

polyurethane, polyurea

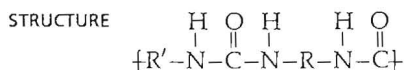
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Polyurea

L. S. RAMANATHAN, S. SIVARAM, AND MUNMAYA K. MISHRA

ACRONYMS PU, PUR

CLASS Polyureas



R = isocyanate unit

R' = diamine unit

MAJOR APPLICATIONS The most important practical applications of polyurea elastomers are in the production of automobile parts. High-modulus RIM (reaction-injection molded) and RRIM (reinforced reaction-injection molded) polyureas are suitable for producing high-impact external body panels. It is also useful in the forming microporous films for artificial leather. Ultrathin membranes of polyurea are used in water desalination by reverse osmosis. Polyureas are effective in making lubricant greases, medical equipment and artificial organs. Polyurea is also applied as a wall material for encapsulating drugs, pesticides, catalysts, and other products.

PROPERTIES OF SPECIAL INTEREST Polyurea fibres have high melting points, low specific gravity, excellent dyeability, and good acid and alkaline resistance. Polyurea coatings have lower solvent and better water resistance compared to polyurethanes. They have good blood compatibility.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	g cm ⁻³	1,9-Nonane diamine (NDA)/ethylene bis chloroformate (EBC)	1.175	(1)
		1,10-Decane diamine (DDA)/EBC	1.75	(1)
		Polyisocyanate/polyetheramine/diethyl toluene diamine (DETDA)	1.1	(2)
		Aliphatic-aromatic copolyureas	1.012-1.214	(3)

Unit cell dimensions

Sample	Lattice	Cell dimensions (Å)			Cell angles (degrees)			Reference
		a	b	c	α	β	γ	
4,4'-Dicyclohexyl methane diisocyanate (CHMDI)/1,10 DDA	—	9.30	6.06	45	—	—	—	(4)
4,4'-diphenyl methane diisocyanate (MDI)/1,4-butane diamine (BDA)	Triclinic	4.63	5.83	25.23	90.7	91.58	102.9	(5)

Refractive indices of polyurea before poling⁽⁶⁾

System	Wavelength (μm)	RI	
		n_{TE}	n_{TM}
MDI/4,4'-methylene bis(cyclohexyl amine)	0.532	1.6052	1.5834
	0.6328	1.5962	1.5761
	1.064	1.5762	1.5644
MDI/1,4-diaminocyclohexane	0.532	1.6152	1.6012
	0.6328	1.6089	1.5949
	1.064	1.5838	1.5762
MDI/2,2-dimethyl-1,3-propane diamine	0.532	1.6223	1.6127
	0.6328	1.6091	1.5995
	1.064	1.5919	1.5833
MDI/4,4'-diaminodimethyl sulfone	0.532	1.7088	1.6715
	0.6328	1.6872	1.6564
	1.064	1.6577	1.6340

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Piezoelectric ' e ' constant	mC m^{-2}	MDI/4,4'-diaminodiphenylmethane (MDA)	15	(7)
Heat capacity	—	MDI/polyether amine/DETDA	0.41	(8)
Glass transition temperature	K	1,9-NDA/EBC	277	(1)
		1,10-DDA/EBC	333.8	(1)
		Octafluoro hexamethylene-1,6-diamine (OFHMDA)/1,6-hexamethylene bis(chlorocarbonate) [HMCC]	278	(9)
		Hexamethylene diamine (HMDA)/HMCC	271	(9)
		MDI/polyether amine/DETDA	215	(10)
		Amino terminated polysilanes/MDI/DETDA	186	(11)
		Amino terminated polysilanes/MDI+HMDI/1,3-propane sulfonate	180	(11)
		Amino terminated polysilanes/MDI+HMDI/ethylene diamine (EDA)	176	(11)
		4,4'-methylenebis[N-methyl aniline]/2,2-dimethyl-1,3-propanediol bis(chloroformate)	443-463	(12)
		4,4'-methylenebis[N-methyl aniline]/ COCl_2	523-553	(12)
Melting temperature	K	$\text{ClCON}(\text{CH}_3)\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)\text{COCl}/\text{HN}(\text{CH}_3)(\text{CH}_2)_6(\text{CH}_3)\text{NH}$	383-453	(12)
		4,4'-diamino-1,3-diphenyl propane/EBC	480	(1)
		4,4'-diamino-1,3-diphenyl butane/EBC	547	(1)
		1,9-NDA/EBC	441	(1)
		1,10-DDA/EBC	447	(1)
		OFHMDA/HMCC	457	(9)
		HMDA/HMCC	443	(9)

