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Comparison of Some Soft Unplasticized Cast Polyurethane Rubbers

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ABSTRACT

Different types of unplasticized cast polyurethanes with hardness around 60 Shore A have been compared. The tensile properties, tear strength, resistance to hydrolysis, and swelling in solvents and water were examined. The influence of composition on the properties of cast polyurethanes prepared from a polyadipate polyol and diisocyanates, including the effect of a range of fillers, was investigated in detail. Fumed silica, fumed alumina, and carbon black significantly increased the hardness and tensile strength of the rubber, whereas kaolin and talc gave small increases. Ground silica, calcite, and rutile had no effect. No significant increases in tensile strength were obtained with silane and titanate coupling agents with a fumed silica filler. The rate of hydrolysis or extent of swelling in xylene was unchanged by fillers.

INTRODUCTION

A soft rubber (between 50 and 70 Shore A hardness) with good oil, hydrolysis, and tear resistance, as well as high strength, was required for a textile machine. In our preliminary work, unplasticized

cast polyurethanes met these requirements better than other types of rubber; consequently different types of soft polyurethanes have been compared in detail.

The properties of cast polyurethanes can be varied widely by using different starting materials and reaction pathways. All are prepared from the following components: polyols, diisocyanates, crosslinking agents (usually containing hydroxyl or amino groups), and additives such as fillers, plasticizers, stabilizers, and pigments. The chemical reaction and casting may be done in one step, referred to as "one-shot" methods. Alternatively prepolymers may be first prepared from polyols and diisocyanates, and crosslinking agent is added just before casting. In a further variation, blocked rather than free isocyanates can be used.

Most of the literature [1, 2] on unplasticized cast polyurethanes describes materials harder than 80 Shore A.

The normal method for softening polyurethanes (e. g., addition of plasticizers or reduced crosslinking) usually results in poor oil resistance and may reduce the strength [1, 2]. This paper reports on the influence of composition on physical properties of soft cast polyurethanes.

EXPERIMENTAL

Materials

The polyester polyol, Daltorol PR 1 (ICI Australia), was used as received without drying; its water content was below 0.05% by weight. The commercial diisocyanates, fillers, and additives (Table 1) were used as received. Other chemicals were laboratory grade.

Casting of Rubber Sheets

One-Shot Method. Unless otherwise stated, reaction mixtures contained equal number of equivalents of isocyanates and hydroxyl groups i. e., $[NCO]:[OH] = 1:1$, based on an equivalent weight of 711 for Daltorol PR1.

The polyol, fillers, and/or additives (e. g., coupling agents) were heated in a flanged multineck flask in an oven for 30 min at 110°C. The flask was transferred to an oil bath at 80°C, and a vacuum (1-2 mm Hg) applied. The mixture was stirred mechanically until the filler was uniformly dispersed. This usually took about 3 hr, after which the diisocyanate was added. The mixture was degassed and stirred for a further 10-15 min at 80°C, and then poured into aluminum molds, 110 mm × 90 mm × 2.5 mm, fitted with a steel cover with venting slits. The molds were either greased with silicone high-vacuum grease or treated with Indpol mold-release agent (Synair

TABLE 1. Materials

Brand name	Supplier	Type
Polyols		
Daltorol PR1	ICI	A liquid polyester polyol from adipic acid and diethylene glycol
PCP 0240	Union Carbide	Polycaprolactone diol OH No. 57
PCP 0300	Union Carbide	Polycaprolactone triol OH No. 310
Q-2-8026	Dow Corning	Silicone carbinol, 2% primary hydroxyls
Q-4-3557	Dow Corning	Silicone carbinol, 4.5% secondary hydroxyls
Heat-Curable, Isocyanate-Free Systems		
Indpol	Synair	(Probably contains blocked polyisocyanates with polyester backbone)
Monothane A30, A60 and A80		
Isocyanate-Terminated Prepolymers		
Adiprene L83	Du Pont	Polyether backbone, 3.2% NCO
Adiprene L100	Du Pont	Polyether backbone, 4.1% NCO
Adiprene L167	Du Pont	Polyether backbone, 6.3% NCO
Solithane 291	Thiokol	Polyester backbone, 3.3% NCO
Isocyanates		
Suprasec PR	ICI	65/35 Mixture of 2,4- and 2,6- isomers of tolylene diisocyanate = (TDI)
Desmodur T100	Bayer	2,4-Tolylene diisocyanate

