

Mechanical Properties of HTPB–IPDI-Based Elastomers

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ABSTRACT: A polyurethane elastomer having mechanical and adhesive properties suitable for liner applications in solid rocket propellants was developed using HTPB as the prepolymer and IPDI as the curing agent. The effects of the NCO/OH ratio (R value) and the triol/diol ratio on the mechanical properties of the polyurethane matrix were investigated. The reaction of HTPB and IPDI is followed by monitoring the changes in the IR absorption bands of the NCO stretching at 2255 cm^{-1} and the CO stretching at 1730 cm^{-1} . It was found that the rate of the polyurethane formation obeys an overall second-order kinetics. At an R value of 1.15, the elastomer shows the maximum tensile strength and 200% elongation at break. The hardness, elongation, and the tensile strength reach a steady value around the same R value. The elastomers having a triol/diol ratio less than 0.03 show a decrease in the tensile strength and modulus with a concomitant increase in elongation. At a triol/diol ratio greater than 0.05, the tensile strength increases to about the same value for the liner composition without any triol component. The elongation reaches a steady level at a triol/diol ratio of 0.10 and one observes a steady increase in hardness up to about 0.5. The modulus for the compositions having a triol/diol ratio greater than 0.1 is about 50% higher than that for the composition without triol. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2347–2354, 1997

Key words: elastomer; polyurethane; HTPB; liner; diisocyanate

INTRODUCTION

Polyurethane elastomers are widely used engineering materials and are well known for their outstanding mechanical, thermal, and adhesive properties. Polyurethanes are also used as a liner material for HTPB-based composite solid propellants.¹ In the development of such a liner material, knowledge of the mechanical, thermal, and adhesive properties of the material is of great importance. These properties substantially depend on the degree of crosslinking,² which has been shown to be controlled by the use of polyfunctional groups such as triols or by the NCO/OH ratio (R

value) in the polyurethane matrix.³ The effect of crosslinking agents on the structure and properties of polyurethane elastomer composite polymers has been studied for various mixtures of dicumyl peroxide and toluene diisocyanate dimer,⁴ trimethylolpropane and toluene diisocyanate,^{5,6} and trimethylolpropane and 4,4'-diphenylmethane diisocyanate.^{7,8} The NCO/OH ratio was found to affect the properties of the composite polymers.^{9,10}

Here, we report on the effect of the R value and the triol/diol ratio on the mechanical properties of a liner matrix which can be used to hold an HTPB-based solid propellant in the rocket chamber. The liner is prepared using the same prepolymer (HTPB) and the same curing agent (isophorone diisocyanate, IPDI) to assure the optimum compatibility and effective bonding between the

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liner and propellant matrices. The liner matrix is plasticized and reinforced with dioctyladipate and carbon black, respectively. Triethanolamine is used as the crosslinking agent of the polyurethane matrix. In what follows, we discuss the adhesive properties of the same liner-propellant system.

EXPERIMENTAL

Materials

HTPB (R45-M, number-average molecular weight of 2700, ARCO Chemical Co., Philadelphia, PA), isophoron diisocyanate (IPDI, Fluka AG, Leverkusen, Germany), triethanolamine (TEA, E. Merck, Darmstadt, Germany), carbon black (25 nm particle diameter, 98% carbon content, 0.7% sulfur content, 110 m²/g surface area, pH 4, Printex-U, Degussa A.G., Frankfurt, Germany), and dioctyladipate (DOA, Kimtaş, Istanbul, Turkey) were used as purchased.

Polyurethane Matrix Preparation

For matrix preparation, all the ingredients except the curing agent and the curing catalyst are blended thoroughly in a sigma blade mixer for about 10 min at 65°C. The mixing is then continued under a vacuum for another 45 min. After addition of the curing agent to the slurry, the mixture is blended for another 15 min. A dry nitrogen gas blanket is maintained throughout the mixing. The freshly prepared matrix is cast into Teflon molds. The molds are cured for 7 days at 65°C. The dog-bone-shaped matrix specimens are used in the tests.

Method of Testing

The tensile properties of the polyurethane elastomers are determined in the form of dog-bone test specimens under predetermined conditions of pretreatment and temperature.¹¹ The cured samples are tested for their mechanical properties (tensile strength, elongation at break) at room temperature and with a cross-head speed of 50 mm/min using a conventional uniaxial testing system (Hewlett-Packard 1185 type Instron).

