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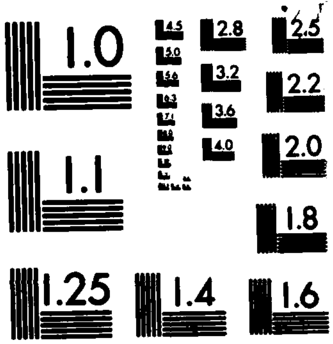

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PREPARATION AND PROPERTIES OF POLYURETHANE AND POLYURETHANEUREA ELASTOMERS FROM METHYLENE BIS(4-CYCLOHEXYLISOCYANATE)

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POLYMER RESEARCH DIVISION

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ABSTRACT

Transparent polyurethane elastomers have been prepared and evaluated as flexible lens materials. The main ingredients of the polymers include methylene bis(4-cyclohexylisocyanate), poly(tetramethylene oxide) polyols, and 1,4-butanediol, with small amounts of ethylene glycol and trimethylol propane added to improve properties. The polymers exhibit very good mechanical properties for the desired use, however, the low temperature (-20°C) bend recovery needs to be improved. Additional problems include the lack of a completely suitable mold release system, in which the molds could be used repeatedly and produce consistently good optical quality samples. This difficulty arises from the exceptionally strong adherence of polyurethane elastomers to mold surfaces compared to other polymers. Excellent samples were prepared on polypropylene sheets which had been press polished, but the repeated use of this material as a mold at 100°C under pressure might not be possible.

CONTENTS

Page

DIFFERENTIAL SCANNING CALORIMETRY

THERMOMECHANICAL ANALYSIS

DYNAMIC MECHANICAL ANALYSIS

BEND RECOVERY

HARDNESS

TENSILE PROPERTIES

MOLDS AND MOLD RELEASES

ADDITIVES TO POLYMERS

INTRODUCTION

Polyurethane elastomers can be prepared with numerous compositional variations. The polymers which result have great differences in properties, including strength, flexibility, hydrolytic and ultraviolet stability, and degree of opacity. The goal of this work is to prepare polyurethanes of moderate strength which are transparent and non-yellowing for flexible lens applications. The materials should exhibit good flexibility at temperatures below zero and recovery from storage in a folded configuration.

For the polyurethanes, methylene bis(4-cyclohexylisocyanate) (H_{12}MDI, Table 1) was chosen, because aliphatic diisocyanates lead to minimal yellowing in the product. It is supplied as a mixture of three geometric isomers (shown in Figure 1); the exact ratio depending on the method of preparation. The trans-trans diisocyanate isomer, present as about 50% of the diamine from which the diisocyanate is synthesized, precipitates out of the isomer mixture at 25°C. When the amount of trans-trans is reduced to 20% to 30%, the mixture remains liquid and is easier to handle. The trans-trans isomer is removed in practice as the amine, which is commercially important for the production of nylon fibers. The diisocyanate mixture which is marketed is, thus, about 20% to 30% trans-trans, 65% cis-trans, and about 5% cis-cis isomer.[1,2,3] Use of this mixture leads to little or no crystallinity in the hard segment microdomains and transparent polymers are produced. Poly(tetramethylene oxide) polyols (PTMO) were emphasized rather than polyesters because of their hydrolytic stability and lower glass transition temperature with superior low temperature properties. Amine cured polymers were first prepared to maximize phase segregation but were not sufficiently flexible. Diol cures were then used and it was found that reasonable mechanical properties could be attained with properly catalyzed samples.

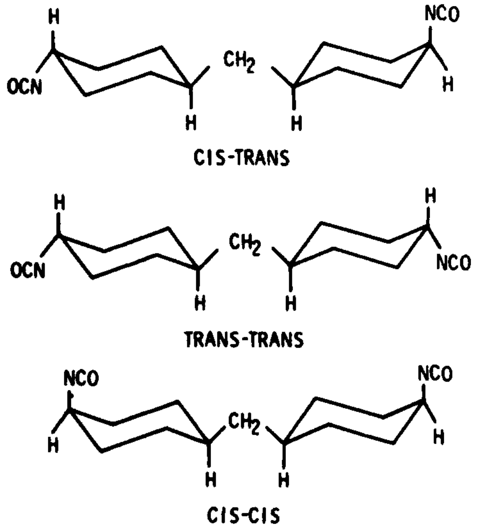


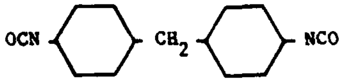
Figure 1. Isomers of methylene bis(4-cyclohexylisocyanate).

1. VAN BOGART, J. W. C., LILAONITKUL, A., LERNER, L. E., and COOPER, S. L. *Morphology and Properties of Short Segment Block Copolymers.* J. Macromol. Sci.-Phys., v. B17, no. 2, 1980, p. 267-301.
2. IRWIN, C. F. Canadian Patent No. 971,184, issued to DuPont, 1975.
3. British Patent No. 1,220,715, issued to Allied Chem. Corp., 1971.

Table 1. REACTANTS FOR POLYURETHANES AND POLYURETHANEUREAS

Isocyanate

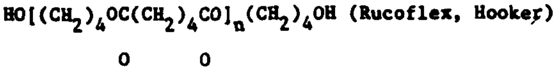
Methylene bis(4-cyclohexylisocyanate) [H_{12}MDI, Hylene W, DuPont (discontinued); Desmodur W, Mobay]



Polyols

PTMO 2900, 2000, 1000, 650 $HO(CH_2CH_2CH_2CH_2O)_nH$ (Teracol, DuPont; Polymeg, Quaker Oats)

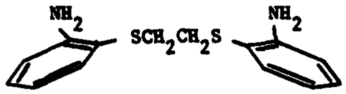
PBA 1000



$HO[(CH_2)_4O\overset{}{\underset{O}{C}}(CH_2)_4\underset{O}{C}O]_n(CH_2)_4OH$ (Rucoflex, Hooker)

Amine

1,2-bis(2-aminophenylthio)ethane



(Apocure 601, M&T Chemical; Cyanacure, American Cyanamid)

Low Molecular Weight Diols and Triols

1,4-Butanediol

Trimethylol Propane $C_2H_5C(CH_2OH)_3$

Ethylene Glycol

3-Methyl-2,4-Pentanediol

1,6-Hexanediol

Catalyst

Dibutyl tin dilaurate (T-12, M&T Chemical)

This report is divided into sections in which a short experimental description of the technique used is followed by a discussion of the results. The topics included are synthesis, differential scanning calorimetry, thermomechanical analysis, dynamic mechanical analysis, bend recovery, Shore A hardness, tensile properties, molds and mold releases, additives, surface treatment, pyrolysis - gas chromatography - mass spectroscopy, and Fourier transform infrared spectroscopy.

SYNTHESIS

A representative synthesis includes the preparation of a large batch of the prepolymer from which portions were withdrawn for cure with diol or diamine. In a 500 ml three-necked round-botton flask 247.87 g PTMO 1999 (0.124 mole, Polymeg, Quaker Oats) were stirred under vacuum in an oil bath at 100°C for at least 2 hours. The vacuum was broken and nitrogen was bubbled in while 85.4 g H_{12}MDI (0.326 mole, Desmodur W, Mobay) were added from a 50 ml syringe, as well as 350 ℓ of a solution of T-12 catalyst (4 wt-vol %) in MEK (a mixture containing dibutyl tin dilaurate, M&T chemical). This mixture was stirred under vaccum at 100°C for 1-1/2 hours. The resulting prepolymer was stored under nitrogen in the refrigerator until needed.