Polyurea

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Water absorption	%	MDI based polyurea at 25°C, 7 days	2.13	—
Solubility parameter	(MPa) ^{1/2}	MDI/EDA	24.9	(13)
		MDI/DETDA	23.9	
		MDI/methylene bis(2,6-isopropyl aniline) (MMIPA)	21.6	
		MDI/methylene bis(2-methyl-6-isopropyl aniline) [MDIPA]	20.4	
Tensile strength	MPa	Aminopropyl terminated poly(dimethyl siloxane) [ATPDMS]/MDI	16.6	(14)
		ATPDMS/TDI	10.0	(14)
		ATPDMS/HMDI	9.0	(14)
		MDI/polyether amine/DETDA	4.61	(10)
		MDI/polyether amine/DETDA	15.9	(8)
		Amino terminated polysilanes/MDI/DETDA	9.1	(11)
		Amino terminated polysilanes/MDI+HMDI/ 1,3-propane sulfonate	22.4	(11)
		Amino terminated polysilanes/MDI+HMDI/ED	16.1	(11)
Elongation	%	ATPDMS/MDI	430	(14)
		ATPDMS/TDI	520	(14)
		ATPDMS/HMDI	950	(14)
		MDI/polyether amine/DETDA	276	(8)
		MDI/ polyether amine/DETDA	250	(10)
		Amino terminated polysilanes/MDI/DETDA	426	(11)
		Amino terminated polysilanes/MDI+HMDI/ 1,3-propane sulfonate	335	(11)
		Amino terminated polysilanes/MDI+HMDI/EDA	332	(11)
Shore D hardness		Polyisocyanate/polyether amine/DETDA	75	(2)
Tear strength	N m ⁻¹	IPDI based polyurea	70 × 10 ³	(15)
		Tetramethyl xylene diisocyanate (TMXDI) based polyurea	45 × 10 ³	

REFERENCES

1. Lyman, J., J. Heller, and M. Barlow. *Makromol. Chemie.* 84 (1965): 64.
2. Harris, R. F., R. M. Anderson, and D. M. Shannon. *J. Appl. Polym. Sci.* 46 (1992): 1,547.
3. Ibrahim, A. M., V. Mahadevan, and M. Srinivasan. *Eur. Polym. J.* 25 (1989): 427.
4. Barton, R. Jr. *Bull. Am. Phys. Soc.* 32(3) KU10 (1987): 701.
5. Born, L., and H. Hespe. *Colloid Polym. Sci.* 263 (1985): 335 [CA; 103: 7586z].
6. Tao, H. T., et al. *Macromolecules* 28 (1995): 2,637.
7. Takahashi, Y., et al. *J. Appl. Phys.* 70 (1991): 6,983.
8. Rayan, A. J., J. L. Stanford, and N. Wilkinson. *Polym. Bull.* 18 (1987): 517.
9. Malichenko, B. F., Y. V. Sheludko, and Y. Y. Kercha. *Polym. Sci. USSR* 9 (1967): 2,808.
10. Willkokomm, W. R., Z. S. Chen, and C. W. Macosko. *Polym. Eng. Sci.* 28 (1988): 888.
11. Yang, C. Z., C. Li, and S. L. Cooper. *J. Polym. Sci., Polym. Phys. Ed.*, 29 (1991): 75.

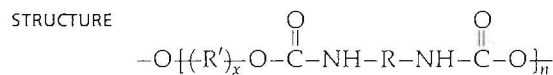
12. Foti, S., P. Maravigna, and G. Mantaudo. *Macromolecules* 15 (1982): 883.
13. Rayan, A. J., J. L. Stanford, and R. H. Still. *Polym. Commun.* 29 (1988): 196.
14. Tyagi, D., et al. *Polymer* 25 (1984): 1,807.
15. Dominguez, R. J. G., D. M. Rice, and R. A. Grigsby. *Plas. Eng.* 43(11) (1987): 41.

Polyurethane

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ACRONYMS PU, PUR

CLASS Polyurethanes



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R' = polyol segment

MAJOR APPLICATIONS Polyurethane flexible foams find applications in protective packaging, gaskets, textile laminates, protective cushioning in automobiles, and two component injection-grouting resins. Rigid polyurethane foams are used as thermal insulating materials in refrigerators, freezers, and water heaters. It is also used as a roof proofing material.