(continued)

TABLE 1 (continued)

Brand name	Supplier	Type
Isonate 143L	Upjohn	Liquified 4,4'-diisocyanatodiphenylmethane (MDI)
Desmodur H (rein)	Bayer	1,6-Hexamethylene diisocyanate
Desmodur TT	Bayer	Toluene diisocyanate dimer
Isophorone diisocyanate	Veba-Chemie	3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate
Xylylene diisocyanate	Takeda	70% m- and 30% p-isomer
Fillers		
Ultrasil VN-3	ICI	Fumed silica, surface area 170 m ² /g
Cabosil M-5	Cabot	Fumed silica, surface area 230 m ² /g
Cabosil EH-5	Cabot	Fumed silica, surface area 390 m ² /g
Syloid 161	W. R. Grace	Fumed silica, average particle size 7 μm
Syloid 244	W. R. Grace	Fumed silica, average particle size 4 μm
Silancox	Cabot	Fumed silica treated with silane
Imasil A 10 H	Illinois Minerals	Fumed silica + aminosilane
Imasil A 10 S	Illinois Minerals	Fumed silica + mercaptosilane
Novakup L337-1100-1	Malvern Minerals	Laminar silica + silane
Aerosil 380	Degussa	Fumed silica surface area 380 m ² /g
300 WQ	Steelley Industries	Ground silica

Alon	Cabot	Fumed alumina
Vulkasil Al	Bayer	Precipitated sodium aluminum silicate
FY 10	Rodda	Calcite
Tioxide R-CR2	Tioxide Australia	Rutile coated with silica and alumina
Tioxide R-PP5	Tioxide Australia	Rutile coated with silica and alumina and an organic coating
K 10	Steeley Industries	Kaolin
TXF	Steeley Industries	Talc
Tintacarb 300	Australian Carbon Black	Carbon black (industry classification HAF-LS), surface area 80 m ² /g
Tintacarb 25	Australian Carbon Black	Carbon black (industry classification SRF-HMNS) surface area 30 m ² /g
Coupling Agents		
Silane Z-6020	Dow Corning	Aminoalkoxysilane
Tetrabutyl titanate	Du Pont	
Ken-React TTOP1-41B	Kenrich Petrochemicals	Phosphito-titanate ester
Ken-React TSN2-37S	Kenrich Petrochemicals	Amino-titanate ester
Ken-React GTDOP-112S	Kenrich Petrochemicals	Oxyacetate-titanate phosphate ester
Ken-React GTDN-152S	Kenrich Petrochemicals	Oxyacetate-titanate amino ester
Ken-React ETNS-226S	Kenrich Petrochemicals	Ethylene titanate amino ester
Ken-React TTBS-9S	Kenrich Petrochemicals	Ethylene titanate ester

(continued)

TABLE 1 (continued)

Brand name	Supplier	Type
Ken-React ETDOP-212	Kenrich Petrochemicals	Ethylene titanate phosphate
Ken-React TTLPI-36B	Kenrich Petrochemicals	Phosphito-titanate
Ken-React TB2NS-26S	Kenrich Petrochemicals	Amino-titanate
Ken-React TTEE-44	Kenrich Petrochemicals	Amino-titanate
Antihydrolysis Agents		
Daltogard PR	ICI	Monomeric carbodiimide
Epikote 828	Shell Chemical	Bisphenol-A diglycidyl ether
1,4-Butanediol diglycidyl ether	Aldrich Chemical	
Paraplex G62	Rohm & Haas	Epoxidized soya bean oil

Corp., Tustin, Calif.). The polyurethanes were cured by heating the molds for 16 hr at 110°C in an oven. Normally, acidic materials are recommended to be added to this type of cast polyurethane to retard reaction and increase the pot-life [1-2]. However, small amounts (~0.03%) of either tartaric acid or benzoyl chloride caused little change in the pot-life and curing time and no apparent change in the rubber properties, so no addition was made in the work reported.