To prepare a polymer with mole ratio 2.625 $H_{12}MDI$, 1.0 PTMO 2000, and 1.5 1,4-butanediol, the prepolymer was heated to 80°C and withdrawn wtih a 50 ml disposable syringe. In a polyethylene beaker, 57.13 g prepolymer and 2.87 g 1,4-butanediol at 80°C were weighed and mixed at high speed using a regular laboratory mechanical stirrer for 1-1/2 minutes. The polymer was degassed in a vacuum dessicator for 1-1/2 minutes and poured into a mold preheated to 100°C. The mold was placed in a press at approximately 150 psi for 1 hour at 100°C and was then post cured in the oven for 15 hours at 100°C. Samples were aged for a minimum of two weeks before analysis.

Many samples have been synthesized and their compositions will be indicated in sections where their properties are discussed. The sample composition in the synthetic description above will be referred to as the standard composition. It is the sample type which has been characterized and utilized most frequently throughout the work.

DIFFERENTIAL SCANNING CALORIMETRY

Experimental

A Perkin-Elmer DSC-2 cooled with liquid nitrogen and purged with helium was used for the thermal analysis. Samples weighing 10 mg to 15 mg were encapsulated in standard crimped aluminum pans and placed in the DSC sample chamber. The samples were chilled to 150°K at 80°/min and then heated from 150°K to 300°K at 20°/min to determine the T_{g1}.* It was necessary to scan up to 400°K when looking for the T_{g2}. Analyses of the resulting curves were performed using a Perkin-Elmer Thermal Analysis Data Station to determine the glass transition temperatures. This procedure was repeated three times on each sample and an average was taken of the results.

Results and Discussion

Polyurethaneureas

A small number of samples with Apocure 601 amine chain extender (M&T chemical) were prepared early in this investigation. This was done because it was believed that polyurethanes cured with diols would not exhibit the desired mechanical properties. The yellowing sometimes associated with the use of amines was thought to be a solvable problem. When good mechanical properties were achieved on proper cure with diols, the amine chain extenders were abandoned. Only thermal analysis data is available for the amine cured polymers.

In Table 2, two polyurethaneureas prepared from PTMO 2000 are reported with T_{g1}* elevated 15°C to 25°C above the T_g of the pure polyol. For both samples using polyols of 1000 molecular weight, elevations of 30°C to 40°C above the T_g occur. Generally, the lower the soft segment molecular weight, the greater the elevation of T_{g1}, which is a measure of phase mixing. The effects seen here will be constrasted with those for polyurethanes where phase mixing occurs to a lesser extent, as indicated by thermal analysis. Phase mixing of PTMO 1000 soft segments with hard segments has also been reported for amine cured polymers prepared from 2,4-toluene diisocyanate.[4]

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*T_{g1} is the glass transition temperature of the soft segment; T_{g2} is that of the hard segment.

[4] PAIK SUNG, C. S., HU, C. B., and WU, C. S. *Properties of Segmented Poly(urethaneureas) Based on 2,4-Toluene Diisocyanate. 1. Thermal Transitions, X-Ray Studies, and Comparison with Segmented Poly(urethanes).* Macromolecules, v. 13, no. 1, 1980, p. 111.

Table 2. POLYMER COMPOSITIONS AND T_{g1}'S* FROM DSC

a. POLYURETHANEUREAS

Moles H_{12}MDI/Polyol/Amine	Polyol	$\frac{NCO}{NH_2+OH}$	Wt% Hard Segment	T_{g1}(°C)
2.0-1-0.9	PBA 1000	1.08	41.7	-35.8
	PBA 2000		0.0	-65
1.8-1-0.7	PTMO 1000	1.06	40.1	-49.7
	PTMO 2000		0.0	-85
3.0-1-1.9	PTMO 2000	1.05	40.3	-63.7
4.0-1-2.6	PTMO 2000	1.13	47.6	-70.3

b. POLYURETHANES

1. H_{12}MDI-PTMO 2000-1,4-Butanediol

Moles H_{12}MDI/PTMO/BD	NCO/OH	Wt% Hard Segment	T_{g1}(°C)
4.0-1-3.0	1	39.8	-75.4
2.5-1-1.5	1	28.3	-74.0
2.0-1-1.0	1	23.5	-75.1
2.6-1-1.5	1.05	29.2	-73.8
2.1-1-1.0	1.05	23.9	-73.6
2.5-1-1.1	1.18	27.1	-72.4
2.5-1-1.9	0.85	28.9	-77.0

2. With Various Mol. Wt. PTMO

Moles H_{12}MDI/PTMO/BD			
2.6-1-1.5 (3)†	1.05	22.1	-76.1
2.6-1-1.5 (2)	1.05	29.2	-73.8
2.6-1-1.5 (1)	1.05	46.0	-60.0
2.6-1-1.5 (0.6)	1.05	55.9	+15.4

3. With 1,4-Butanediol and Ethylene Glycol, PTMO 2000

Moles H_{12}MDI/PTMO/BD/EG			
2.6-1-0.0-1.5	1.05	28.1	-76.1
2.6-1-1.35-0.15	1.05	29.4	-74.2

4. With Trimethylol Propane, PTMO 2000

Moles H_{12}MDI/PTMO/BD/TMP			
2.5-1-1.2-0.2	1.0	27.9	-76.1
3.0-1-1.7-0.2	1.0	32.2	-75.9

---

*T_{g1} is the glass transition temperature of the soft segment.

†Designation (3) refers to PTMO 2900, (2) to PTMO 2000, etc. Samples without designation are samples prepared from PTMO 2000.

Polyurethanes

DSC was used mainly to determine the low temperature transitions of the polyurethanes. All of the PTMO 2000 samples exhibit T_{g1} elevated only about 10°C above that of the pure polyol. This indicates a low degree of phase mixing. The same is true for the polyurethane prepared from PTMO 2900 shown in Figure 2a and Table 2. As is generally the case, the samples prepared from lower molecular weight polyols, PTMO 1000 and 650,* exhibit elevated T_{g1} which represent evidence of phase mixing and loss of mobility.