PROPERTIES OF SPECIAL INTEREST Excellent dampening property, good mechanical and physical properties even at low temperatures, high combustion resistance, and low thermal conductivity.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	g cm^{-3}	4,4'-Diphenylmethane diisocyanate (MDI)/1,4-butane diol (BD)	1.297	(1)
Flory-Huggins polymer solvent interaction parameter	—	TDI/1,4-BD (DMF)	0.122	(2)

Unit cell dimensions

Sample	Lattice	Cell dimensions (Å)			Cell angles (degrees)			Reference
		a	b	c	α	β	γ	
Hexamethylene diisocyanate (HMDI)/Ethylene glycol (EG)	Triclinic	4.59	5.14	13.9	90	90	119	(3)
HMDI/1,3-propane diol (PD)	Monoclinic	4.70	8.36	33.9	—	—	115	(3)
HMDI/BD	Triclinic	4.98	4.71	19.4	116	105	109	(3)
HMDI/1,5-pentane diol (PtD)	Monoclinic	4.70	8.36	39.0	—	—	115	(3)
HMDI/1,6-hexane diol (HD)	Triclinic	5.05	4.54	21.9	112	108	108	(3)
Trimethylene diisocyanate (TMDI)/BD	Triclinic	5.06	5.04	30.1	112	113	110	(4)
TMDI/HD	Triclinic	5.04	5.04	34.6	111	111	111	(4)
MDI/BD	Triclinic	5.2	4.8	35	115	121	85	(5, 6)
MDI/BD	Triclinic	4.92	5.66	38.4	124	104	86	(7)

Conformational characteristics

Sample	Solvent	Mark-Houwink parameters		$[\langle R^2 \rangle / M]^{1/2} \times 10^9$	Reference
		$K \times 10^{-4} (\text{ml g}^{-1})$	a		
Toluene diisocyanate (TDI)/BD	—	5.4	0.74	—	(2)
MDI/EG	100 DMF	3.64	0.71	10.11	(8)
	95/5 DMF/acetone	6.29	0.65	10.19	(8)
	90/10 DMF/acetone	7.19	0.63	10.25	(8)
	85/15 DMF/acetone	10.02	0.59	10.04	(8)
	79/21 DMF/acetone	14.19	0.56	9.97	(8)
	71/29 DMF/acetone	30	0.50	—	(8)
MDI/BD	DMA (at 25°C)	870	1.43	—	(9)

Refractive index gradient

Sample	Condition			$dn/dc (\text{ml g}^{-1})$	Second virial coefficient $A_2 \times 10^4$	Reference
	Solvent	$\lambda (\text{nm})$	Temp (°C)			
TDI/BD	DMF	546	—	0.14	—	(2)
MDI/1,6-HD	DMF/acetone	—	—	0.159–0.203*	3.0–4.5*	(10)
	DMF/toluene	—	—	0.123–0.154*	2.3–8.0*	(10)

*Variable with respect to DMF volume fraction.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion	kJ mol^{-1}	MDI/BD	5.3	(9)
Heat capacity	$\text{cal g}^{-1} \text{°C}^{-1}$	HMDI/BD		(11)
		–50 to 10°C	0.422	
		45–120°C	0.495	
		195–210°C	0.665	
		HMDI/DEG		
		–50 to –5°C	0.422	
		50–100°C	0.512	
		140–160°C	0.623	
Crystallization half time	min	HMDI/BD	6	(12)
		HMDI/diethylene glycol (DEG)	10.5	
Crystallization enthalpy	cal cm^{-3}	HMDI/BD	40	(12)
		HMDI/DEG	45	
Glass transition temperature	K	HMDI/BD	295	(12)
		HMDI/DEG	272	(12)
		HMDI/octafluoro1,6-hexane diol (OFHD)	271	(13)
		MDI/EG	363	(14)
		Desmodur/1,6-HD	322	(15)
		Desmodur/cyclohexane dimethanol (CHDM)	302	(15)

Polyurethane

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting temperature	K	HMDI/BD	476	(12)
		HMDI/DEG	396	(12)
		HMDI/OFHD	399	(13)
		TDI/EG	453	(14)
		MDI/EG	498	(14)

