

Low-Temperature Behavior of Polyurethane Elastomers

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Synopsis

A study of the performance at low temperatures of various polyurethane elastomer systems, prepared from polyether and polyester diols with 2,4-toluene diisocyanate and 4,4'-methylenebis(2-chloroaniline), *p,p'*-diphenylmethane diisocyanate and 1,4-butanediol, and 4,4'-methylenebis(cyclohexylisocyanate) and methylenedianiline, has shown the polytetramethylene ether diols to impart the best low-temperature behavior to the elastomers. The properties studied were the apparent modulus of rigidity with the Clash and Berg torsional apparatus, the hardness with a Shore D Durometer, and the resiliency with the Bashore Resiliometer.

INTRODUCTION

Since the introduction of polyurethane elastomers, the versatility and the outstanding properties of these systems have become well known to the rubber industry. One important application area for these materials is where good low-temperature performance is necessary. Some applications require that elastomers retain their elasticity at temperatures as low as -40°C . To learn more about the behavior of the various types of polyurethane elastomers at low temperatures, a study was undertaken to obtain information that would be useful to polyurethane fabricators interested in developing elastomers with good low-temperature properties.

Since the variety of components—polymeric diols, diisocyanates, and curatives—used to fabricate polyurethane elastomers is quite large, it was decided to restrict this study to commercially available polyether and polyester diols and the most widely used diisocyanate–curative systems as follows:

Polymeric Diols: polytetramethylene glycol (PTMEG), polypropylene glycol (PPG), polycaprolactone diol (PCL), polyethylenepropylene adipate glycol (PEPAG), and polybutylene adipate glycol (PBAG).

Diisocyanates: 2,4-toluene diisocyanate (TDI), *p,p'*-diphenylmethane diisocyanate (MDI), and 4,4'-methylenebis(cyclohexylisocyanate) (H_{12} -MDI).

Curatives: 4,4'-methylenebis(2-chloroaniline) (MOCA), 1,4-butanediol (1,4BD), and methylenedianiline (MDA).

The elastomer formulations used in the study were as follows: PTMEG 1000–TDI–MOCA, PTMEG 1000–MDI–1,4BD, PTMEG 1000– H_{12} MDI–

MDA, PTMEG 2000-TDI-MOCA, PTMEG 2000-MDI-1,4BD, PCL 1250-TDI-MOCA, PCL 1250-MDI-1,4BD, PCL 2000-TDI-MOCA, PCL 2000-MDI-1,4BD, PEPAG 1000-TDI-MOCA, PEPAG 2000-TDI-MOCA, PPG 1000-TDI-MOCA, PPG 2000-TDI-MOCA, PBAG 1000-MDI-1,4BD, PBAG 1000-H₁₂MDI-MDA, and PBAG 2000-MDI-1,4BD.

The elastomers were prepared via the prepolymer technique. The preparation of the prepolymers and the casting procedures are described in the experimental section. The TDI prepolymers and the H₁₂MDI prepolymers were prepared with a NCO/OH ratio of 2; however, it was necessary to prepare the MDI prepolymers with a NCO/OH ratio of 3 to obtain elastomers with similar hardness. All extensions of the prepolymers were made with a 95% stoichiometry of the curatives used.

EXPERIMENTAL

Prepolymer Preparation

The prepolymers were prepared from the various diols after they had been stripped of moisture at 100°C for 1 hr under vacuum (1 mm Hg) and cooled under nitrogen to 45–60°C, in the case of the polyesters the lowest temperature at which the diol will remain liquid. The prescribed amount of diisocyanate was added to the diols under nitrogen with good agitation, and the temperature was then gradually raised to 80°C and held for 3 hr for the TDI and MDI prepolymers. The H₁₂MDI prepolymers were heated at 140°C for 3 hr. Table I gives the NCO analyses of the prepolymers.

TABLE I
Prepolymer Properties

| NCO/OH | Components | % NCO | Mixing temp., °C |
|--------|--------------------------------|-------|---------------------|
| 2/1 | PTMEG 1000-TDI | 6.2 | 85 |
| 2/1 | PTMEG 2000-TDI | 3.5 | 100 |
| 2/1 | PCL 1250-TDI | 5.1 | 85 |
| 2/1 | PCL 2000-TDI | 3.5 | 100 |
| 2/1 | PEPAG 1000-TDI | 6.2 | 85 |
| 2/1 | PEPAG 2000-TDI | 3.6 | 100 |
| 2/1 | PPG 1000-TDI | 6.4 | 85 |
| 2/1 | PPG 2000-TDI | 3.7 | 100 |
| 3/1 | PTMEG 1000-MDI | 9.7 | 60 |
| 3/1 | PTMEG 2000-MDI | 6.1 | 65 |
| 3/1 | PCL 1250-MDI | 8.2 | 60 |
| 3/1 | PCL 2000-MDI | 5.5 | 65 |
| 3/1 | PBAG 1000-MDI | 9.1 | 60 |
| 3/1 | PBAG 2000-MDI | 5.7 | 65 |
| 2/1 | PTMEG 1000-H ₁₂ MDI | 5.5 | 100 |
| 2/1 | PBAG 1000-H ₁₂ MDI | 5.5 | 100 |

Elastomer Preparation

To make the elastomers, each prepolymer was degassed at the mixing temperature given in Table I. When the prepolymers were bubble free, the amount of molten MOCA, 1,4-butanediol, or molten MDA that was necessary to provide 95% stoichiometry was added and blended in well. The resins were cast into $6 \times 6 \times 0.075$ in. molds (ASTM D15) and compression-set disc molds (ASTM D395) and cured at 110°C for 16 hr. The elastomers were then demolded and kept at room temperature (77°F) for at least a week before they were tested. The specimens used for obtaining the tensile properties (ASTM D412) in Table II were conditioned at 50% R.H. for 48 hr before testing.

TABLE II
Tensile Properties

| Elastomer | Tensile, psi | Elongation, % | M_{100} , psi | M_{300} , psi |
|------------------------------------|--------------|---------------|-----------------|-----------------|
| PTMEG 1000-TDI-MOCA | 5650 | 435 | 1700 | 2750 |
| PTMEG 2000-TDI-MOCA | 4250 | 625 | 670 | 1020 |
| PCL 1250-TDI-MOCA | 6800 | 550 | 880 | 1500 |
| PCL 2000-TDI-MOCA | 3850 | 645 | 400 | 650 |
| PEPAG 1000-TDI-MOCA | 7300 | 525 | 1600 | 2775 |
| PEPAG 2000-TDI-MOCA | 6570 | 750 | 580 | 885 |
| PPG 1000-TDI-MOCA | 5000 | 385 | 1550 | 3490 |
| PPG 2000-TDI-MOCA | 1940 | 595 | 485 | 820 |
| PTMEG 1000-MDI-1,4BD | 5430 | 430 | 1680 | 3100 |
| PTMEG 2000-MDI-1,4BD | 5100 | 540 | 710 | 1400 |
| PCL 1250-MDI-1,4BD | 5600 | 440 | 1200 | 2500 |
| PCL 2000-MDI-1,4BD | 5350 | 490 | 700 | 1500 |
| PBAG 1000-MDI-1,4BD | 5460 | 420 | 2200 | 3200 |
| PBAG 2000-MDI-1,4BD | 5300 | 460 | 800 | 1900 |
| PTMEG 1000-H ₁₂ MDI-MDA | 5280 | 330 | 1580 | 4250 |
| PBAG 1000-H ₁₂ MDI-MDA | 7000 | 330 | 1900 | 5560 |