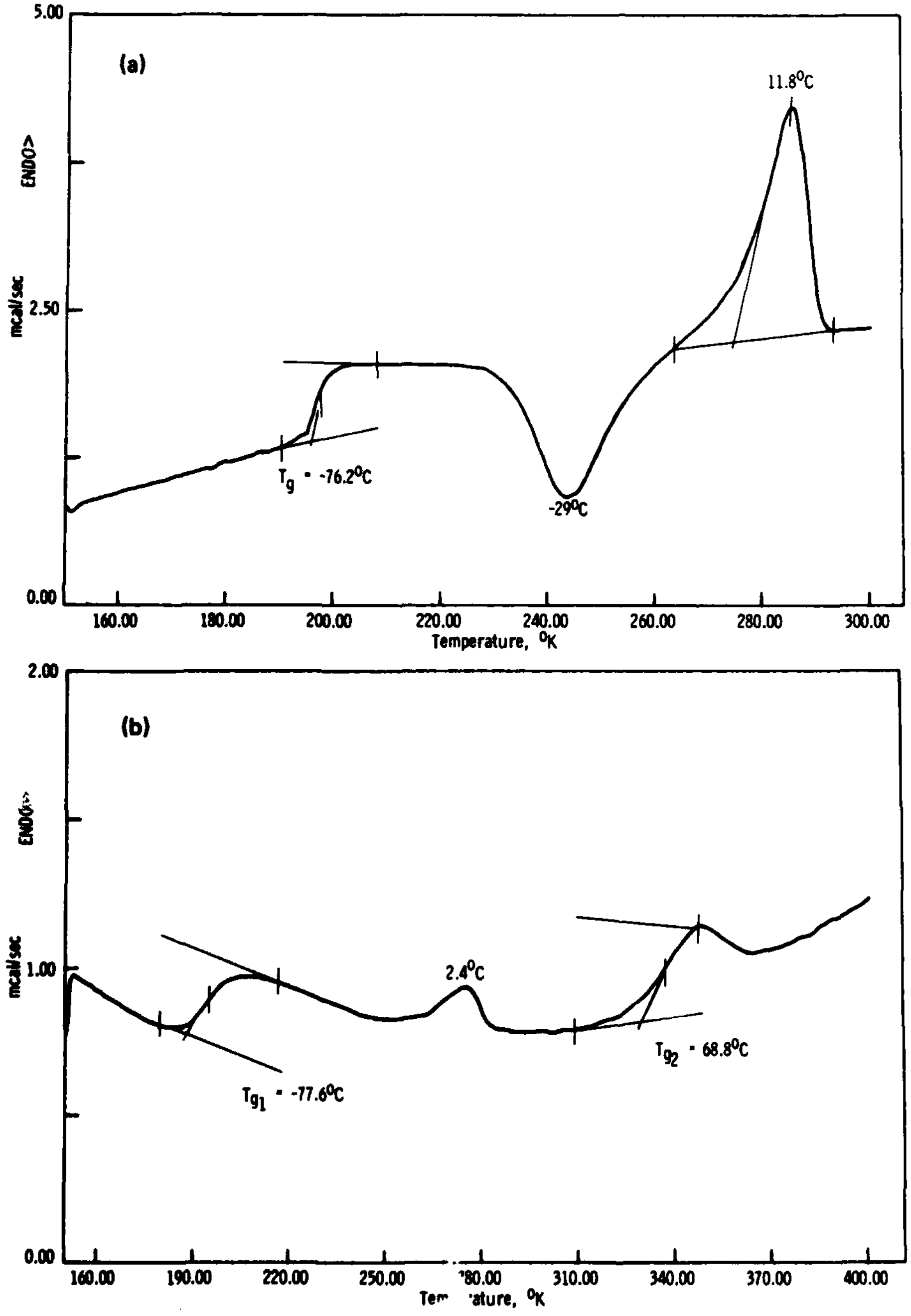

Figure 2. DSC trace of (a) sample 2.6-1-1.5(3) in Table 2b prepared from Teracol PTMO 2900; and (b) sample 2.6-1-1.5(2) in Table 2b. Sample weight is 11.17 mg. Scan rate is 20°K/min.

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*Designated 2.6-1-1.5(3) for PTMO 2900 samples and 2.6-1-1.5(0.6) for PTMO 650 samples, etc. Samples without designation are PTMO 2000 samples.

The T_{g1} for the PTMO 650 sample is anomalously high and broad, indicating the extreme effect of tying down the polyol chain ends on the T_{g1} of the soft segment. Several other thermal transitions are observed for these samples. Polymers prepared from PTMO 2900 exhibit a crystallization exotherm at -29°C and melting of the soft segment at 11.8°C (Figure 2a) compared to about 23°C for the pure polyol. Crystallinity in the hard segment domains is not observed in these polymers because the diisocyanate used is a mixture of geometric isomers, as was discussed in the Introduction. A hard segment, T_{g2}, at about 70°C is observed in the DSC trace for the standard composition (Figure 2b). A small endotherm at 2.4°C is an indication of a small amount of crystallinity in the PTMO 2000 soft segment.

THERMOMECHANICAL ANALYSIS

Experimental

Thermomechanical analysis (TMA) was performed using a Perkin-Elmer Thermomechanical Analyzer, TMS-1, with a Perkin-Elmer Model UU-1 temperature program controller. Results were recorded on a Hewlett-Packard 7100B Strip Chart Recorder. Samples were heated in a helium atmosphere from -100°C to the softening point of the sample. Two specimens were run from each sample material tested. Sample thickness ranged from 0.020" to 0.065". The weight used on the TMA was 20 grams. The heating rate was 20°/min and the chart speed was 1"/min.

Results and Discussion

The results obtained from TMA (Figure 3) using a temperature programmed penetrometer are more variable than those obtained by DSC because TMA results depend to some extent on the geometry and surface conditions of the sample. The result of representative TMA experiments are shown in Table 3. The lowest transition, the T_{g1} occurs at a slightly higher temperature than that measured by DSC. The second value represents the T_{g2}. For the polymer prepared from PTMO 2900, the transition at -31°C corresponds to the soft segment crystallization exotherm shown in Figure 2a. The second value for the polymer prepared from PTMO 1000, 103°C, is probably a T_{g2}, elevated by the ends of the hard segment being held by a soft segment. The hard segment length is statistically the same as that for sample 2.6-1-1.5 prepared from

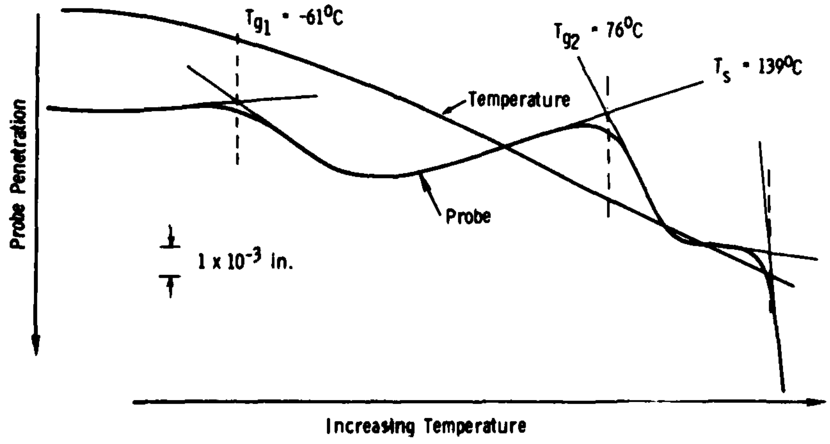


Figure 3. Thermomechanical analysis curve for sample 2.6-1-1.5 in Table 3.