Optical properties

System	Temp. (°C)	Solvent	Optical rotation $[\alpha]_D$	Reference
MDI/(1S,2S)-diphenyl propane diol	25	DMSO	-71.6	(16)
HMDI/(1S,2S)-diphenyl propane diol	25	DMSO	-14.7	(16)
HMDI/(2R,4R)-pentanediol	25	DMSO	-80.6	(16)
MDI/(1S,2S)-(+)-2-acetamido-1-phenyl-1,3-propanediol	25	DMF	-24.6	(17)
TDI/(1S,2S)-(+)-2-acetamido-1-phenyl-1,3-propanediol	25	DMF	-20.6	(17)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Photoconductivity	ohms ⁻¹ cm ⁻¹	Polyurethane with pendant chromophore	1.3×10^{-13}	(18)
Refractive index	—	Polyurethane with pendant chromophore		(18)
		At 532 nm	1.879	
		At 690 nm	1.812	
		At 1,064 nm	1.763	
Water vapor absorption	%	MDI/EG	2.5	(14)
Solubility parameter	(MPa) ^{1/2}	MDI/BD	27	(1)
		MDI/EG	21	(19)
Elongation	%	MDI/EG	36	(14)
Adhesion strength	psi	Desmodur/1,6-HD	220	(15)
		Desmodur/CHDM	220	

REFERENCES

1. Camberlin, Y., and J. P. Pascaut. *J. Polym. Sci., Polym. Phys. Ed.* 22 (1984): 1,835.
2. Malichenko, B. F., et al. *Polym. Sci. USSR* 9 (1967): 2,975.
3. Sato, Y., S. Nansai, and S. Kinoshita. *Polym. J.* 3 (1972): 113.
4. Sato, Y., K. Hara, and S. Kinoshita. *Polym. J.* 14 (1982): 19.
5. Blackwell, J., and K. H. Gardner. *Polymer* 20 (1979): 13.
6. Blackwell, J., and M. Ross. *J. Polym. Sci., Polym. Lett. Ed.*, 17 (1979): 447.
7. Born, L., et al. *J. Polym. Sci., Polym. Phys. Ed.*, 22 (1984): 163.
8. Beachell, H. C., and J. C. Peterson. *J. Polym. Sci., Part A-1*, 7 (1969): 2,021.

9. Hwang, K. K. S., et al. *J. Polym. Sci., Polym. Chem. Ed.*, 22 (1984): 1,677.
10. Tuzar, Z., and H. C. Beachell. *J. Polym. Sci., Polym. Lett. Ed.*, 9 (1971): 37.
11. Godovskii, Y. K., and Y. S. Lipatov. *Polym. Sci. USSR* 10 (1968): 34.
12. Godovskii, Y. K., and G. C. Slomimsky. *J. Polym. Sci., Polym. Phys. Ed.*, 12 (1974): 1,053.
13. Malichenko, B. F., Y. V. Sheludks, and Y. Y. Kercha. *Polym. Sci. USSR* 9 (1967): 2,808.
14. Lyman, D. J. *J. Polym. Sci.* 45 (1960): 49.
15. Chung, F. H. *J. Appl. Polym. Sci.* 42 (1991): 1,319.
16. Kobayashi, T., M. Kakimoto, and Y. Imai. *Polym. J.* 25 (1993): 969.
17. Chen, Y., and J. Tsay. *Polym. J.* 24 (1992): 263.
18. Chen, M., et al. *Appl. Phys. Lett.* 64 (1994): 1,195.
19. Nishimura, H., et al. *Polym. Eng. and Sci.* 26 (1986): 585.

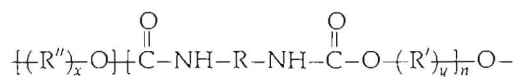
Polyurethane elastomers

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ACRONYMS PU, PUR

CLASS Polyurethanes

STRUCTURE



R = isocyanate unit

R' = polyol segment

R'' = diol segment

MAJOR APPLICATIONS Polyurethane elastomers find applications in adhesives, laminates for textiles, covering of conveyor and drive belts, welded bodies, roof underlay sheeting, magnetic tape coatings, water line tubing, and ski boot manufacture. Elastomeric RIM polyurethanes are useful in making automotive parts such as bumpers and fascia. Reinforced RIM polyurethane has been used for car windows door panels and wind shields. Foamed elastomeric polyurethanes are also used in making automotive parts such as arm rests, steering wheels, and rear deck air domes.