Elastomer Testing

The behavior of the elastomers at low temperatures was observed using the Clash and Berg torsional apparatus as described in ASTM D1043, the Bashore Resiliometer, and the Shore D Durometer (ASTM D676). Using two specimens from each elastomer type, the apparent modulus of rigidity (G) was determined over a temperature range on the Clash and Berg. If the modulus of elasticity (E) is desired, the formula $E = 2G(1 + \lambda)$ can be used, where the λ is equal to 0.5. The T_r value is the temperature at which the apparent modulus of rigidity is 45,000 psi, or the modulus of elasticity is 135,000 psi. The T_4 value is the temperature at which the E is 10,000 psi and the G is 3,333 psi. These values for each elastomer were obtained from their plots of apparent modulus of rigidity versus temperature.

To obtain resiliency and hardness profiles of the different elastomers, at least two compression set discs from each elastomer type were conditioned as described below before they were measured for hardness (Shore D) and rebound (Bashore).

77°F: Samples stabilized at 76–78°F for 48 hr.

45°F: Samples from –15°F placed in 50°F chamber for 3 hr. Chamber cooled to 45°F for 1 hr. Samples removed individually and tested immediately. Samples also cooled from room temperature to 45°F and conditioned for 3 hr. Samples removed individually from the chamber and tested immediately.

35°F: Samples cooled from room temperature to 35°F and conditioned for 3 or 67 hr. Samples removed individually from the chamber and tested immediately.

25°F: Samples cooled from room temperature to 25°F and conditioned for 3 hr. Samples removed individually from the chamber and tested immediately.

10°F: Samples cooled from room temperature to 10°F and conditioned for 19 hr. Samples removed individually from the chamber and tested immediately.

0°F: Samples cooled from room temperature to 0°F and conditioned for 3, 19, or 67 hr. Samples tested in chamber.

–15°F: Samples cooled from room temperature to –15°F and conditioned for 3, 16, or 67 hr. Samples tested in chamber.

Materials

TDI-Hylene T (du Pont), MDI-Multrathane M (Mobay Chemical), H₁₂MDI-Nacconate H₁₂ (Allied Chemical), PTMEG 650, 1000, and 2000 (Quaker Oats), polycaprolactone diols Niox D-540 and D-560 (Union Carbide), polypropylene glycols Pluracol 1010 and 2010 (Wyandotte), polyethylenepropylene adipate glycols Formrez F10-91, L8-71 (Witco), polybutylene adipate glycols Formrez F13-35, F9-30 (Witco), 4,4'-methylenebis(2-chloroaniline) (du Pont), 1,4-butanediol (anhydrous) (General Aniline & Film), methylenedianiline (Allied Chemical).

DISCUSSION

Previous work¹ has dealt with the modulus-temperature profile of polyurethane systems using a modified Gehman Tester. Also, some Clash and Berg torsional stiffness curves showing the modulus of elasticity of some PCL polyurethane elastomers have been reported.² In this study, to evaluate the low-temperature properties of the formulated elastomers, the Clash and Berg torsional apparatus was used to obtain the apparent modulus of rigidity-versus-temperature curves for each elastomer type. Also, the rebound and the hardness of the elastomers were measured from room temperature (77°F) to –15°F using the Bashore Resiliometer and the Shore D Durometer to obtain their resiliency and hardness profiles.

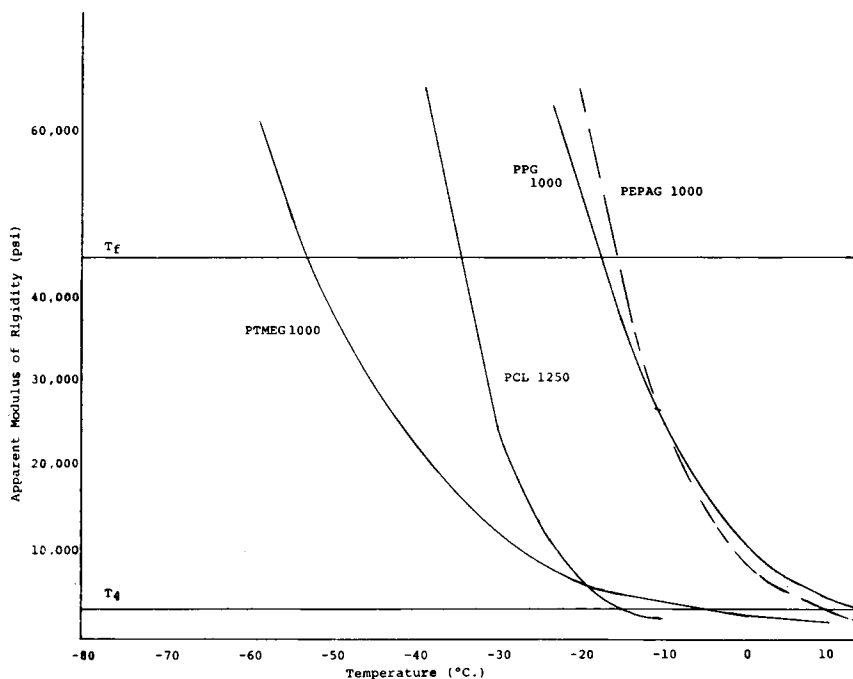


Fig. 1. Low-temperature properties of diol-TDI-MOCA systems.

An overall comparison of the performance of the different elastomers as depicted by their apparent modulus of rigidity-versus-temperature curves has shown the polytetramethylene ether chain to impart the best torsional flexibility to a polyurethane elastomer system. Figures 1 and 2 compare the TDI-MOCA elastomers prepared from the 1000 MW and 2000 MW diols, respectively. Figure 3 is a composite of the MDI-1,4BD elastomers. Figure 4 shows the curves for two H_{12} MDI-MDA elastomers. To obtain low-temperature flexibility similar to that of the PTMEG 1000, polypropylene glycols and polyesters of 2000 MW must be used (see Figs. 3 and 5).

To place a representative measurement on the low-temperature properties, the arbitrary values T_f and T_4 are commonly used by the elastomer industry. The T_f is the temperature ($^{\circ}\text{C}$) at which the apparent modulus of rigidity (G) is 45,000 psi, and the T_4 is the temperature ($^{\circ}\text{C}$) at which G is 3,333 psi. Thus, the elastomers having the lower values should exhibit the better overall low temperature behavior (Table III).

