</sup> x 10 <sup>10</sup>	7.0	Chen, Y; Wang, R; Zhou, J; Fan, H; Shi, B, Polymer, 52, 1856-67, 2011.
Diffusion coefficient of nitrogen	cm <sup>2</sup> s <sup>-1</sup> x10 <sup>7</sup>	2.2	Chen, Y; Wang, R; Zhou, J; Fan, H; Shi, B, Polymer, 52, 1856-67, 2011.
Diffusion coefficient of oxygen	cm <sup>2</sup> s <sup>-1</sup> x10 <sup>7</sup>	3.5	Chen, Y; Wang, R; Zhou, J; Fan, H; Shi, B, Polymer, 52, 1856-67, 2011.
<b>MECHANICAL &amp; RHEOLOGICAL PROPERTIES</b>			
Tensile strength	MPa	17-66	
Tensile modulus	MPa	120-330	
Tensile stress at yield	MPa	39-54.2	
Elongation	%	300-1500	
Flexural strength	MPa	5.5-75.2	
Flexural modulus	MPa	17-1,990	
Young's modulus	MPa	33-72	Ojha, U; Kulkarni, P; Faust, R, Polymer, 50, 3448-57, 2009.
Tear strength	kN m <sup>-1</sup>	33-256	
Compression set, 24h 70°C	%	11-87	
Shore A hardness	-	62-98	
Shore D hardness	-	28-73	
Shrinkage	%	0.3-0.8	
<b>CHEMICAL RESISTANCE</b>			
Alcohols	-	good	
Aliphatic hydrocarbons	-	good	
Aromatic hydrocarbons	-	poor	
Esters	-	poor	
Greases & oils	-	good	
Ketones	-	poor	
Good solvent	-	DMF, THF, MEK	
<b>FLAMMABILITY</b>			
Ignition temperature	°C	400	
Autoignition temperature	°C	>393	
<b>WEATHER STABILITY</b>			
Activation wavelengths	nm	313, 334, 365, 405, 435	
Excitation wavelengths	nm	320, 372	
Emission wavelengths	nm	420, 423, 455, 489	

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<b>Important initiators and accelerators</b>	-	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	
<b>Products of degradation</b>	-	photo-Fries rearrangement, yellowing, chains scission, hydroperoxides, carbonyls	
<b>Stabilizers</b>	-	<p>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 &amp; 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-ethanediy-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-hexanediy][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, 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; 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-hydroxyphenyl)propionamide); 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-dimethylethyl)-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)</p>	

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PARAMETER	UNIT	VALUE	REFERENCES
<b>BIODEGRADATION</b>			
Biodegradable TPUs		biodegradable polyurethanes are typically prepared from polyester polyols, aliphatic diisocyanates and chain extenders	Tatai, L; Moore, T G; Adhikari, R; Malherbe, F; Jayasekara, R; Griffiths, I; Gunatillake, P A, <i>Biomaterials</i> , 28, 5407-17, 2007.
<b>PROCESSING</b>			
Typical processing methods	-	blow molding, calendaring, coating, extrusion, injection molding, slush molding	
Preprocess drying: temperature/time/residual moisture	°C/h/%	80-110/0.03	
Processing temperature	°C	185-240 (injection molding); 170-235 (extrusion)	
Applications	-	wearing parts (mine screens, strippers, cyclones); wheels and solid tires; rollers (transport, office equipment); seals (U and V packing rings, O-rings, cup seals); damping components (spacers, grippers, pickers, handles); drive elements (clutch components, timing belts, round belts, cog wheels); animal identification tags, automotive products, belts, cable sheathing, castors, coated fabrics, films, hoses, membranes, profiles, shoe soles	
Outstanding properties	-	abrasion resistance, resistance to oils and greases, rebound resilience, load-bearing capacity, damping properties	
<b>BLENDS</b>			
Suitable polymers	-	NR, PEO, phenoxy, POM, PP (functionalized), PR, PVB, PVC, PVDF, SBS	
<b>ANALYSIS</b>			
FTIR (wavenumber-assignment)	cm <sup>-1</sup> /-	NH - 3455, 3320; amide - 1714, 1697, 1666; hydrogen bonded NH - 3316; hydrogen bonded C=O - 1708; C-N - 1525	Barick, A K; Tripathy, D K, <i>Composites</i> , A41, 1471-82, 2010.
Raman (wavenumber-assignment)	cm <sup>-1</sup> /-	soft phase - 1115; hard phase - 1080; C=O - 1800, 1650	Ferry, A; Jacobsson, P; van Heumen, J D; Stevens, J R, <i>Polymer</i> , 37, 5, 737-44, 1996.
NMR (chemical shifts)	ppm	OH - 3.6; CH <sub>2</sub> - 4.1	Sonnenschein, M F; Guillaudeu, S J; Landes, B G; Wendt, B L, <i>Polymer</i> , 51, 3685-92, 2010.
x-ray diffraction peaks	degree	10, 11.2, 12	Buckley, C P; Prisacariu, C; Martin, C, <i>Polymer</i> , 51, 3213-24, 2010.