Prepolymer Method. With rubbers prepared from isocyanate-containing prepolymers, the prepolymer and filler were heated as above for 30 min at 110°C and then degassed by stirring under vacuum for about 3 hr at 80°C. The polyol crosslinking agent was added and, after degassing for a further 15-30 min, the mixture was cast and cured as before.

Heat-Curable Isocyanate-Free Systems. The Monothane preparations were used as received. The material was poured into heated molds and cured for 16 hr at 110°C. Degassing was unnecessary.

Testing Methods

Tensile testing was carried out according to ASTM method D412-75, using dumbbell-shaped samples with a gauge length of 37 mm. ASTM method D624-73 was followed for the tear tests using both dies B and C. Swelling tests were carried out in distilled water or organic solvents at 20°C following ASTM procedure D471-75. The maximum variation between the three replicate samples in these tests was 5% for swelling, 10% for tear and tensile tests, and 20% for elongation. Hardness was determined with a Zwick Shore A durometer. The variability in hardness between sheets from different batches of the one formulation was ± 2 Shore A units.

Hydrolytic Degradation Experiments

Two sets of conditions were used: (A) exposure at 50°C in a desiccator containing saturated potassium nitrate solution, which produces an atmosphere of approximately 80% R. H. [3]; (B) immersion in boiled distilled water in screw-top jars placed in a water bath thermostatted to 50°C.

Periodically, the samples were removed and the hardness was tested immediately. Before the sheets were cut into strips for tensile testing they were allowed to equilibrate at room temperature (22°C, 50% RH).

RESULTS AND DISCUSSION

One-shot, prepolymer, and blocked-isocyanate cast polyurethanes were examined (Tables 2-4). A variety of polymer backbones were investigated, but most of the work (Tables 2 and 3) was on one-shot types prepared from a commercial liquid polyadipate polyester polyol and tolylene diisocyanate (65% 2,4- and 35% 2,6-isomer mixture). In this system, the use of fillers to increase strength was studied in detail (Table 2). The effect of diisocyanate structure was also examined (Table 3).

Effect of Fillers

The effect of fillers on the properties of conventional rubbers has been investigated very extensively [4, 5], but very little has been published on cast polyurethanes containing fillers [6-8]. In the present study a range of fillers was incorporated into a one-shot polyurethane formulation by using a polyadipate polyol and tolylene diisocyanate (Table 2).

The amount of filler (up to about 20 parts phr) which could be practically incorporated in the cast polyurethanes studied was much lower than normally added to rubbers. This was because it was difficult to produce uniform dispersions and the increase in viscosity at high filler loadings, especially with carbon black and high-surface-area fumed silica, made it difficult to produce bubble-free rubbers. In some cases, (e. g., the Syloids and Vulkasil Al) the fillers considerably reduced the pot-life of the casting mixture.

Different fillers had different effects (Table 2). Firstly, with fumed silica, fumed alumina, and carbon black tensile and tear strengths were markedly increased, hardness was significantly increased, but the extent of swelling in xylene or water was unchanged. These fillers are commonly used [4, 5] as reinforcing fillers for other rubbers. Presumably they can interact strongly with the polyurethane, e. g., through hydrogen bonds.

With a second group of fillers—kaolin and talc—the increase in strength and hardness was small. With a third group—ground silica, calcite, and rutile—the properties of the polyurethanes were unchanged.

Results with carbon black fillers were variable, probably because of the problem of producing uniform dispersions, even though printing ink grade (i. e., powdered rather than granular) carbon black was used. Better dispersion, e. g., by using high-shear mixing, might have enhanced reinforcement but is unlikely to have reduced the viscosity and/or increased the pot-life of the casting mixture.