A closer examination and comparison of the curves by relating the position and the shape of the curves to the composition of the elastomers have shown that several factors affect the behavior of the elastomers. These factors are the molecular length of the polymeric diol, the molecular mobility of the polymeric diol, and the intermolecular bonding (hydrogen bonding) of the polymeric diol and the elastomer. These three factors all

TABLE III

| Elastomer | T_f , °C | T_4 , °C |
|------------------------------------|------------|------------|
| PTMEG 2000-TDI-MOCA | -75 | -43 |
| PTMEG 2000-MDI-1,4BD | -73 | -57 |
| PTMEG 1000-H ₁₂ MDI-MDA | -57 | -2 |
| PTMEG 1000-TDI-MOCA | -53 | -5 |
| PPG 2000-TDI-MOCA | -49 | -32 |
| PTMEG 1000-MDI-1,4BD | -47 | -10 |
| PCL 2000-MDI-1,4BD | -47 | -35 |
| PCL 2000-TDI-MOCA | -44 | -32 |
| PBAG 2000-MDI-1,4BD | -44 | -29 |
| PBAG 1000-H ₁₂ MDI-MDA | -35 | 15 |
| PCL 1250-TDI-MOCA | -34 | -15 |
| PCL 1250-MDI-1,4BD | -34 | -14 |
| PEPAG 2000-TDI-MOCA | -32 | -18 |
| PBAG 1000-MDI-1,4BD | -27.5 | 15 |
| PTMEG 650-TDI-MOCA | -18 | — |
| PPG 1000-TDI-MOCA | -17.5 | 15 |
| PEPAG 1000-TDI-MOCA | -16 | 10 |

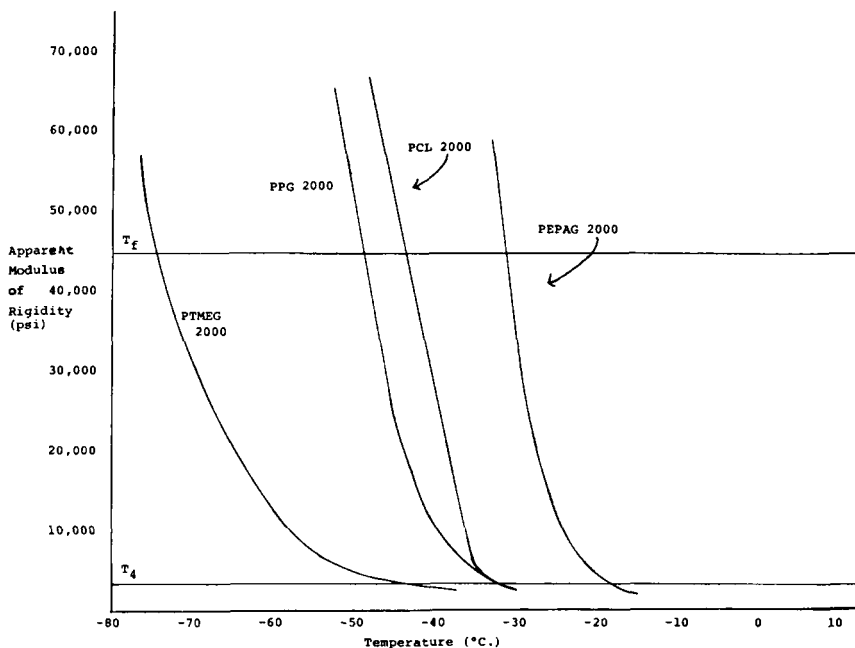


Fig. 2. Low-temperature properties of diol-TDI-MOCA.

affect the tendency of the elastomers to crystallize and thus define the low-temperature performance of the elastomers.

Polyurethane elastomers can be classified as block polymers composed of alternating blocks of soft segments—the polyether or polyester component—and hard segments—the urethane and urea component.³ The molecular

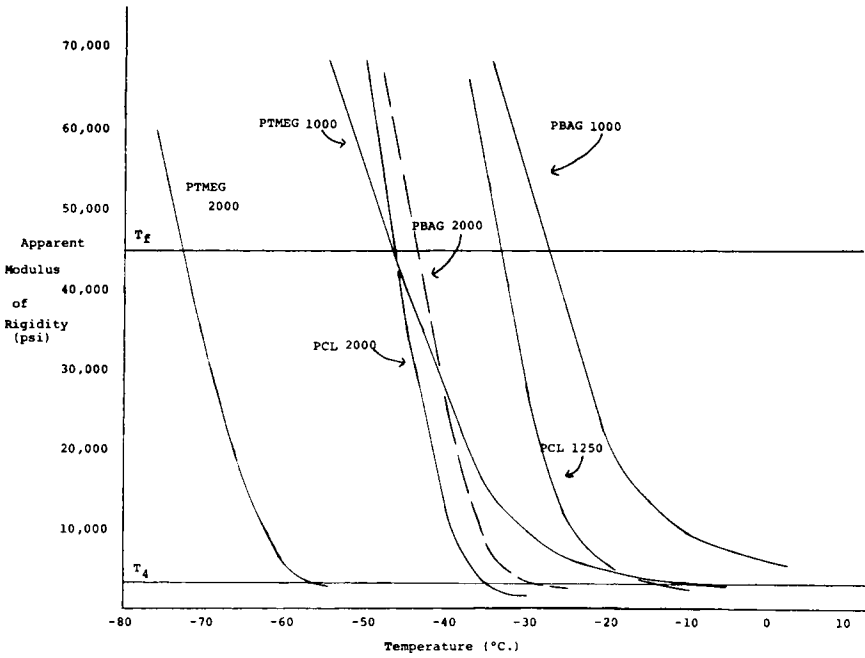


Fig. 3. Low-temperature properties of diol-MDI-1,4-butanediol systems.

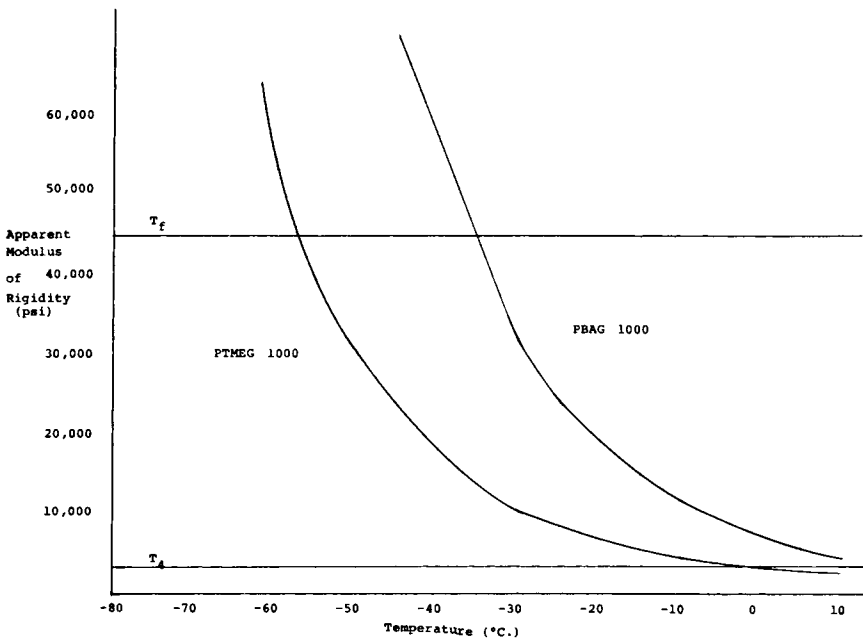


Fig. 4. Low-temperature properties of diol-H₁₂MDI-MDA systems.