PROPERTIES OF SPECIAL INTEREST Excellent toughness and wear resistance with a broad temperature range for use. Polyurethane has good blood and tissue compatibility.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	g cm ⁻³	Oxyester/toluene diisocyanate (TDI)/1,4-butane diol(BD)	1.240	(1)
		Oxyester/4,4'-diphenylmethane diisocyanate (MDI)/BD	1.213	(1)
		Oxyester/hexamethylene diisocyanate (HDI)/BD	1.163	(1)
		Oxyester/Isophorone diisocyanate (IPDI)/BD	1.160	(1)
		Poly(oxyethylene) (PEO) diol/MDI/BD	0.986	(2)
		Poly(tetramethyleneoxide) PTMO/MDI/BD	1.004	(2)
		Poly(propyleneoxide) PPO/MDI/BD	0.976	(2)

Unit cell dimensions

Sample	Lattice	Cell dimensions (Å)			Cell angles (degrees)			Reference
		a	b	c	α	β	γ	
PTMO/MDI/BD	Triclinic	5.05	4.67	37.9	116	116	83.5	(3)
PTMO/MDI/Hexane diol (HD)	Triclinic	4.99	—	41.5	114.5	113.8	84.3	(4)
Poly(tetramethyleneadipate) [PTMA]/MDI/HD	Triclinic	5.1	5.1	41.6	116	116	85	(5)

Polyurethane elastomers

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Flory-Huggins interaction parameter	—	PEO/MDI/BD	-0.27	(2)
		PTMO/MDI/BD	-0.33	
		PPO/MDI/BD	-0.08	
Flory-Huggins polymer solvent interaction parameter	—	Chloroform	0.228	(6)
		Benzene	0.333	
		MEK	0.417	
		Dibutyl ether	0.521	
		Acetonitrile	0.606	
		Cyclohexane	0.660	

Conformational characteristics⁽⁷⁾

Sample	Mark-Houwink parameters		K_0 (g ^{-3/2} mol ^{1/2} cm ³)	$\bar{R}_0^2$ (Å ² mol g ⁻¹)
	K (ml g ⁻¹)	a		
Poly (caprolactone) diol (PCL)/MDI/BD	0.257	0.54	0.25	1.0
PTMA/MDI/BD	0.043	0.70	0.20	0.84

Refractive index gradient^(7,8)

Sample	Conditions			dn/dc (ml g ⁻¹)
	Solvent	λ (nm)	Temp (°C)	
PCL/MDI/BD	DMF	546	25	0.102
PTMA/MDI/(BD)	DMF	546	25	0.110
TDI/poly (propylene) glycol (PPG)	Benzene	435.8	—	0.031
TDI/PPG	Butanone	435.8	—	0.094
TDI/PPG	Methanol	435.8	—	0.148

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion	kJ mol ⁻¹	PEO/MDI/BD	197	(9)
		PEO/MDI/BD	155	
Glass transition temperature	K	PPG/MDI/BD	222	(10)
		PCL/MDI/BD	250	(11)
		Poly(ethyleneadipate)[PEA]/MDI/BD	230	(12)
		Hydroxy terminated poly(butadiene) [HTPB]/TDI/BD	246	(13)
		PTMO/2,4-TDI/BD	208	(14)
		PTMO/2,6-TDI/BD	200	(14)
Melting temperature	K	PCL/MDI/BD	358; 426	(11)
		PPG/MDI/BD	462; 468	(10)
		PTMG/poly (dimethylsiloxane) [PDMS]/MDI/EG	505	(15)