Infrared Analysis

Infrared spectra (400–4000 cm⁻¹) of thin polyurethane films are recorded on a Nicolet 20-SX Fou-

Table I Composition and Characteristics of an Elastomeric Liner Matrix

Composition of a Typical Matrix	%
Prepolymer	60–80
Plasticizer	2–10
C-black	5–20
Curing agent	2–10
Physical Properties of the Matrix	
Density at 25°C	0.90–1.10 g/cm ³
Linear thermal expansion coefficient	About 120 · 10 ⁶ /°C
Potlife at 20°C	20–30 min.
Mechanical Properties of the Matrix (Tensile Loading Rate 50 mm/min at 20°C)	
Tensile strength	4–15 kg/cm ²
Elongation	150–900%
Modulus	0.5–12 kg/cm ²

rier transform infrared spectrometer. The polyurethane formation is followed by monitoring the IR spectra of a mixture of starting materials prepared at room temperature and squeezed between two potassium bromide pellets in an inert nitrogen atmosphere.

RESULTS AND DISCUSSION

A typical matrix composition and its characteristics are given in Table I. The effects of the triol/diol ratio and *R* value are tested as follows:

Effect of NCO/OH Ratio on Liner Properties

To study the influence of the NCO index (*R* value) on the mechanical properties of the matrix, experiments are carried out at NCO/OH ratios ranging from 0.9 to 1.3 by keeping the total number of functional groups, the triol/diol ratio (0.054), and the concentrations of all the other components constant. The matrix processing is done in a small sigma blade mixer at the 300g level. The values given are the average of at least a minimum of four measurements for each composition in all sets of experiments.

Table II Mechanical Properties of the Elastomer Matrices with Various NCO/OH Ratios

<i>R</i> Value	Tensile Strength (kg/cm ²)	Elongation at Break (%)	Initial Modulus (kg/cm ²)	Hardness (Shore A)
0.90	4.1 ± 0.4	880 ± 60	0.54 ± 0.02	8
1.00	6.1 ± 0.6	430 ± 160	1.84 ± 0.91	28
1.05	7.7 ± 0.3	250 ± 20	3.20 ± 0.89	30
1.10	6.9 ± 0.7	230 ± 30	3.30 ± 0.05	34
1.15	9.2 ± 1.2	245 ± 30	3.61 ± 0.08	32
1.20	6.9 ± 0.1	190 ± 8	5.00 ± 0.30	32
1.30				28

Mechanical properties of the elastomer matrix samples with various *R* values are given in Table II. The tensile strength and elongation of the matrix material are plotted as a function of the NCO/OH ratios in Figures 1 and 2, respectively. In general, as the *R* value increases, the tensile strength increases and elongation decreases, reaching a plateau level eventually. Among the compositions tested, the matrix formulation with an *R* value of 0.90 is found to be quite elastomeric (about 900% elongation before rupture) in nature. However, the tensile strength of this matrix, which is found to be 4 kg/cm², is too low, as expected, and sufficient mechanical strength cannot be obtained due to the diisocyanate deficiency. The tensile strength of the elastomeric matrix increases with an increasing NCO/OH ratio up to *R* = 1.15 and then starts to decrease. Excess diisocyanate leads to a fast diminishing of hydroxyl groups which can be detrimental to the mechanical properties at *R* = 1.2.

In a complex system such as that used in this study, it is not easy to relate the tensile strength to the *R* values. The optimum conditions for the formation of higher molecular weights or the amount of crosslinks may depend on the *R* value in a complicated manner. The presence of triols, the molecular weight distribution of HTPB, and the average functionality and its distribution in HTPB may be coupled with the diffusivities of —NCO and —OH groups as the extent of reaction increases and they can all be factors that govern the overall MW and crosslink density of the cured matrix. In addition, the functional groups that are present on the fine powdered carbon black filler can react with the diisocyanate. The observation of a maximum for the tensile strength at *R* values greater than 1.00 might be attributed to the consumption of excess diisocyanate by the functional groups on the filler surface.