TABLE IV

| Polymeric diol | $A_n, \text{\AA}$ | MWD |
|----------------|-------------------|------|
| PTMEG 650 | 38 | 1.34 |
| PPG 1000 | 38 | 1.07 |
| PEPAG 1000 | 49 | 1.56 |
| PBAG 1000 | 52 | 1.62 |
| PTMEG 1000 | 55 | 1.52 |
| PCL 1250 | 58 | 1.59 |
| PPG 2000 | 65 | 1.13 |
| PEPAG 2000 | 70 | 1.90 |
| PCL 2000 | 78 | 1.72 |
| PBAG 2000 | 82 | 1.97 |
| PTMEG 2000 | 93 | 1.80 |

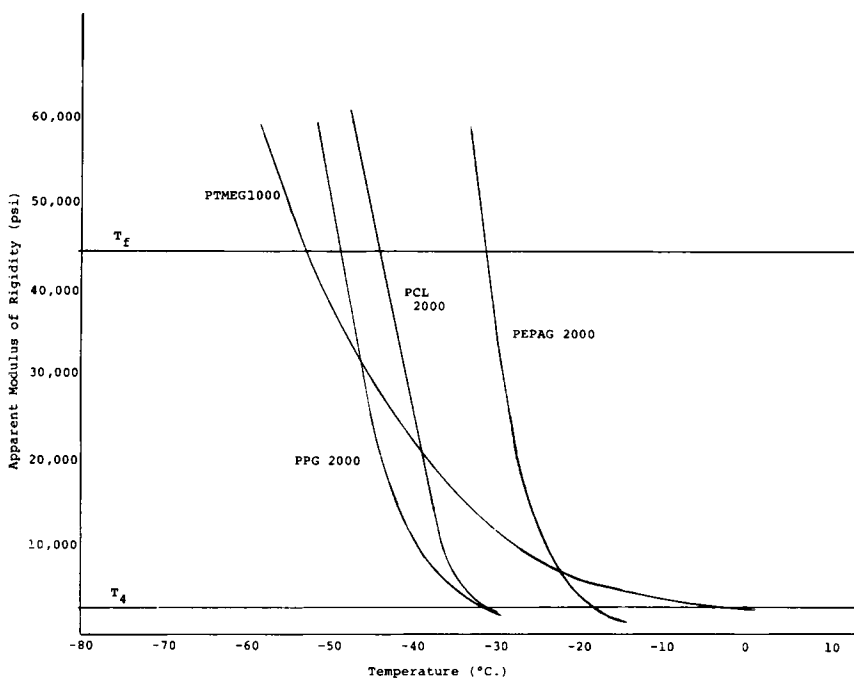


Fig. 5. Low-temperature properties of diol-TDI-MOCA systems.

length of the polymeric diol is very important because it controls the distances between the very polar urethane and urea groupings of the elastomer. As these hard segments are brought closer together in the polyurethane sequence, the elastomers become harder and more rigid. Table IV lists the molecular lengths by number (A_n) and the molecular weight distribution (MWD) of the various diols as determined by gel permeation chromatography. The gel permeation chromatography of the diols was run on a Water Associates apparatus with columns 2×10^4 , 1×10^3 , 250, and 100 \AA and tetrahydrofuran as the solvent. The A_n , the number-

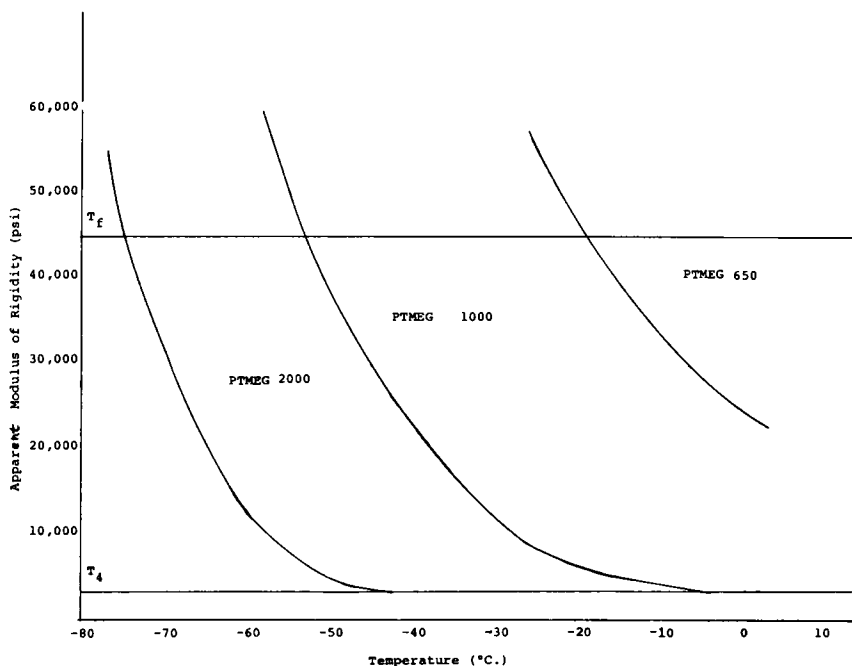


Fig. 6. Low-temperature properties of PTMEG-TDI-MOCA. Molecular length comparison.

average molecular length, was chosen since the hydroxyl number used for the diol is a number-average endgroup determination.

A good example of the importance of the molecular length of a diol in determining the rigidity of an elastomer is shown in Figure 6 which compares the three different MW PTMEGs—650 (A_n 38 Å), 1000 (A_n 55 Å), and 2000 (A_n 93 Å). In a particular formulation (e.g., diol-TDI-MOCA), the shorter the molecular length of the polymeric diol, the more rigid the elastomer and the poorer the low-temperature properties.

Figure 7 compares the two polyether systems (PTMEG-TDI-MOCA and PPG-TDI-MOCA). Though the molecular length of PTMEG 650 (A_n 38 Å) and PPG 1000 (A_n 38 Å) are identical and their plots are in the same area, the slopes of the curves are quite different. The PTMEG 1000 (A_n 55 Å) and PPG 2000 (A_n 65 Å) combination also shows the distinct difference in slope. The polypropylene glycols exhibit better flexibility at the intermediate temperatures but become rigid quite rapidly with decreasing temperature. The PTMEGs exhibit a more gradual slope and are more flexible at the lower temperatures. A likely explanation is that the bulky methyl groups of the polypropylene glycols interfere with the intermolecular bonding forces of the molecules causing the PPG elastomers to be less rigid at the moderately low temperatures. The methyl groups also hinder the molecular mobility such that as the temperature is lowered the elastomers become rigid more rapidly. On the other hand, the poly-