The effect of concentration of filler was examined with one silica and one carbon black (Table 2). With both, tensile and tear strength increased with filler concentration. The hardness increased with silica concentration (up to 20%). With carbon black, maximum

TABLE 2. Properties of Daltorol PR1 - Suprasec PR Rubbers

Filler and concn ^a	Additive ^b	Hardness Shore A	Tensile strength (N/mm ²)	Elongation (%)	Tear strength (N/mm)	
					Die B	Die C
None	None	57	1.4	150	4.8	5.3
Fumed Silica Fillers						
Ultrasil VN3 (2%)	-	59	1.9	200	6.1	5.5
Ultrasil VN3 (5%)	-	62	2.2	200	7.2	6.9
Ultrasil VN3 (10%)	-	65	3.4	250	13.1	11.6
Ultrasil VN3 (20%)	-	72	5.2	300	14.6	18.6
Cabosil M-5 (5%)	-	65	3.5	250	7.4	
Cabosil EH-5 (5%)	-	64	3.0	200	8.3	7.4
Imsil A 10 H (10%)	-	62	2.3	200	6.7	6.9
Imsil A 10 S (10%)	-	58	2.0	300	6.9	6.9
Novakup 337-1100-1 (10%)	-	57	2.0	250	8.8	6.7
Silanox (10%)	-	61	2.3	200	9.7	
Aerosil 380 (5%)	-	64	3.0	250	8.0	8.0
Syloid 161 (10%)	-	Gelled before casting				
Syloid 244 (10%)	-	Gelled before casting				

(continued)

TABLE 2 (continued)

Filler and concn ^a	Additive ^b	Hardness Shore A	Tensile strength (N/mm ²)	Elongation (%)	Tear strength (N/mm)	
					Die B	Die C
Carbon Black Fillers						
Tintacarb 300 (2%)	-	59	2.7	150	5.4	6.3
Tintacarb 300 (5%)	-	64	2.5	150	8.2	7.0
Tintacarb 300 (10%)	-	65	3.1	200	8.3	7.3
Tintacarb 300 (20%)	-	55	4.5	400	12.2	14.2
Tintacarb 25 (10%)	-	64	3.6	250	8.0	8.4
Miscellaneous Fillers						
Vulkasil A1 (10%)	-	Gelled before casting				
Alon (10%)	-	65	2.9	200	8.4	9.0
FY10 (10%)	-	57	1.9	200	5.8	5.1
Tioxide R-CR2 (10%)	-	54	1.3	150	5.9	5.3
Tioxide R-PP5 (10%)	-	55	1.8	250	5.8	5.3
TXF (10%)	-	60	2.0	200	6.1	5.2
K 10 (10%)	-	58	2.1	200	6.6	6.4
300 WQ (10%)	-	55	1.2	300	4.4	
300 WQ (10%)	Silane Z-6020	Gelled before casting				

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Antihydrolysis Additives						
Ultrasil VN3 (10%)	Epikote 828	63	3.1	250	8.3	7.9
Ultrasil VN3 (10%)	Paraplex G62	63	3.0	250	7.5	8.1
Ultrasil VN3 (10%)	1,4-Butanediol diglycidyl ether	61	3.0	250	7.7	8.0
Ultrasil VN3 (10%)	Daltogard PR	64	3.3	250	11.4	10.6
Polyol Additives						
Ultrasil VN3 (10%)	Q-4-3357 (17%)	47	1.7	250		
Ultrasil VN3 (10%)	Q-2-8026 (33%)	60	1.4	150		
Ultrasil VN3 (10%)	Castor oil	72	4.5	150	10.6	8.8
Silica + Coupling Agents						
Ultrasil VN3 (10%)	Ken-React TTOPI-41B	64	3.0	300	10.3	9.6
Ultrasil VN3 (10%)	Ken-React TSN2-37S	57	2.4	300	10.5	9.6
Ultrasil VN3 (10%)	Ken-React GTDOP-112S	60	2.6	300	9.7	9.9
Ultrasil VN3 (10%)	Ken-React GTDN-152S	40	2.7	600	9.5	8.9
Ultrasil VN3 (10%)	Ken-React ETNS-226S	60	3.1	400	10.5	10.8
Ultrasil VN3 (10%)	Ken-React TTBS-9S	65	2.6	350	9.4	8.9
Ultrasil VN3 (10%)	Ken-React ETDOP-212	70	4.0	250	11.4	10.2
Ultrasil VN3 (10%)	Ken-React TTLPI-36B	61	1.9	200	8.2	8.6
Ultrasil VN3 (10%)	Ken-React TB2NS-26S	70	1.7	300	9.5	8.3
Ultrasil VN3 (10%)	Ken-React ETDOP-212 (0.1%)	67	3.2	200	9.7	9.0