Table 3. THERMOMECHANICAL RESULTS

Moles

1. H_{12}MDI-PTMO 2000-1,4-Butanediol

H_{12}MDI/PTMO/BD	TMA TRANSITIONS (°C)
2.1-1-1.0	-64, 74, 133
2.3-1-1.2	-66, 79
2.5-1-1.4	-59, 75, 132
2.6-1-1.5	-69, 81, 160

2. With Various Mol. Wt. PTMO

Moles H_{12}MDI/PTMO/BD	
2.6-1-1.5 (3)	-72, -31, 72
2.6-1-1.5 (2)	-69, 81, 160
2.6-1-1.5 (1)	-65, 103

3. With 1,4-Butanediol and Ethylene Glycol, PTMO 2000

Moles H_{12}MDI/PTMO/BD/EG	
2.6-1-1.43-0.08	-57, 68, 135

4. With Trimethylol Propane, PTMO 2000

Moles H_{12}MDI/PTMO/BD/TMP	
2.5-1-1.2-0.2	-60, 60, 239
2.5-1-0.9-0.4	-71, 69, 259

PTMO 2000 and butanediol but the soft segment is half as long and the total wt % hard segment is higher. The third transition is the final softening temperature and occurs in the region of allophanate bond dissociation. Note that this final softening temperature is dramatically elevated for cross-linked samples prepared from trimethylol propane. This suggests that lightly cross-linked samples could meet required mechanical strengths at higher temperatures.

DYNAMIC MECHANICAL ANALYSIS

Experimental

A Rheometrics Dynamic Spectrometer, RDS-7700, was used for dynamic mechanical analysis. The samples were cut to 1/2" x 2-1/2" and were 50 mils to 60 mils thick. A liquid nitrogen controller was used to achieve the desired temperature. Measurements were taken at 10° temperature increments, with an equilibration time of 2 min at each temperature. The range studied was from -100°C to +100°C, with a strain setting of 1% and a rate of 6.28 rad/sec.

During Rheometrics analysis, a torsional motion is imposed on the sample and the torque, and normal forces resulting from the motion are measured by a transducer. From these values the storage modulus, G', the loss modulus, G'', and the ratio of the latter to the former, the loss tangent (tan δ) can be calculated. Peaks in either the G'' or the tan δ curve (Figure 4) indicate glass transition temperatures (T_g's).

Results

A typical experimental set of curves is shown in Figure 4. The G" curve for these samples showed a sharper low temperature peak than the loss tangent, allowing determination of the soft segment T_{g1} which it represents, with greater accuracy. The high temperature peak corresponds to the T_{g2} of the polyurethane hard segment. T_{g2}'s not reported in Table 4 were not apparent in the Rheometrics analysis, or the amount of scatter in the data above room temperature obscured the peaks (2.1-1-1.0 and 2.5-1-1.5). Values for T_{g1} obtained by DSC are about 5°C higher than the temperature of the maxima in the G" curves and about 10°C to 15°C lower than the T_{g1} obtained from the tan δ curve. Additional comments on the loss modulus and loss tangent curves are included in the discussion of the bend recovery test results below.

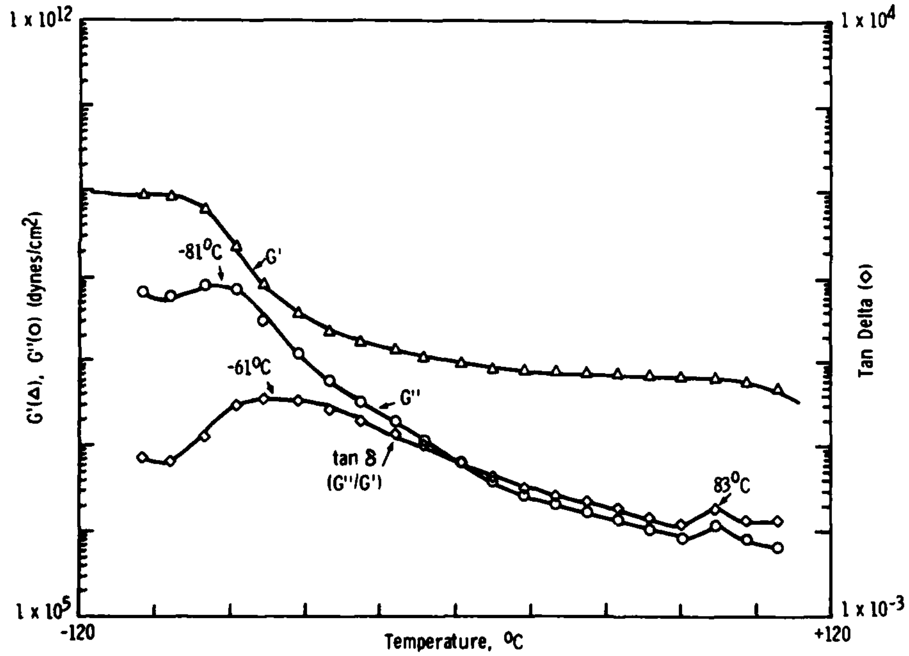


Figure 4. Dynamic mechanical spectrum of sample 2.6-1-1.5 in Table 4.

BEND RECOVERY

Experimental

Samples cut to 1/2" x 3" are bent around a horizontal 1/2"-diameter rod and the ends are clamped together. For room temperature testing (21°C) the clamps are removed after 24 hours. Measurements of deviation from 180° are made by placing the samples on edge on a sheet of paper marked with angles from 0° to 180° in 10 increments. For cold temperature testing, the samples are clamped for 1 hour and the measurements of deviation from 180° are made in the cold chamber.

Table 4. DYNAMIC MECHANICAL RESULTS

1. H_{12} MDI-PTMO 2000-1,4 Butanediol

Moles		TRANSITION (°C)		
H_{12} MDI/PTMO/BD	T_{g1}*(G'')	T_{g1} (tan δ)	T_{g2}†(G'')	T_{g2} (tan δ)
2.1-1-1	-71	-61		
2.5-1-1.5	-81	-61		
2.5-1-1.4	-72	-57	87	
2.6-1-1.5	-78	-61	83	83

2. With 1,4 Butanediol and Ethylene Glycol, PTMO 2000

Moles H_{12} MDI/PTMO/BD/EG	T_{g1} (G'')	T_{g1} (tan δ)	T_{g2} (G'')	T_{g2} (tan δ)
2.6-1-1.35-0.15	-72	-51	71	

3. With Trimethylol Propane, PTMO 2000

Moles H_{12} MDI/PTMO/BD/TMP	T_{g1} (G'')	T_{g1} (tan δ)	T_{g2} (G'')	T_{g2} (tan δ)
2.6-1-1.5-0.01	-73		98	
3.0-1-1.7-0.2	-80	-65	82	82

*T_{g1} is the glass transition temperature of the soft segment.
†T_{g2} is the glass transition temperature of the hard segment.

Results and Discussion

The bend recovery test results are summarized in Table 5 for recoveries after 2 min. This time period was chosen to conform to that used at Battelle Labs for testing of other candidate lens materials. The bend recoveries of these samples differ, even though the T_{g1}'s are very similar. The bend recoveries improve as the hard segment content is reduced but are poor for all compositions at -23°C to -21°C. The rise of G'' and tan δ with decreasing temperature in Figure 4 from +20°C indicates increasing viscoelastic behavior and accounts for the delayed elastic recovery at the low temperature. Note that the bend recoveries for sample 2.6-1-1.5 are poorer at the low temperature than those for the companion stoichiometric sample, 2.5-1-1.5 in Table 5, resulting from presumed allophanate formation in the sample with NCO/OH = 1.05 (2.6-1-1.5).