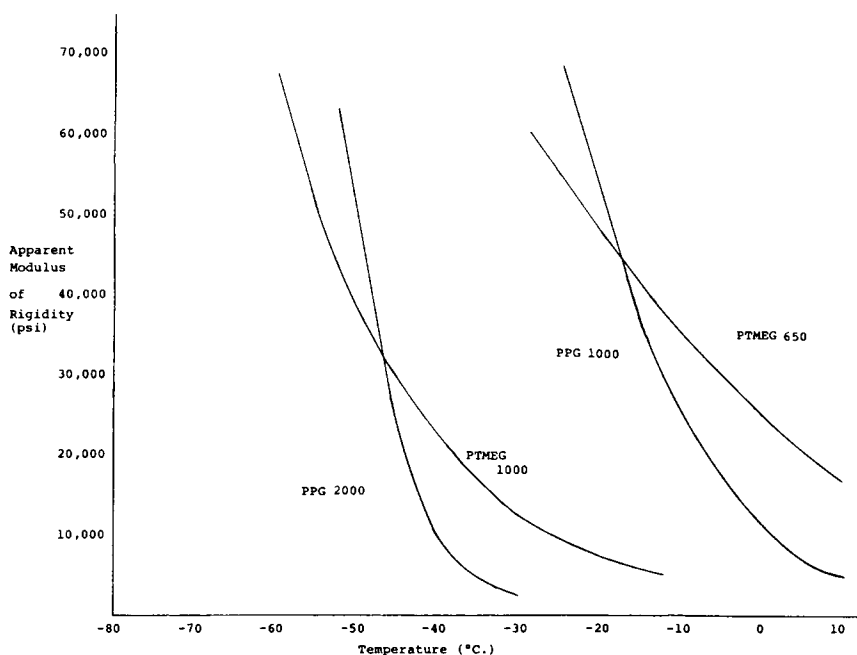


Fig. 7. Low-temperature properties of diol-TDI-MOCA. Polyether comparison.

tetramethylene oxide chain is linear and more mobile causing a more gradual increase in rigidity.

Though the diols PTMEG 1000 (A_n 55 Å), PCL 1250 (A_n 58 Å), PBAG 1000 (A_n 52 Å) and PEPAG 1000 (A_n 49 Å) have similar molecular lengths, their curves, as shown in Figures 1 and 3, show the polyester elastomers to be far less flexible at low temperatures than the PTMEG elastomer. This is also shown in Figures 2 and 3 with the 2000 MW diols, PTMEG 2000 (A_n 93 Å), PCL 2000 (A_n 78 Å), PBAG 2000 (A_n 82 Å), and PEPAG 2000 (A_n 70 Å). Since molecular length of the diols has made the effects of the hard segments of the elastomers nearly constant, one reason for this difference is that the intermolecular bonding of the more polar polyesters is greater than that of the polyethers. The tendency of the polyesters to be more crystalline than the polyethers is imparted to the elastomers prepared from them and as the result a more rigid elastomer is obtained. Table V shows that the molar cohesive energy⁴ (or the intermolecular bonding potential) of the ester grouping is much higher than the ether grouping.

Since an elastomer cast from an MDI prepolymer with a NCO/OH ratio of 2 would be too soft, it is necessary to use MDI prepolymers with a NCO/OH ratio of 3 to obtain elastomers with properties similar to those of the TDI-MOCA elastomers. Table VI shows the difference in tensile properties, and Figure 8 shows the low-temperature rigidity comparison of

TABLE V

| Group | Cohesive energy, kcal/mole |
|---|-------------------------------|
| —CH ₂ — (hydrocarbon) | 0.63 |
| —O— (ether) | 1.00 |
| —COO— (ester) | 2.90 |
| —C ₆ H ₄ — (aromatic) | 3.90 |
| —OCONH— (urethane) | 8.74 |
| —NHCONH— (urea) | >urethane |

TABLE VI
PTMEG 1000-MDI Elastomer Comparison

| Prepolymer NCO/OH | 2/1 | 3/1 |
|-------------------------------|------|------|
| 1,4BD, % | 5.5 | 8.9 |
| Hardness-Shore A | 86 | 96 |
| Tensile, psi | 3630 | 5430 |
| <i>M</i> ₁₀₀ , psi | 720 | 1680 |
| <i>M</i> ₃₀₀ , psi | 1550 | 3100 |
| Elongation, % | 440 | 430 |
| Split tear, pli | 130 | 170 |
| Resiliency, Bashore % | 52 | 48 |

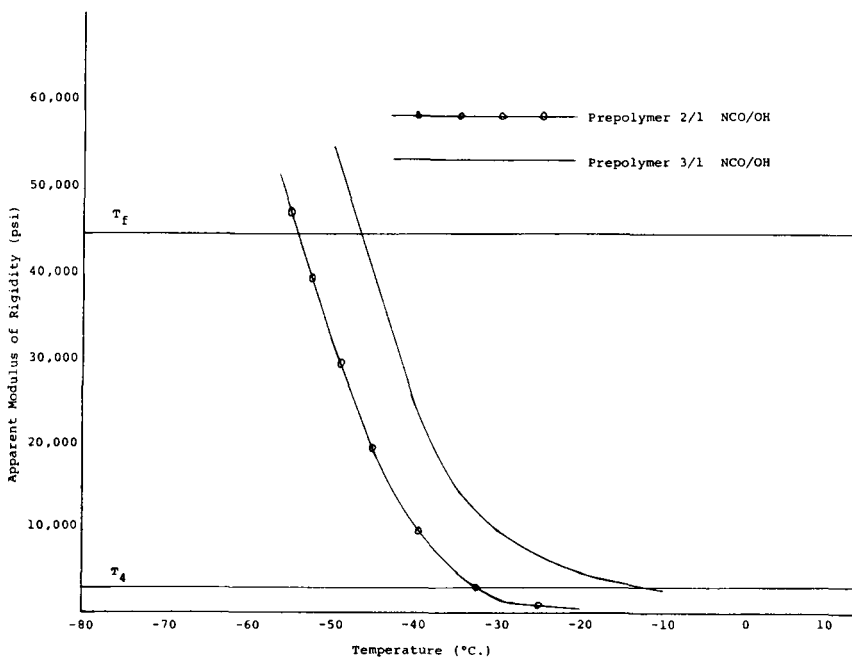


Fig. 8. Low-temperature properties of PTMEG 1000-MDI-1,4BD. MDI prepolymer comparison (—○—○—○—○—) prepolymer 2/1 NCO/OH; (————) prepolymer 3/1 NCO/OH.