(continued)

TABLE 2 (continued)

Filler and concn ^a	Additive ^b	Hardness Shore A	Tensile strength (N/mm ²)	Elongation (%)	Tear strength (N/mm)	
					Die B	Die C
Ultrasil VN3 (10%)	Ken-React GTDN-152S (0.1%)	72	3.4	150	11.6	6.3
Ultrasil VN3 (10%)	Ken-React TTEE-44	Gelled before casting				
Ultrasil VN3 (10%)	Tetrabutyl titanate	Gelled before casting				
Ultrasil VN3 (10%)	Silane Z-6020	67	3.2	150	8.5	

^a Figures in brackets refer to percentage (w/w) based on amount of Daltorol PR1.

^b 1% w/w unless otherwise stated.

TABLE 3. Effect of Diisocyanate Structure and [NCO]:[OH] Ratio on Daltorol PR1-Based Rubbers Containing Ultrasil VN3 (10%)

Diisocyanate	[NCO]:[OH] ratio	Hardness Shore A	Tensile strength (N/mm ²)	Elongation (%)	Tear strength (N/mm)		
					Die B	Die C	Die C
2,4- and 2,6-Tolyene diisocyanate (65/35)	1:1	65	3.4	250	13.1	11.6	11.6
2,4- and 2,6-Tolyene diisocyanate (65/35)	0.8:1	30	1.3	800			
2,4- and 2,6-Tolyene diisocyanate (65/35)	1.2:1	71	2.8	150			8.1
2,4-Tolyene diisocyanate	1:1	66					
Isophorone diisocyanate	1:1	60	2.9	250	11.3		
m-Xylylidene diisocyanate	1:1	44	1.9	250	7.4	6.3	
1,6-Hexamethylene diisocyanate	1:1	63	2.7	200	7.7	5.7	
4,4'-Diisocyanatodiphenylmethane	1:1	72	4.1	200	9.9	8.4	
Dimer of 2,4-tolyene diisocyanate	1:1	67	4.0	200	8.4	10.7	

TABLE 4. Properties of Some Unplasticized Cast Polyurethane Rubbers with Hardness 35-85 Shore A

Formulation type ^a	Formulation ^b	Hardness Shore A	Tensile strength (N/mm ²)	Elongation (%)	Tear strength (N/mm)		
					Die B	Die C	Die A
One-shot method							
(a)	Daltorol PR1 + TDI + Ultrasil VN3 (10%)	65	3.4	250	13.1	11.6	
(c)	PCP0240/PCP0300 (4:1) + TDI	63	6.8	500	6.7	17.7	
Two-step prepolymer method							
(b)	Adiprene L83 + Ultrasil VN3 (6%) + trimethylolpropane/1,4-butanediol (1:0.8)	64	12.0	800		21.3	
(b)	Adiprene L100 + 1,4 butanediol	62	13.5	1200			
(b)	Adiprene L100 + trimethylolpropane/1,4-butanediol (1:3.6)	65	5.4	500		13.9	
(b)	Adiprene L100 + trimethylolpropane/1,4-butanediol (1:0.8)	67	3.4	200	12.0	13.9	
(b)	Adiprene L100 + Ultrasil VN3 (6%) + trimethylolpropane/1,4-butanediol (1:0.8)	69	7.2	300	11.6	12.1	
(b)	Adiprene L100 + Ultrasil VN3 (6%) + triisopropanolamine/1,4-butanediol (1:2.3)	67	10.7	1000			