Table 5. POLYURETHANE BEND RECOVERY RESULTS

1. H_{12}MDI/PTMO 2000-1,4-Butanediol			
Moles H_{12}MDI/PTMO/BD	Thickness (mil)	Temperature ($^{\circ}$C)	Residual Angle($^{\circ}$) After 2 Minutes
4.0-1-3.0	35	21	85
3.0-1-2.0	70	21	39
2.5-1-1.5	50	21	20
		-21	39
2.0-1-1.0	65	21	20
2.6-1-1.5	50	21	19
	65	21	35
	53	-23	87
2. With Various Mol. Wt. PTMO			
Moles H_{12}MDI/PTMO/BD			
2.6-1-1.5 (3)	53	21	38
2.6-1-1.5 (2)	50	21	19
2.6-1-1.5 (1)	51	21	84
3. With 1,4-Butanediol and Ethylene Glycol, PTMO 2000			
Moles H_{12}MDI/PTMO/BD/EG			
2.6-1-0.00-1.50	50	21	85
2.6-1-0.75-0.75	50	21	25
2.6-1-1.35-0.15	50	21	25
		-21	47
2.6-1-1.43-0.08	65	21	28
		-21	33
4. With Trimethylol Propane, PTMO 2000			
Moles H_{12}MDI/PTMO/BD/TMP			
3.0-1-1.70-0.20	50	21	28
3.0-1-1.88-0.08	60	21	42
		-21	122
2.5-1-1.20-0.20	40	21	15
2.6-1-1.20-0.20	54	21	17
		-21	102
2.6-1-1.40-0.05	60	21	15
		-21	69
2.6-1-1.46-0.03	62	21	39
		-21	105
2.6-1-1.23-0.09-0.14*	60	21	20
		-21	93
5. MDI/PTMO 1000-1,4-BD			
Moles MDI/PTMO/BD			
3.0-1-2.0 (1)	48	21	49
		-23	88
	75	21	103

*Ethylene glycol added

In addition, there is a mild thickness dependence with the thicker samples exhibting poorer recovery. Samples cross-linked with TMP recover well at ambient temperature. but stiffen up at the lower test temperature. Commercial MDI samples which were used in injection molding experiments with a lens mold, and are shown in Table 5, section 5, recover better than the H_{12}MDI couterpart, sample 2.6-1-1.5.[1] Both of these polymers were prepared with PTMO 1000.

HARDNESS

Experimental

A hand held Shore Durometer, hardness type "A-2," was used to determine the hardness of the polyurethane samples, according to ASTM 2240-75. Specimens were rectangular, 1" x 1/2". Since the thickness of the polymer samples tested was approximately 50 mils, four plies of sample were used to achieve a thickness of 0.25". Three readings were taken, 0.25" apart on the surface of the four plies.

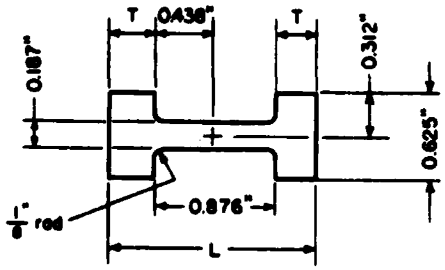
Results and Discussion

For the polyurethanes with only butanediol as the chain extender, the hardness values in Table 6 increase significantly with wt % hard segment. When trimethylol propane and/or ethylene glycol are added, there is some variability in the measured Shore A hardness values shown in Table 6 (sections 3 and 4). This may be related to poorer packing in the hard segment domains, resulting in a lower density of the polymers.

TENSILE PROPERTIES

Experimental

Tensile strength was measured using an Instron Model 1122 tensile tester with a 100-kg cell. Due to the small amount of sample available, specimens were cut with a microdie made to specifications in ASTM D1708 (Figure 5). Results reported were an average of data from five specimens. Crosshead speed and chart speed were both 200 mm/min. The samples were mounted in pneumatic grips with 1-1/2" x 1" serrated faces. Air pressure in the pneumatic grip was 35 psi.



Tolerance: ±0.051 mm (±0.002 in.)
Thickness = thickness of sheet.
Minimum tab length, T = 7.9 mm (0.312 in.) (Larger tabs shall be used wherever possible.)
Minimum length, L = 38.1 mm (1.50 in.)

Figure 5. Microdie specifications from ASTM D1708.

Results and Discussion

Mechanical properties of samples with varying hard segment lengths are shown in Table 7. The first three samples in the table were prepared by a one shot technique and the other two by a prepolymer technique described under synthesis. (The ways in

Table 6. HARDNESS VALUES FOR VARYING COMPOSITIONS

1. H_{12}MDI/PTMO 2000-1,4-Butanediol		
Moles		
H_{12}MDI/PTMO/BD	Hardness, Shore A	Wt% Hard Segment
3.0-1-2.0	84.0	32.6
2.6-1-1.5	75.0	29.2
2.5-1-1.5	78.0	28.3
2.1-1-1.0	71.3	23.9
2. With Various Mol. Wt. PTMO		
Moles		
H_{12}MDI/PTMO/BD		
2.6-1-1.5 (3)	72.8	22.1
2.6-1-1.5 (2)	75.0	29.2
2.6-1-1.5 (1)	92.7	46.0
2.6-1-1.5 (0.6)	94.3	55.9
3. With 1,4-Butanediol and Ethylene Glycol, PTMO 2000		
Moles		
H_{12}MDI/PTMO/BD/EG		
2.6-1-0.00-1.50	69.6	28.2
2.6-1-0.75-0.75	72	28.7
2.6-1-1.35-0.15	75.3	29.4
2.6-1-1.43-0.08	70	29.4
4. With Trimethylol Propane, PTMO 2000		
Moles		
H_{12}MDI/PTMO/BD/TMP		
3.0-1-1.70-0.20	74.6	32.2
2.6-1-1.42-0.05	73.1	29.6
2.6-1-1.20-0.20	68.0	29.6
2.5-1-1.20-0.20	70.0	27.9
2.6-1-1.23-0.09-0.14*	67.2	29.7

*Ethylene glycol

Table 7. TENSILE PROPERTIES OF POLYURETHANES

H_{12}MDI/PTMO-2000/BD	Wt% Hard Segment	100% M (psi)	300% M (psi)	Tensile (psi)	Elongation (%)	Tear Strength Graves Die C (psi)
4.0-1-2.9*	39.6	905±63	1761±181	3868±295	544±25	279±36
3.0-1-2.0*	32.6	692±27	1333±99	3626±342	584±61	309±35
2.0-1-0.1*	23.8	435±34	828±55	3966±46	631±41	310±11
2.6-1-1.5†	29.2	622±50	1301±80	3561±245	480±20	
2.5-1-1.5†	28.3	603±30	1371±69	3293±275	545±25	

*Prepared by a one shot method.
†Prepared by a prepolymer method.

which the polymers produced by the two synthetic methods differ has not been fully explored at AMMRC but have been examined in detail at the University of Detroit.)[5] In general, increasing hard segment content increases the modulus values (100% and 300%). Elongation at break and tear strength tend to decrease with increasing hard segment length, but the tensile strength is relatively constant. There is little difference exhibited by the one sample at NCO/OH = 1.05 in this table compared to its companion stoichiometric sample (2.5-1-1.5), both prepared by the prepolymer method. Compression set (ASTM D395-78) varies between 10% and 25% (not shown) for samples in the range of compositions noted in the table. The tensile strength of the samples increases with a decrease in temperature (Figure 6), but remains approximately the same for -20°C and -40°C. These temperatures are much higher than the T_{g1} of the soft segment and much lower than the T_{g2} of the hard segment. Adding trimethylol propane (TMP) or a mixture of TMP and ethylene glycol during cure has an adverse effect on properties (Figures 7a and 7b) due to the disruption of hard segment domains by cross-linking or diol carbon chain length. Below the composition 2.6-1-1.5-0.025 (TMP) in trimethylol propane (not shown), the tensile strength and elongation compare well with those values for 2.6-1-1.5, the standard composition.