TABLE VII
Polyurethane System Comparison

| | PTMEG 1000 | | | PTMEG 2000 | |
|-------------------------------|------------|-----------|-------------------------|------------|-----------|
| | TDI-MOCA | MDI-1,4BD | H ₁₂ MDI-MDA | TDI-MOCA | MDI-1,4BD |
| Hardness | | | | | |
| Shore D | 50 | 50 | 50 | — | — |
| Shore A | 96 | 96 | — | 88 | 86 |
| Tensile, psi | 5650 | 5430 | 5280 | 4250 | 5100 |
| <i>M</i> ₁₀₀ , psi | 1700 | 1680 | 1580 | 670 | 710 |
| <i>M</i> ₃₀₀ , psi | 2750 | 3100 | 4250 | 1020 | 1400 |
| Elongation, % | 435 | 430 | 330 | 625 | 540 |
| Split tear, pli | 200 | 170 | 95 | 70 | 66 |
| Resiliency, | 46 | 48 | 48 | 61 | 65 |
| Bashore % | | | | | |

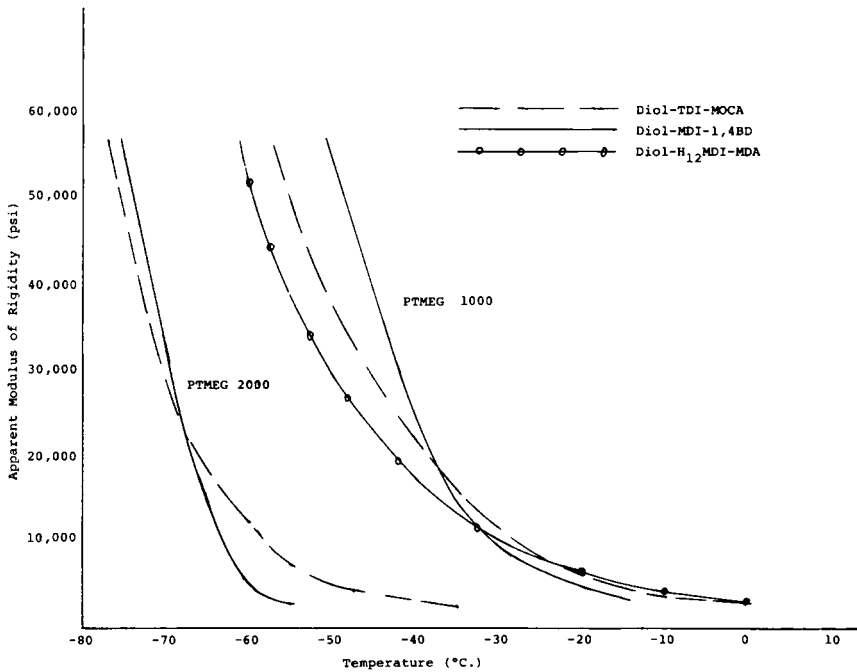


Fig. 9. Low-temperature properties. Comparison of diisocyanate-curative systems. (---) diol-TDI-MOCA; (—) diol-MDI-1,4BD; (—○—○—○—) diol-H₁₂MDI-MDA.

the elastomers obtained from the two different prepolymers prepared with PTMEG 1000.

A comparison of the polyurethane systems TDI-MOCA, MDI-1,4BD, and H₁₂MDI-MDA was made with PTMEG 1000 and PTMEG 2000. Table VII shows that the overall elastomeric properties of the three systems are similar, and in Figure 9 the low-temperature flexibility is compared.

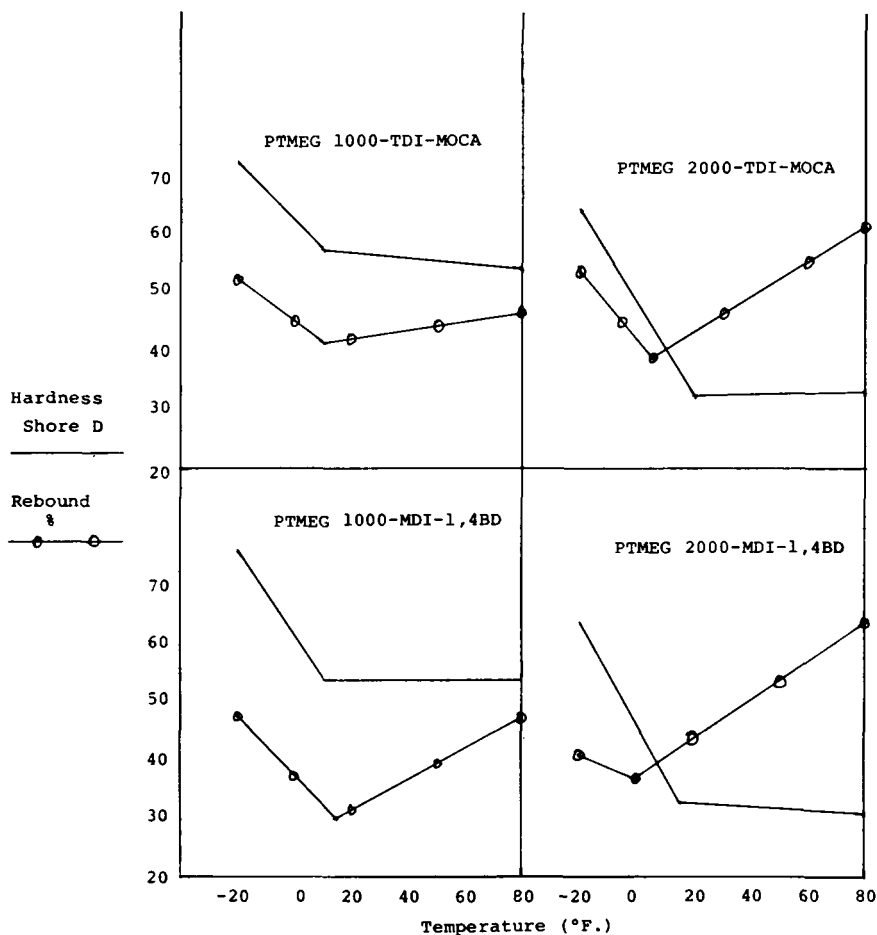


Fig. 10. Hardness-rebound profiles of PTMEG.

Since the diol soft segments of the elastomers in the two cases are held constant, the small differences in flexibility could only be caused by the different hard segments of the elastomers and the relative linearity of the molecules in the elastomers. As a result, the MDI-1,4BD systems show good flexibility at the moderately low temperatures, and the partially aliphatic H_{12} MDI-MDA system has the best overall low-temperature performance.

The tendency of an elastomer to crystallize at low temperatures can be detrimental to its overall low-temperature performance. If the elastomer crystallizes, it will lose its elastic characteristics and become very hard. The temperature at which an elastomer becomes crystalline is dependent on the composition of the elastomer. To explore the effects of the different diols on the crystallinity of the formulated polyurethane elastomers, the cast compression set discs of the different elastomers were subjected to