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(b)	Adiprene L100 + Ultrasil VN3 (6%) + triisopropanolamine	64	7.8	650	18.2
(b)	Adiprene L100 + Daltoral PR1	58	2.1	350	
(b)	Adiprene L167 + Ultrasil VN3 (6%) + trimethylolpropane/1,4- butanediol (1:0.8)	70	5.4	300	12.3
(d)	Solithane 291 + trimethylolpropane/ 1,4-butanediol (1:1) ^c	60	> 6.2	> 850	40.5
(d)	Solithane 291 + trimethylolpropane/ 1,4-butanediol (3:1) ^c	60	> 19.3	> 1300	20.2
(d)	Solithane 291 + Ultrasil VN3 (10%) + trimethylolpropane/1,4- butanediol (3:1) ^c	68	21.8	750	29.6
(d)	Solithane 291 + trimethylolpropane/ triisopropanolamine (2:1)	61	21.0	800	25.4
(d)	Solithane 291 + PCP0300 ^c	58	19.7	900	25.1
(d)	Solithane 291 + Daltoral PR1 + Daltogard PR (1%)	45	7.1	1200	
Heat-curable, isocyanate-free systems					
(e)	Indpol Monothane A30	35	4.8	1000	8.6
(e)	Indpol Monothane A60	65	> 8.7	> 1100	16.8
(e)	Indpol Monothane A80	85	14.1	900	32.4

^a Classification used in conclusions section.

b [NCO]:[OH] ratio = 1:1 unless otherwise stated.

c [NCO]:[OH] ratio = 0.95:1.

hardness was attained at 5-10%, and the reduction at 20% may have been the result of poor dispersion.

The addition of about 10% fumed silica or carbon black filler produced a useful practical improvement in tensile and tear strength, although hardness was also increased. Silica with moderate surface area (e. g., Ultrasil VN3) was preferable to either high-surface-area silica or carbon black because viscosity of the casting mixture and pot-life were less affected and production of bubble-free castings was facilitated.

Effect of Silane and Titanate Coupling Agents

Some silane [9] or titanate [10, 11] coupling agents to have been reported to improve the physical properties of filled elastomers. In the present study (Table 2) tensile strength was not increased significantly in the systems examined. These included the use of amino- and mercapto-functional silane pretreated silicas, or the addition of various silane or titanate coupling agents to the mixture of polyol and fumed silica before the diisocyanate was added. Strength was actually reduced in some systems, and the addition of titanates caused a considerable variation in hardness. Reduction in hardness was usually associated with the use of a coupling agent containing groups capable of reaction with isocyanates. This presumably reduces the isocyanate-hydroxyl stoichiometry below 1:1, which has been shown (below) to reduce hardness and tensile strength. Two titanates (tetrabutyl titanate and the aminofunctional Ken React TTEE-44) caused rapid gelation of the reaction mixture.

Effect of Diisocyanate and Polyol Structure

The physical properties of cast polyurethanes can be changed [1, 2] by varying the diisocyanate and polyol structure. In the present study, variation in diisocyanate structure and concentration (Table 3) caused trends similar to those found earlier [2, 12]. For example, hardness increased with TDI concentration; with isocyanate-hydroxyl ratios of 0.8:1, 1:1, and 1.2:1, hardness values of 30, 65, and 71 were obtained, respectively. Aromatic isocyanates gave stronger and harder rubbers than aliphatic diisocyanates, and the materials incorporating MDI and TDI dimer were stronger than those containing TDI. However, with MDI, pot-life was reduced slightly. Whether pure 2,4-tolylene diisocyanate or the 65% 2,4-, 35% 2,6-isomer mixture was used had no effect on hardness.

Addition of castor oil to the polyadipate polyol-TDI cast polyurethane increased strength and hardness, whereas addition of silicenes with hydroxyl-functional groups had the opposite effect (Table 2).