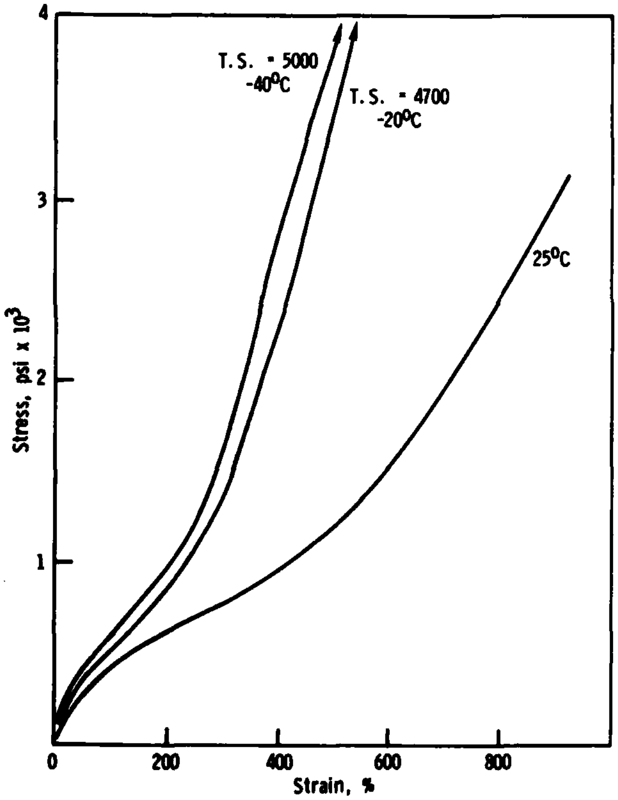


Figure 6. Stress-strain curves for sample 2-1-1 in Table 7 at different temperatures.

Effect of Cure on Tensile Strength

In one experiment, stress-strain curves were obtained for 2.6-1-1.5 cured for varying times from 1 hour to 16 hours and aged for two weeks. Except for some minor experimental error variations, the stress-strain curves were superimposable. This

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[5] WONG, S. W., CORMIER, G. J., FRISCH, K. C., SCHNEIDER, N. S., and BYRNE, C. A. Org. Coat. Appl. Polym. Sci. Preprints, v. 49, 1983, p. 63.

calls into question the importance of a 16-hour cure cycle for these polymers. Assuming that the purpose of this long cure is annealing, and that annealing is of value for polyurethanes with crystalline regions, perhaps it is not of use for these highly amorphous polymers.

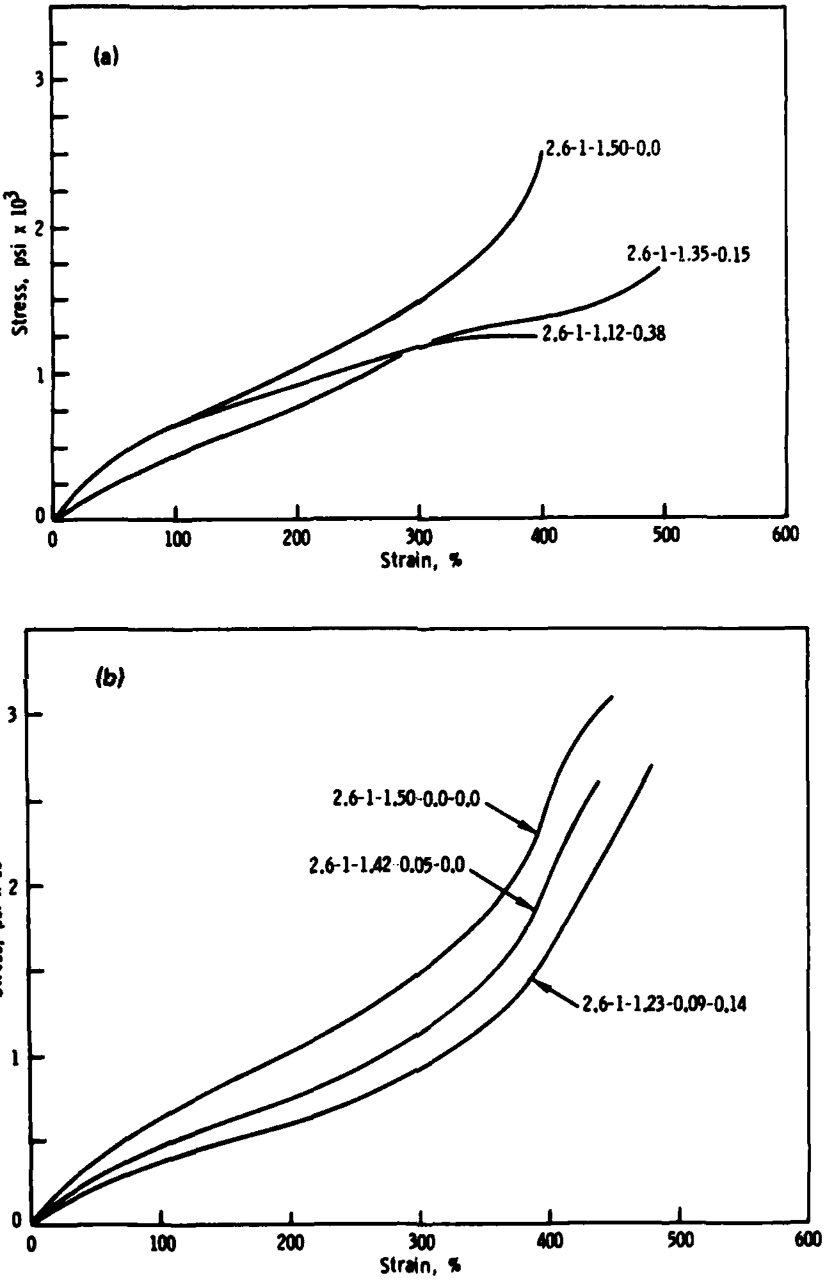

Figure 7. Stress-strain curves for H_{12}MDI/PTMO/BD/EG samples prepared with (a) butanediol/ethylene glycol mixtures as chain extenders compared to the standard compositions; and (b) stress-strain curves for H_{12}MDI/PTMO/BD/TMP/EG samples prepared with butanediol and trimethylol propane or with butanediol, trimethylol propane and ethylene glycol compared to the standard composition.

MOLDS AND MOLD RELEASES

External Release Agents

Previous experience with polyurethane elastomer synthesis indicated that Ram 225 and Kraxo 1711 (Table 8) were good external release agents for chrome-plated steel molds, prepared according to ASTM D3182-74 and D3183-73. SS-61 released the polyurethanes, but XMR-254 from Chem-Trend did not. External release agents of this type, which must be applied before each use, in general, provide good release but leave streaked or mottled surfaces on the samples.