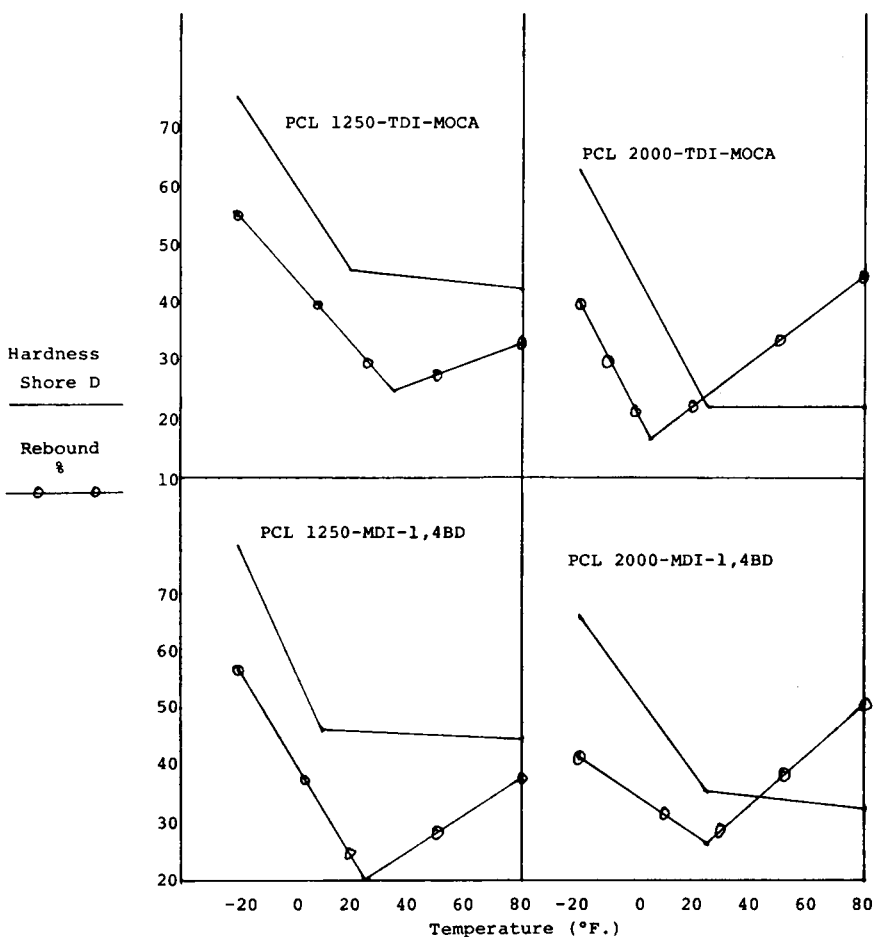


Fig. 11. Hardness-rebound profiles of polycaprolactone.

conditioning at various temperatures between room temperature and -15°F . After conditioning for either 3, 19, or 67 hr, the samples were measured for hardness and resiliency. The results of the tests are tabulated in Table VIII. For each formulation, plots of hardness versus temperature and rebound versus temperature were drawn and are shown in Figures 10 to 13.

In general, with cooling the hardness of each elastomer remains fairly constant until crystallization occurs and an abrupt increase results. The rebound decreases as expected until below a certain temperature it also rapidly increases. Below this temperature the elastomer becomes very hard and loses its elasticity, such that its resiliency is no longer an elastic rebound but similar to a recoil off a hard metal surface. The PEPAG 1000-TDI-MOCA elastomer is unusual because it has only a slight hardness break and an increasing rebound profile. The aliphatic H_{12} MDI

TABLE VIII
Low-Temperature Properties: Hardness and Resiliency

| Elastomer ^a | 77°F | | 45°F | | 35°F | | 25°F | | 10°F | | 0°F | | -15°F | |
|-----------------------------------|------------------|------------|------------------|------------|------------------|------------|------------------|------------|------------------|------------|------------------|------------|------------------|------------|
| | Hardness Shore D | Rebound, % | Hardness Shore D | Rebound, % | Hardness Shore D | Rebound, % | Hardness Shore D | Rebound, % | Hardness Shore D | Rebound, % | Hardness Shore D | Rebound, % | Hardness Shore D | Rebound, % |
| P1000-TDI-MOCA | 54 | 46 | 58 | 43 | 51 | 50 | 42 | 41 | 57 | 41 | 64 | 67 | 43 | 44 |
| P2000-TDI-MOCA | 33 | 61 | 35 | 32 | 32 | 31 | 49 | 50 | 42 | 43 | 46 | 47 | 59 | 38 |
| P1000-MDI-1,4BD | 55 | 48 | 56 | 50 | 39 | 35 | 49 | 50 | 52 | 33 | 65 | 61 | 66 | 36 |
| P2000-MDI-1,4BD | 31 | 65 | 40 | 37 | 58 | 50 | 32 | 32 | 33 | 42 | 39 | 40 | 55 | 37 |
| P1000-H ₁₂ MDI-MDA | 50 | 48 | 54 | — | 46 | — | 58 | 51 | 52 | 46 | 67 | 62 | 66 | 46 |
| PCL 1250-TDI-MOCA | 41 | 33 | 45 | 43 | 28 | 27 | 43 | 44 | 46 | 33 | 68 | 64 | 66 | 43 |
| PCL 2000-TDI-MOCA | 22 | 44 | 23 | 21 | 32 | 32 | 27 | 29 | 21 | 21 | 42 | 45 | 44 | 21 |
| PCL 1250-MDI-1,4BD | 45 | 38 | 46 | 42 | 27 | 24 | 47 | 45 | 46 | 28 | 66 | 62 | 64 | 38 |
| PCL 2000-MDI-1,4BD | 33 | 50 | 34 | 41 | 40 | 31 | 37 | 37 | 32 | 26 | 45 | 51 | 60 | 15 |
| PEPAG 1000-TDI-MOCA | 56 | 31 | 69 | 58 | 40 | 37 | 62 | 66 | 72 | 43 | 87 | 86 | 86 | 48 |
| PEPAG 2000-TDI-MOCA | 28 | 33 | 38 | 28 | 25 | 27 | 30 | 32 | 31 | 21 | 60 | 44 | 64 | 34 |
| PBAG 1000-MDI-1,4BD | 62 | 42 | 67 | 63 | 38 | 38 | 63 | 65 | 66 | 29 | 78 | 78 | 76 | 45 |
| PBAG 2000-MDI-1,4BD | 40 | 45 | 48 | 40 | 35 | 32 | 39 | 45 | 42 | 32 | 61 | 58 | 64 | 33 |
| PBAG 1000-H ₁₂ MDI-MDA | 59 | 46 | 63 | — | 47 | — | 68 | 62 | 66 | 46 | 78 | 75 | 78 | 50 |

^a P = PTMEG.

^b Conditioning: 3 hr 50°F, 1 hr 45°F.