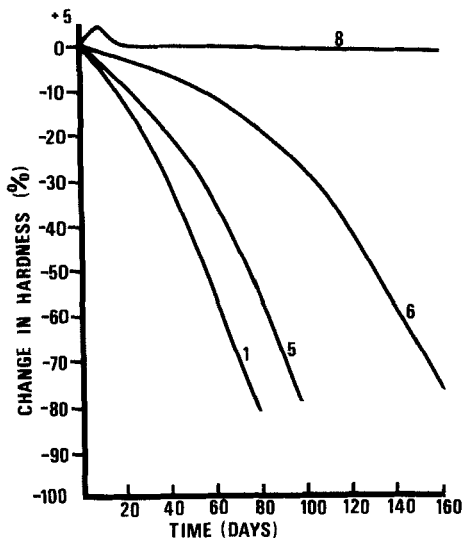


FIG. 1. Change in hardness of polyurethane rubbers after immersion in water at 50°C: (1) Daltorol PR1/TDI with and without Ultrasil VN3 (10%); (2) Daltorol PR1/TDI + Tintacarb 300; (3) Daltorol PR1/TDI + Epikote 828; (4) Solithane 291/1,4-butanediol/trimethylolpropane; (5) Daltorol PR1/TDI with and without Ultrasil VN3 (10%) + Daltogard PR; (6) PCP0240/PCP0300/TDI; (7) PCP0240/PCP0300/TDI + Daltogard PR; (8) Adiprene L100/1,4-butanediol/trimethylolpropane.

Resistance to Hydrolytic Degradation

Results of tests for resistance to hydrolytic degradation are shown in Figs. 1 and 2 mainly for the polyadipate-TDI rubbers as well as some other cast polyurethane rubbers of similar hardness. The expected order [13-16] of stability of polyether > polycaprolactone > polyester was found. The antihydrolysis agent, Daltogard PR (a carbodiimide), stabilized both polycaprolactone and polyester against hydrolysis. Patent claims [17, 18] that the hydrolysis resistance of polyester polyurethanes can be improved by adding epoxides could not be substantiated. Silica and carbon black filler had no effect on the rate of hydrolysis of the polyadipate-TDI polyurethane. One commercial polyester prepolymer (Solithane 291) cured with 1,4-butanediol/trimethylolpropane was more resistant to hydrolysis than the one-shot polyadipate polyester polyurethane.

As degradation proceeded with the polyadipate polyurethane rubber,

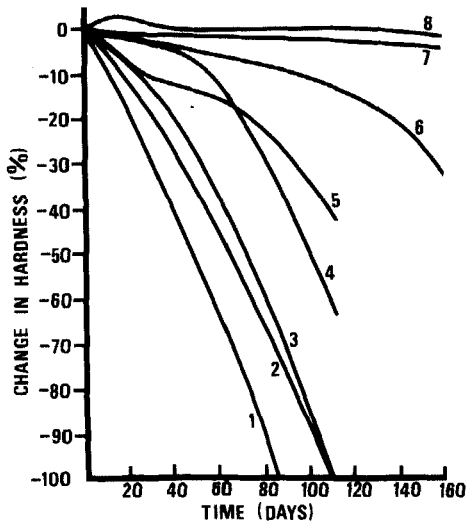


FIG. 2. Change in hardness of polyurethane rubbers after exposure to 80% humidity at 50°C. Key to curves as in Fig. 1.

the elongation increased but the modulus and hardness decreased. The tensile strength also decreased, but at a lower rate than the hardness or modulus. In our work measuring hardness was found to be a simple and sensitive method of monitoring degradation.

Why the polycaprolactone polyurethane should have better hydrolysis resistance than polyadipates is not clear. It may be due to polarity differences, as there are more methylene groups per oxygen atom in a polycaprolactone than in a poly(diethylene glycol adipate). At 20°C in water there was little difference in swelling (2-4%). However, in a polar solvent such as dimethylformamide, the polycaprolactone (Table 4) and the silica filler (10% Ultrasil VN3) polyadipate polyurethane swelled similarly (185 and 170%, respectively). In contrast, in the nonpolar xylene, swelling was 82% and 25%, respectively, which appears to confirm such a polarity difference.

CONCLUSIONS

The properties of cast polyurethane rubbers of hardness between 50 and 70 Shore A have been compared. As good resistance to oil swelling was required, formulations containing plasticizers were not examined. With the isocyanate-terminated prepolymers it was necessary to use polyol crosslinking agents, as agents containing

primary amino groups gave much harder rubbers; for example, 4,4'-methylene-bis-2-chloroaniline (MOCA) gave rubbers with a hardness above 90 Shore A.