A reasonably extensive search of available release methods was undertaken in the hope of finding a way to prepare a large quantity of optical quality sheets of the

Table 8. MOLD RELEASES

Release	Supplier	Sample Condition
RAM 225	Ram Chemical Co. 210 E. Alondra Blvd. Gardena, CA 90248	streaked, mottled
Kraxo 1711	Contour Chemical Co. 70 Concord St. N. Reading, MA 01864	streaked, mottled
SS-61	Chem-Trend Inc. 3205 E. Grand River Howell, MI 48843	streaked, mottled
XMR-254	Chem-Trend Inc.	no release
Dow Corning 233A	Midland, MI 48640	slippery, mottled
Frekote #20 experimental urethane release	2300 N. Emerson Ave. Indianapolis, IN 46218	greasy
Nonstickenstoffe	Contour Chemical Co.	grainy
Duralease 1070	Hydro-Kinetics & Res. Inc. P.O. Box 646 Newtown, PA 18940	cloudy
Acrawax C	Glyco Inc. Greenwich Ofc Park 1 Greenwich, CT 06830	no sample
Mold Wiz	Axel Plastics Res. Labs, Inc. 58-20 Broadway Woodside, NY 11377	blurry to see through
Dow Corning Q2-7119		cloudy
Silicone coating, base cure	uncertain, but possibly General Electric	tacky
Teflon impregnated electroless nickel	Poly-plating, Inc. 4610 Westover Rd. Westover Industrial Air Park Chicopee, MA 01022	see text
Plasma-deposited fluorocarbon on glass	Dr. N. Morosoff Chemical & Life Sciences Group Research Triangle Inst. NC 27709	slightly cloudy

transparent polyurethane. Most of the samples which were characterized were prepared on polished polypropylene which offered the best optical surface and no contamination by mold release.

Several semi-permanent release agents are available and have been tested, using disposable, photographic ferrotype olates instead of steel molds, and using the manufacturer's directions for application. Dow Corning 233A releases well, but again leaves a mottled surface. Frekote #20 releases with difficulty. Nonstickenstoffe, apparently a very fine dispersion of teflon powder, releases very well, but leaves a pebbly surface. Duralease 1070 releases but leaves a very cloudy surface. A base-cured silicone coating releases well, but yields an unusually tacky sample, probably due to interference of the silicone with the polyurethane cure. The surface of the silicone becomes damaged after two or three uses.

Release from other miscellaneous surfaces was investigatied. A plain highly polished ferrotype plate does not release the polyurethane. A teflon impregnated electroless nickel coating on a ferrotype plate does not release a sample cured on it, but can be used to press polish an already cured sample. This will be discussed later. Plasma-deposited fluorocarbon on glass releases well, but leaves a slight cloudiness. This method is potentially useful, but the variables involved should be examined more completely.

Most of the samples have been prepared on polypropylene sheets, which release well, and give a sample free of greasy release agents. The surface of the plastic can be press polished, but does scratch and begin to pit on repeated use. Preparation of samples of precise thickness of specific curvature in a polypropylene mold would be difficult but perhaps not impossible.

Internal Release Agents

Acrawax, which is an internal release agent used for injection molding at 350°F or above, cannot be used at 250°F because it is insoluble in the polymer and does not melt at the reaction temperature. Mold Wiz, a liquid, has been tested in amounts varying from 0.25 wt % to 1.0 wt %. The polyurethane does not release easily and could not be expected to give optical quality sheets. Dow Corning Q2-7119 releases well but its addition produces a white polymer.

Press Polishing

In attempts to obtain a good quality optical surface, polymer samples were pressed with heating on smooth surfaces. This technique worked best for 60 mil polypropylene which was pressed on photographic ferrotype plates. The sample was pressed at a platen temperature of 150°C for 10 min under approximately 550 $lb/in.^2$. The surfaces produced were flawless to the naked eye and then were used as molds for polyurethanes. Poly(methylpentane) could be prepared in a similar manner using 350°C for 15 min. These 1/2" sheets were very hard and tended to warp when polyurethanes were prepared on them.

Press polishing or transfer molding of a partially cured sample can work very well for polyurethanes if no mold release is used (possible only on a material like polypropylene) and care is taken to use clean dust-free surfaces and samples. No completely suitable mold release agent, either internal or external, has been found which will yield consistently good optical quality samples.

ADDITIVES TO POLYMERS

Alcohols

Polymers prepared from 1,4-butanediol had excellent clarity and a moderately tack-free surface. The same was true of polymers prepared with small amounts of trimethylol propane and ethylene glycol. When larger amounts of ethylene glycol or 1,6-hexanediol were used, very gummy polymers were obtained, which picked up dust and changed the shape or flow readily when subjected to small amounts of pressure, i.e., pressing between thumb and forefinger. There is some evidence that better polyurethanes result when the carbon chain length of the diol and the length of the repeat unit of the polyol are the same.* The present results conform to this expectation.

A methyl-substituted C_{10} diol (Henkel) was added to a preparation because it was thought that increasing the hydrocarbon content would improve the release properties. An observable improvement did not occur, and a slightly gummy sample resulted. The same reasoning dictated the use of 3-methyl-2,4-pentanediol, partially replacing the butanediol, with similar disappointing results.

Antistats

The polyurethanes picked up dust readily, therefore, several antistatic agents were employed. Gafac RD510 and Gafac RE610 (GAF), both liquids, added in 3 wt %, left oily-looking surfaces which picked up fingerprints. Statexan K_1 (Mobay), a solid, was insoluble at 100°C in the polymer reaction mixture. After cure, the polymer looked like little pieces of tissue paper had been dispersed in it.

Silica

A report from Battelle Labs that fumed silica improved the optical clarity of ethylene-propylene copolymers and stimulated attempts to incorporate silica into the polyurethanes. Extensive blooming occurred after a few days in samples prepared using 1, 2, and 5 wt % silica.

Miscellaneous

The antioxidant Irganox 1076 (Ciba-Geigy) was added in amounts from 0.2 wt % to 0.5 wt % to samples prepared at 110°C to 120°C. This material was compatible with the polyurethanes, soluble and non-blooming.

Small amounts of hydroxy terminated poly(butadiene) HTPBD R45M (Arco) down to 0.25 wt % were added during polymer preparation, but slightly cloudy samples were obtained. It was hoped that cross-linking with benzoyl peroxide or another agent at a low level would improve the surface task. Difficulties were encountered, as well, in the addition of the benzoyl peroxide, which is not soluble in a suitable solvent and decomposes rapidly at elevated temperatures. A good way of adding it was not obvious. The HTPBD is known to show poor compatibility with hydrogen bonding components of a polyurethane, which can lead to cloudiness.[6]

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*K. C. Frisch, private communication.

[6] SCHNEIDER, N. S., BRUNETTE, C. M., HSU, S. L., and MacKNIGHT, W. J. *Structure and Properties of Polybutadiene Polyurethanes.* Adv. Urethane Sci. and Tech., v. 8, 1981, p. 49.