TABLE IX

| Formulation | Hardness break, °F | Rebound minimum, °F |
|------------------------------------|--------------------|---------------------|
| PTMEG 2000-MDI-1,4BD | 15 | 0 |
| PTMEG 1000-TDI-MOCA | 10 | 10 |
| PTMEG 1000-MDI-1,4BD | 10 | 15 |
| PTMEG 2000-TDI-MOCA | 20 | 5 |
| PEPAG 2000-TDI-MOCA | 10 | 15 |
| PCL 2000-TDI-MOCA | 25 | 5 |
| PTMEG 1000-H ₁₂ MDI-MDA | 20 | — |
| PCL 1250-MDI-1,4BD | 10 | 25 |
| PBAG 1000-MDI-1,4BD | 15 | 20 |
| PBAG 2000-MDI-1,4BD | 20 | 30 |
| PBAG 1000-H ₁₂ MDI-MDA | 25 | — |
| PCL 2000-MDI-1,4BD | 25 | 25 |
| PCL 1250-TDI-MOCA | 20 | 35 |
| PEPAG 1000-TDI-MOCA | 45 | >77 |

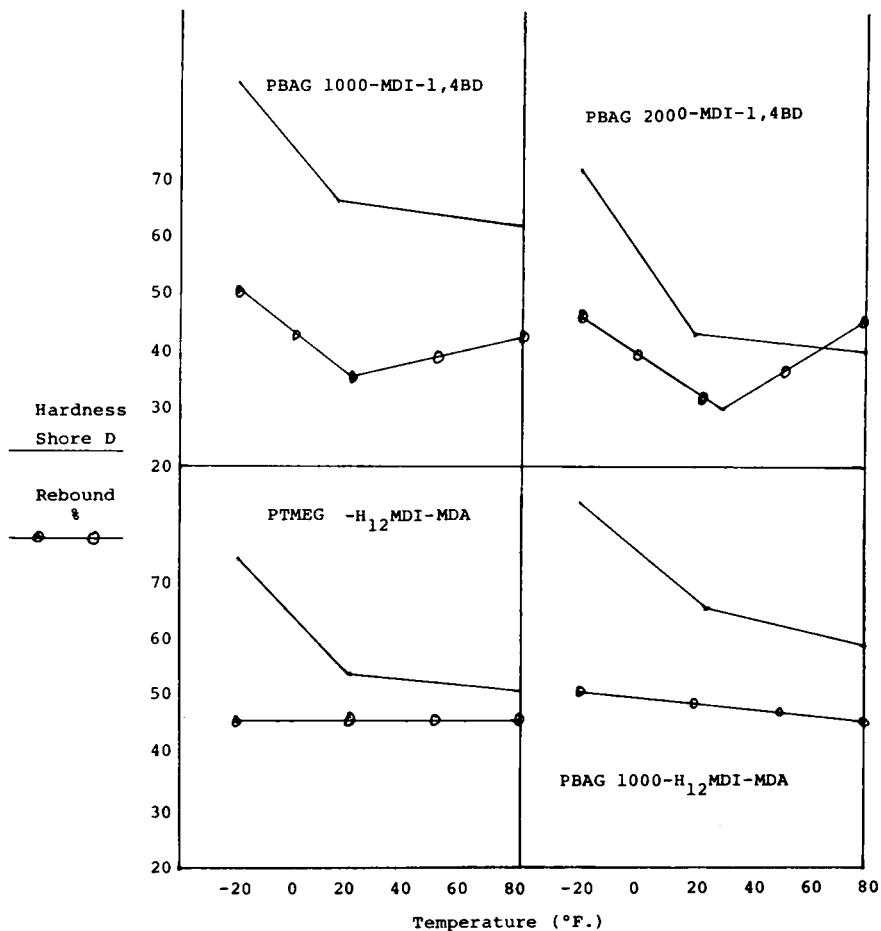


Fig. 12. Hardness-rebound profiles of PBAG and PTMEG.

systems have normal hardness profiles, but their rebound profiles show a relatively constant rebound over the temperature range. Table IX below lists the temperatures at which the elastomers show a hardness curve break and a rebound minimum.

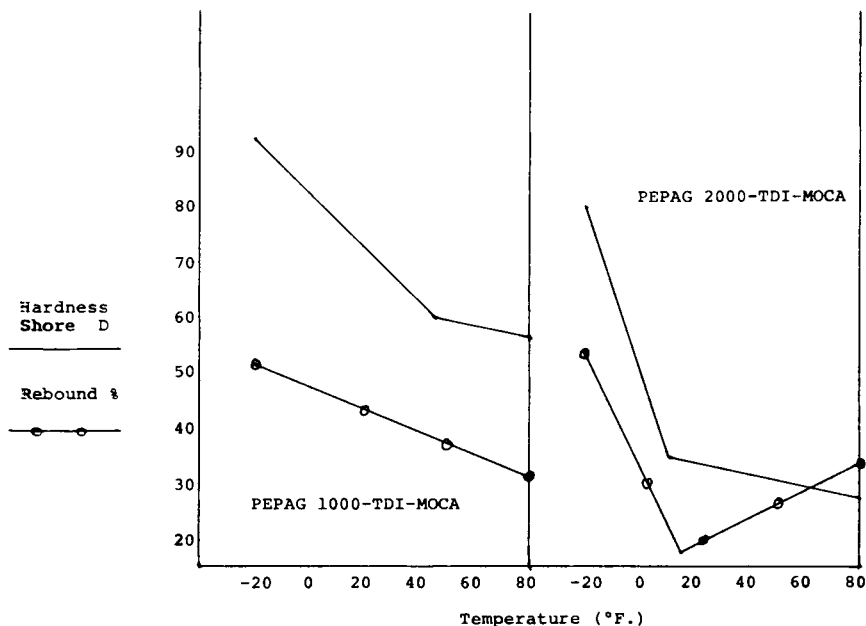


Fig. 13. Hardness-rebound profiles of PEPAG.

TABLE X
Low Temperature Properties Comparison

| Polymeric diol | T_f , °C | T_g , °C | Hardness break | | Rebound minimum | |
|-------------------------|------------|------------|----------------|------|-----------------|------|
| | | | °F | °C | °F | °C |
| TDI-MOCA System | | | | | | |
| PTMEG 1000 | -53 | -5 | 10 | -12 | 10 | -12 |
| PTMEG 2000 | -75 | -43 | 20 | -7.5 | 5 | -15 |
| PCL 1250 | -34 | -15 | 20 | -7.5 | 35 | 2 |
| PCL 2000 | -44 | -32 | 25 | -4 | 5 | -15 |
| PEPAG 1000 | -16 | 10 | 45 | 7 | >77 | >25 |
| PEPAG 2000 | -32 | -18 | 10 | -12 | 15 | -9.5 |
| MDI-1,4BD System | | | | | | |
| PTMEG 1000 | -47 | -10 | 10 | -12 | 15 | -9.5 |
| PTMEG 2000 | -73 | -57 | 15 | -9.5 | 0 | -18 |
| PCL 1250 | -34 | -14 | 10 | -12 | 25 | -4 |
| PCL 2000 | -47 | -35 | 25 | -4 | 25 | -4 |
| PBAG 1000 | -27.5 | 15 | 15 | -9.5 | 20 | -7.5 |
| PBAG 2000 | -44 | -29 | 20 | -7.5 | 30 | -1 |
| H_{12} MDI-MDA System | | | | | | |
| PTMEG 1000 | -57 | -2 | 20 | -7.5 | — | — |
| PBAG 1000 | -35 | 15 | 25 | -4 | — | — |

CONCLUSION

A comparison of the low-temperature performance of polyurethane elastomers as affected by the different polymeric diols is shown in Table X by using the T_f , the T_i , the hardness break, and the rebound minimum as criteria.

By rating the performance of each diol in each category, the best overall diol type for imparting good low-temperature properties to polyurethane systems is the polytetramethylene ether glycol.

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Received March 7, 1973

Revised July 1, 1973