Five types of polyurethane (see Table IV) had a hardness within the desired range: (a) one-shot polyester (polyadipate) polyol-TDI; (b) polyether(polyoxytetramethylene) isocyanate-terminated prepolymers crosslinked with polyols; (c) one-shot polycaprolactone diol/triol mixture and TDI; (d) polyester isocyanate-terminated prepolymer crosslinked with polyols; (e) one-component heat-curable polyurethane containing no free isocyanates.

For these polyurethanes the order of performance was as follows. Tensile and tear strength:

$$d \approx e > c > b > a \text{ containing silica} > a$$

Swelling by water after 8 weeks at 20°C:

$$b (3.3\%) > \text{filled or unfilled } a (2.5\%) > d (2.0\%) > c (1.7\%) \\ > e (-2.2\%)$$

Hydrolysis resistance:

$$b > c \approx e > \text{carbodiimide-stabilized } a > d > a$$

Swelling by solvents:

$$b > c > a$$

Addition of fumed silica filler increased strength and hardness but more so with a or c than with b.

It is also important with polyurethanes to consider performance during casting. Fillers should disperse readily, the pot-life should be as long as possible, and the castings should be bubble-free. The pot-lives of the above casting mixtures were in the order $e \gg b \approx d > c > a > \text{carbodiimide-stabilized } a$. When silica filler (Ultrasil VN3) was added it dispersed most rapidly in a and d, but increased the viscosity of d, so that a and c were the easiest to cast.

The cast polycaprolactone polyurethane rubbers showed the most promise for requirement, and a detailed study of this system will be reported later.

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REFERENCES

- [1] J. H. Saunders and K. C. Frisch, Polyurethanes: Chemistry and Technology, Vol. 2, Interscience, New York, 1964, Chap. IX.
- [2] P. Wright and A. P. C. Cumming, Solid Polyurethane Elastomers, Maclaren and Sons, London, 1969.
- [3] E. W. Washburn, Ed., International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol. I, McGraw-Hill, New York, 1926, p. 67.
- [4] G. Kraus, Reinforcement of Elastomers, Interscience, New York, 1965.
- [5] M. P. Wagner, Rubber Chem. Technol., 49, 703 (1976).
- [6] J. A. Verdol, D. J. Carrow, P. W. Ryan, and K. L. Kuncel, Rubber Age, 57 (July 1966).
- [7] H. R. Bylisma, Ind. Eng. Chem. Prod. Res. Dev., 3, 204 (1963).
- [8] J. M. Buist, G. P. Crowley, H. France, and G. Trappe, Proceedings Rubber Technology Conference 4th, London, 1964, p. 541.
- [9] B. Arkles, Chem. Tech., 7, 766 (1977).
- [10] Kenrich Petrochemicals Inc., Bayonne, New Jersey, Bulletins KR-0975-2 and KR-0376-4, and Paper No. 40.
- [11] S. J. Monte and G. Sugerman, Org. Coatings Plast. Chem., 38, 49 (1978).
- [12] T. L. Smith and A. B. Magnusson, J. Polym. Sci., 42, 391 (1960).
- [13] G. Magnus, R. A. Dunleavy, and F. E. Critchfield, Rubber Chem. Technol., 39, 1328 (1966).
- [14] J. Wright, Eur. Rubber J., 13, (1977).
- [15] J. Matthan, M. Weichers, and K. A. Scott, in Aging and Weathering of Plastics, J. Matthan, K. A. Scott, and M. Weichers, Eds., RAPPRA, England, 1970, p. 5.
- [16] B. E. Brockenbrow, D. Sims and J. Wright, Rubber J., 48 (June 1971).
- [17] S. Kaizerman and A. Singh (American Cyanamid), Austral. Pat. 483, 419 (Oct. 30, 1972).
- [18] A. F. Finelli (Goodyear Tire and Rubber Co.), U. S. Pat. 4,036,906 (Dec. 30, 1969).