Use of small amounts (5% to 10%) of trans-1,4-diisocyanatocyclohexane combined with the H_{12}MDI produced much harder samples which cured more rapidly. Exploration of this avenue to improve surface properties is ongoing.

SURFACE TREATMENT

Because the polymers were more tacky than desired, and because varying the chemical composition of the polymers did not sufficiently reduce the surface drag, several surface treatments were tried in order to improve properties such as dry cleanability.

Polymers were coated with GAFGARD 277 and 280 high-gloss coatings (GAF). These aliphatic coatings were UV-cured on the surface to a thickness of 2 mils. The surfaces were much less tacky and the samples were a bit stiffer, but some delamination and cracking occurred under severe bending.

Several samples were irradiated at High Voltage Engineering (Burlington, Massachusetts) using electron irradiation at 2.5 MeV in 5 Mrad increments to levels of 10, 15, 20, and 30 Mrads. The samples subjected to 15 and 20 Mrad doses had slightly improved blocking characteristics; that at 10 was not affected, and the sample at 30 appeared to melt. All of the samples underwent a very slight yellowing. The tensile strength of the 20 Mrad sample decreased from 3400 psi to 2400 psi after irradiation and the elongation decreased from 500% to 450%. This would not be a significant decrease on mechanical properties for a material to be used as a lens.

The third treatment involved fluorination of the surface in a manner similar to that used at Battelle Laboratories for the ethylene-propylene copolymers. Experiments to test the optical properties of the samples before and after fluorination are shown in Table 9.* The abrasion test was conducted according to ASTM D673-76 using 400 g of sand. The talc test utilized ASTM D1003-77. The abrasion resistance,

Table 9. OPTICAL PROPERTIES OF FLUORINATED AND NONFLUORINATED POLYURETHANES

	ABRASION				TALC TEST					
							After			
	Before		After		Before		Dry Wipe		Wash	
2.6-1-1.5	%T*	%H†	%T	%H	%T	%H	%T	%H	%T	%H
Not Fluorinated	93.2	4.1	79.5	11.7	94.3	1.5	91.9	12.8	93.2	4.7
Fluorinated	94.9	1.5	89.9	4.0	94.7	1.7	92.9	9.6	94.5	2.6

*% Transmission
†% Haze

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*J. T. Mok, and N. Ramos, tests performed by Mask Management Office, Chemical Systems Laboratory, Aberdeen Proving Ground, Maryland.

as well as the cleanability, was favorably affected by fluorination. The seemingly small improvements reflected in Table 9 are considered to be significant in tests of this type.

PYROLYSIS - GAS CHROMATOGRAPHY - MASS SPECTROSCOPY/ FOURIER-TRANSFORM INFRARED SPECTROPHOTOMETRY

It is possible that a trace of isocyanate remains unreacted in the polyurethanes after cure. Pyrolysis-GC-MS (low resolution) yields a substance with molecular ion of Mass 262 corresponding to the isocyanate. The pyrolysis occurs at 160°C and the isocyanate shows up after approximately 5 minutes. Thermolysis of urethane bonds could also be occurring to a small extent. Information about molecular weight distribution and unreacted starting materials, which might be obtained by gel permeation chromatography, would be useful in clarifying this matter. Isocyanate peaks have been observed in the IR for samples which were probably prepared with a catalyst solution which had picked up moisture. The T-12 loses effectiveness on hyrdolysis. The infrared spectra of these 50-mil samples are obtained by FT-ATR (attenuated total reflectance) which is a surface technique useful for analysis of elastomers. The FT-IR in Figure 8 exhibits three peaks in the carbonyl region ranging from 1660 cm^{-1} to 1715 cm^{-1}. This is quite unusual for polyurethanes, most of which exhibit two peaks, which are attributed to hydrogen-bonded and non-hydrogen-bonded carbonyls.[7] It is theorized that the presence of three geometric isomers of $H_{12}MDI$ contributes to the effect. A thorough analysis of the IR spectra is planned.

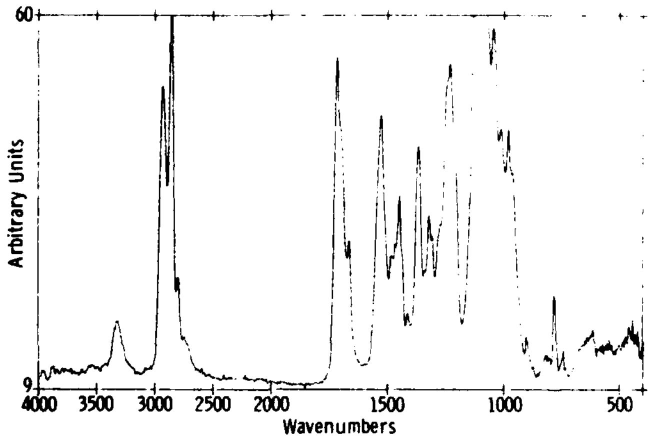

Figure 8. FT-IR of polyurethane sample 2.5-1-1.4 showing three absorption peaks in the carbonyl region, 1660-1720 cm^{-1}.

CONCLUSIONS

The polyurethanes which have been prepared meet or exceed many of the design goals set forth by the Mask Management Office at the Chemical Systems Laboratory in early 1980. The properties investigated at AMMRC are listed in Table 10, along with the desired values for a flexible lens and the best values obtainable for the aliphatic polyurethanes. In general, the urethane mechanical properties are excellent, exceeding

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[7] PAIK SUNG, C. S., and SCHNEIDER, N. S. *Infrared Studies of Hydrogen Bonding in Toluene Diisocyanate Based Polyurethanes.* Macromolecules, v. 8, no. 1, 1975, p. 68.

in every case, the desired properties. The best optical properties, which are in the desired range, were attained for samples which were set aside after preparation, aged for at least two weeks and then fluorinated.

The summary in Table 10 does not completely explain the difficulties still encountered in the preparation of these polyurethanes and their ultimate use as lens materials. No appropriate mold releases are available. Excellent quality sheets can be formed on polished polypropylene surfaces, but the use of a curved plastic mold to make lenses might be difficult. Preparation of the polyurethanes on surfaces which are less chemically inert than polypropylene, for example, silicone, can result in samples with very poor blocking characteristics.

Table 10. SUMMARY OF DESIRED AND ATTAINABLE PROPERTIES FOR THE ALIPHATIC POLYURETHANE LENS MATERIAL

Property	Desired Value	Attained Value
Tensile Strength (psi)	1000	4500
Extension (%)	250	500
Modulus (100%, psi)		620
Compression Set (%)	18	10-25
Hardness, Shore A	60±10	75
Light Transmission (%)*	87 minimum	90
Haze (%)*	4.2 maximum	2-10†
Blocking	none	slight to moderate
Bend Recovery (2 min)	minimal or none	
Residual Angle 21°C		15
-21°C		69

*Tests performed at CSL.
†See Table 9.

Another major source of problems is inadequate bend recovery at low temperatures. The best results at room and low temperatures were attained with samples lightly cross-linked with trimethylol propane. It is quite likely that the low temperature characteristics which would be desirable in a flexible lens are not completely attainable with any available polymers. This means that the best available material must be used. These polyurethanes can be considered to be useful candidate materials for a flexible lens until an elastomer is discovered which possesses markedly better properties in the areas where inadequacies exist for the polyurethanes.

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