Polyurethane elastomers

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric loss	—	PEA/MDI	0.8	(16)
		PPO/MDI/BD (at 12.5°C)	2.2	(9)
Bulk DC conductivity	$\text{ohm}^{-1} \text{cm}^{-1}$	PPO/MDI/BD (at 12.5°C)	22×10^{12}	(9)
Surface resistivity	ohm	Oxyester/MDI/BD	1.8×10^{12}	(1)
Volume resistivity	ohm cm	Oxyester/MDI/BD	6.9×10^{11}	(1)
Contact angle	degrees	Water	89	(17)
		Water/propanol	69	
		α -Br naphthalein	25	
Surface free energy	erg cm^{-2}	Estane 5714 FI (BF Goodrich)	21	(17)
Permeation rate	$\text{mg cm}^{-1} \text{day}^{-1}$	At 25°C		(18)
		Water	0.33	
		LiCl	0.27	
		NaCl	0.24	
		KCl	0.32	
		CsCl	0.28	
Solubility parameter	$(\text{MPa})^{1/2}$	PPG(1000)/MDI/BD	23	(10)
		PPG(2000)/MDI/BD	23	
		PPG(3000)/MDI/BD	23	
Loss factor $\tan \delta$	—	PTMO/MDI/BD	0.072	(19)
Activation energy	kJ mol^{-1}	PEA/MDI/BD	152.5	(16)
		PTMO/MDI/BD	224	(19)
Tensile strength	MPa	PTMO/MDI/BD	45	(18)
		PTMO/MDI/BD (NCO/OH = 2/1)	20.16	(20)
		PTMO/MDI/BD (NCO/OH = 4/1)	37.59	(20)
Elongation	%	PTMO/MDI/BD	850	(21)
		PTMO/MDI/BD (NCO/OH = 2/1)	1,100	(20)
		PTMO/MDI/BD (NCO/OH = 4/1)	649.2	(20)
Shore A hardness	—	Poly(butyleneadipate) [PBA]/MDI/BD	85	(22)
Thermal expansion coefficient	K^{-1}	—	280	(23)

REFERENCES

1. Pandya, M. V., D. D. Deshpande, and D. G. Hundiware. *J. Appl. Polym. Sci.* 32 (1986): 4,959.
2. Hwang, K. K. S., D. J. Hemker, and S. L. Cooper. *Macromolecules* 17 (1984): 307.
3. Blackwell, J., and M. Ross. *J. Polym. Sci., Polym. Let. Ed.*, 17 (1979): 447.
4. Blackwell, J., M. R. Nagarajan, and T. B. Hoitinic. *Polymer* 23 (1982): 950.
5. Blackwell, J., C. D. Lee. *J. Polym. Sci., Polym. Phys.*, 22 (1984): 759.
6. Oberth, A. E. *Rubber Chem. and Technol.* 63 (1990): 56.
7. Simek, L., Z. Tuzar, and M. Bondanecky. *Macromol. Chem. Rapid Commun.* 1 (1980): 215.
8. Moacanin, J. *J. Appl. Polym. Sci.* 1 (1959): 272.
9. North, A. M., and J. C. Reid. *Europ. Polym. J.* 8 (1972): 1,129.
10. Petrovic, Z., Soda-So, and I. Javani. *J. Polym. Sci., Polym. Phys.*, 27 (1989): 545.
11. Russo, R., and E. L. Thomas. *J. Macromol. Sci. Phys. B* 22 (1983): 533.
12. VanBogart, J. W. C., D. A. Bluemke, and S. L. Cooper. *Polymer* 22 (1981): 1,428.
13. Bengtson, B., et al. *Polymer* 26 (1985): 895.
14. Schneider, N. S., and C. S. Paik Sung. *Polym. Eng. and Sci.* 17 (1977): 73.
15. Shibayama, M., et al. *Polymer* 31 (1990): 749.
16. Dieldes, C., and R. A. Pethrick. *Europ. Polym. J.* 17 (1981): 675.
17. Busscher, H. J., et al. *J. Colloidal and Interface Sci.* 95 (1983): 23.
18. Wells, L. A., et al. *Rubber Chem. and Technol.* 63 (1990): 66.
19. Petrovic, Z. S., et al. *J. Appl. Polym. Sci.* 38 (1989): 1,929.
20. Bajsic, E. G., et al. *Polym. Deg. Stab.* 52 (1996): 223.
21. Petrovic, Z. S., and J. B. Simendic. *Rubber Chem. and Technol.* 58 (1985): 701.
22. Nagoshi, K. In *International Progress in Urethanes*, edited by K. Ashida and K. C. Frish. Technomic Publishing, Westport, Conn., 1981, vol. 3, pp. 193.
23. Theocaris, P. S., and A. G. Varias. *J. Appl. Polym. Sci.* 30 (1985): 2,979.

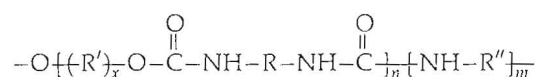
Polyurethane urea

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ACRONYMS PU, PUU

CLASS Polyurethanes

STRUCTURE



x = DP of soft segment; R = isocyanate unit

R' = soft segment; R'' = amine unit

MAJOR APPLICATIONS Polyurethane urea is useful in making interior automobile parts like armrests, head rests, gear shifts, knee protection pad, etc. Rigid integral PU foams are used in electronic and construction fields.

PROPERTIES OF SPECIAL INTEREST High compressive strength, less weight, good weatherability, and excellent properties of electrical insulation.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	g cm^{-3}	4,4'-Diphenylmethane diisocyanate (MDI)/polyether polyol/4,4'-diaminodiphenyl methane (MDA)	0.96	(1)
		MDI/polyether polyol/diethyl toluene diamine (DETDA)	0.98	
		MDI/polyether polyol/3-chloro-3'methoxy-4,4'diamino diphenylmethane (CMOMDA)	0.94	

Unit cell dimensions⁽²⁾

Sample	Lattice	Cell dimensions (Å)			Cell angles (degrees)		
		a	b	c	α	β	γ
MDI/poly(tetramethylene oxide) (PTMO)/MDA	Monoclinic	4.72	11.33	11.64	—	—	116.5

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Electron density (mean square fluctuation)	$\text{mol electron cm}^{-3}$	2,4-Toluenediisocyanate (TDI)/PTMO/ethylenediamine (EDA)	7.14×10^{-3}	(3)
Bragg spacing	Å	2,4-TDI/PTMO/EDA	140	(3)
Flory-Huggins polymer solvent interaction parameter	—	MDI/polycaprolactone diol (PCL)	0.32	(4)
		$M_n = 1,300$ /EDA (dimethylacetamide)		
		MDI/PCL(1,300)/EDA (dimethylformamide)	0.4	
		MDI/PCL(1,300)/EDA (dimethylsulfoxide)	0.45	
		MDI/PCL(2,800)/EDA (dimethylformamide)	0.42	

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Partial specific volume	—	At 25°C in DMF MDI/PCL(1300)/EDA	0.848	(4)
		MDI/PCL(2800)/EDA	0.875	
Heat of fusion	J g^{-1}	MDI/ polyether polyol /MDA	26.4	(1)
		MDI/ polyether polyol /DETDA	11.9	(1)
		MDI/ polyether polyol /CMOMDA	18.6	(1)
		MDI/PTMG/1,2-propylenediamine (PDA)	21.49	(5)
Heat capacity	$\text{J g}^{-1} \text{K}$	MDI/hydroxy terminated polybutadiene (HTPB)/ 4,4'-methyleme bis(2-chloroaniline (MOCA)	0.4	(6)
		MDI/HTPB/1,4-butanediamine (BDA)	0.389	(6)
		IPDI/PTMO/methylene bis(2-methyl-6-ethyl aniline) [MBMEA]	0.44	(7)
		IPDI/PTMO/methylene bis(2-methyl-6-isopropyl aniline) [MMIPA]	0.45	(7)
		Trimethyl hexamethylene diisocyanate/PTMO/ MBMEA	0.513	(7)
Glass transition temperature	K	MDI/polyether polyol/MDA	215.9	(1)
		MDI/polyether polyol /DETDA	220.9	(1)
		MDI/polyether polyol /CMOMDA	232.8	(1)
		MDI/PTMO/EDA	200	(8)
		MDI/PTMO/MDA	199	(8)
		MDI/PTMO/1,6-hexanediamine (HDA)	200	(8)
		TDI/PTMO/EDA	201	(8)
		2,4-TDI/PTMO(1000)/EDA	220	(9)
		2,4-TDI/PTMO(2000)/EDA	199	(9)
		2,4-TDI/PTMO/EDA	199	(3)
		MDI/PTMO/EDA	225	(10)
		MDI/aminopropyl terminated polycyanoethylmethoxysiloxane (ATPCEMS)/ 1,4-butanediol (BD)	194.1	(11)
		Lysinediisocyanate (LDI)/PCL/1,4-BDA	220.9	(12)
		1,4-butanediisocyanate (BDI)/PCL/1,4-BDA	216.3	(12)
		1,6-hexanediisocyanate (HDI)/PCL/1,4-BDA	222	(12)
		Tetramethyl xylene diisocyanate (TMXDI)/PCL/ DETDA	221.7	(13)
Melting temperature	K	TMXDI/HTPB/DETDA	198.8	(13)
Melting temperature	K	MDI/PTMO/EDA	564	(10)
		MDI/PTMG/1,2-PDA	547	(5)
Melting enthalpy	J g^{-1}	MDI/PEG(400)/EDA	60	(14)
		MDI/PEG(1500)/EDA	29	
Dielectric loss	—	TMXDI/PCL/DETDA	0.3	(13)
		TMXDI/HTPB/DETDA	0.04	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric permittivity	—	TMXDI/PCL/DETDA	6.8	(13)
		TMXDI/HTPB/DETDA	3.0	
Activation energy	kJ mol ⁻¹	TDI/POLYESTERDIOL/MOCA	42.7	(15)
		TDI/POLYETHERDIOL/MOCA	66.8	
Tensile strength	MPa	MDI/polyetherdiol/MDA	Brittle	(1)
		MDI/polyetherdiol/DETDA	14.3	(1)
		MDI/polyetherdiol/CMOMDA	10	(1)
		MDI/ATPCEMS/BD	6.65	(11)
		LDI/PCL/1,4-BDA	17	(12)
		BDI/PCL/1,4-BDA	29	(12)
		HDI/PCL/1,4-BDA	38	(12)
		MDI/PPO/DETDA	9.33	(16)
		MDI/PBA/DETDA	14.75	(16)
Elongation	%	MDI/polyetherdiol/MDA	—	(1)
		MDI/polyetherdiol/DETDA	194	(1)
		MDI/polyetherdiol/CMOMDA	103	(1)
		MDI/PTMG/1,2-PDA	360	(5)
		MDI/ATPCEMS/1,4-BD	256	(11)
		MDI/PPO/DETDA	150	(16)
		MDI/PBA/DETDA	267	(16)
Shore A hardness	—	LDI/PCL/1,4-BDA	800	(12)
		BDI/PCL/1,4-BDA	1042	
		HDI/PCL/1,4-BDA	1168	
Shore D hardness	—	2,4-TDI/PTMG/dimethylthio-2,4-toluenediamine (DM-2,4-TDA)	45	(17)
		2,4-TDI/PTMG/trimethylthio-m-phenylenediamine (TM-m-PDA)	36	
Tearing energy	kg m ²	LDI/PCL/1,4-BDA	36	(12)
		BDI/PCL/1,4-BDA	161	
		HDI/PCL/1,4-BDA	137	
Resilience	—	2,4-TDI/PTMG/DM-2,4-TDA	46	(17)
		2,4-TDI/PTMG/TM-m-PDA	37	

REFERENCES

1. Gao, Y., et al. *J. Appl. Polym. Sci.* 53 (1994): 23.
2. Ishihara, H., I. Kimura, and N. Yoshihara. *J. Macromol. Sci. Phys. B* 22 (1983-1984): 713.
3. Wilkes, G. L., and S. Abouzahr. *Macromolecules* 14 (1981): 456.
4. Sato, H. *Bull. Chem. Soc. Japan* 39 (1966): 2,335.
5. Shibayama, M., et al. *Polym. J.* 18 (1986): 719.
6. Camberlin, Y., and J. Pascault. *J. Polym. Sci., Polym. Chem. Ed.*, 21 (1983): 415.
7. Knaub, P., and Y. Camberlin. *J. Appl. Polym. Sci.* 32 (1986): 5,627.

8. Hu, C.B., and R. S. Ward, Jr. *J. Appl. Polym. Sci.* 27 (1982): 2,167.
9. Sung, C. S. P., and C. B. Hu. *Macromolecules* 14 (1981): 212.
10. Sung, C. S. P., and S. L. Cooper. *Macromolecules* 16 (1983): 775.
11. Li, C., et al. *J. Polym. Sci., Polym. Phys. Ed.*, 26 (1988): 315.
12. de Groot, J. H., et al. *Polym. Bull.* 38 (1997): 211.
13. Capps, R. N., et al. *J. Appl. Polym. Sci.* 45 (1992): 1,175.
14. Gustafson, I., and P. Flodin. *J. Macromol. Sci. Chem. A* 27 (1990): 1,469.
15. Xiaolie, L., L. Jin, and M. Dezhü. *J. Appl. Polym. Sci.* 57 (1995): 467.
16. Yiu, Y., et al. *J. Appl. Polym. Sci.* 48 (1993): 867.
17. Davis, R. L., and C. J. Nalepa. *J. Polym. Sci., Polym. Chem. Ed.*, 28 (1990): 3,701.