The hardness and the modulus of the polyurethane elastomers increase with an increasing *R*

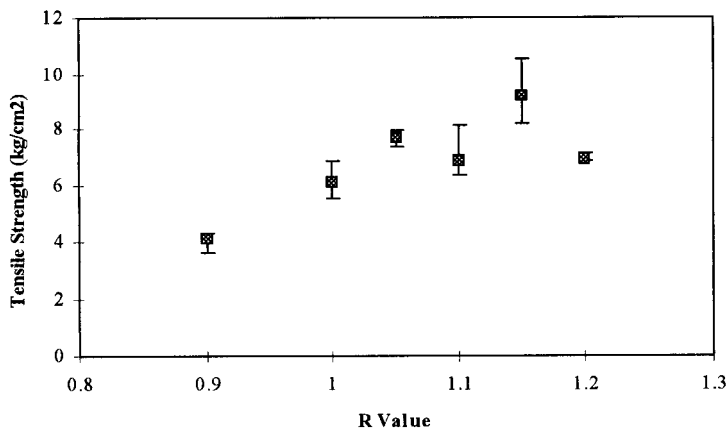


Figure 1 Effect of *R* value on the maximum tensile strength of an HTPB-based polyurethane elastomer.

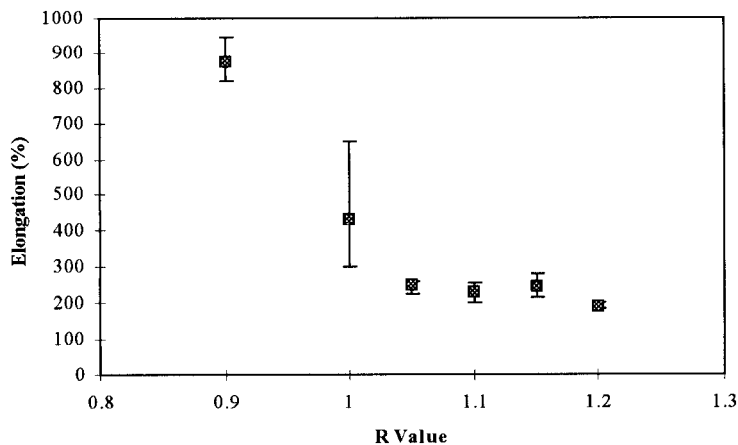


Figure 2 Effect of R value on elongation at break of an HTPB-based polyurethane elastomer.

value, as shown in Figures 3 and 4, respectively. Hardness is governed by the polyurethane structures formed. When the matrix system solidifies, the polyurethane formation is terminated, and the hardness reaches to a plateau because no more polyurethane structures or crosslinks can be formed. The polyurethane formation is restricted by the limited number of hydroxyls in the system at high R values ($R > 1.0$).

Kothandaraman et al.² showed that crosslinking at a higher diisocyanate ratio proceeds through the formation of allophanate and isocyanurate linkages. However, it was later shown that allophanate linkages can only be formed above 140°C in a considerably long reaction time (8 h).¹² Thus, in the present study, the allophanate formation can be neglected under the given experimental conditions. The other possible reaction, isocyanurate linkage formations, can only be

formed by heating the polymer with a strong organic base; therefore, it is conceivable that the only major reaction is between the diisocyanates and hydroxyl groups. Indeed, the comparison of the FTIR spectra taken before and after curing (Fig. 5) provides compelling evidence for the reaction between the diisocyanates and hydroxyl groups to yield polyurethane linkages.

The Cure Mechanism for the Polyurethane Matrix

The reaction of the HTPB prepolymer with the diisocyanate was followed by monitoring the changes in the IR absorption bands of the NCO stretching at 2255 cm^{-1} and the CO stretching growth at 1730 cm^{-1} (Fig. 5). The IR absorption band of the NCO stretching at 2255 cm^{-1} loses intensity and the band for the CO stretching at 1730 cm^{-1} gains intensity while there is almost

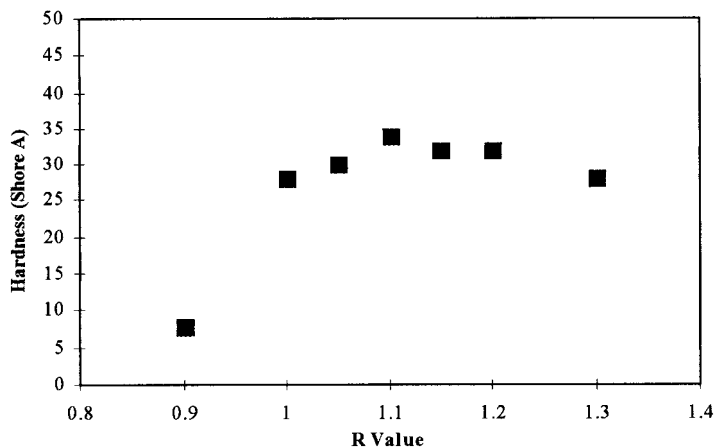


Figure 3 Effect of R value on hardness of cured matrix elastomers.

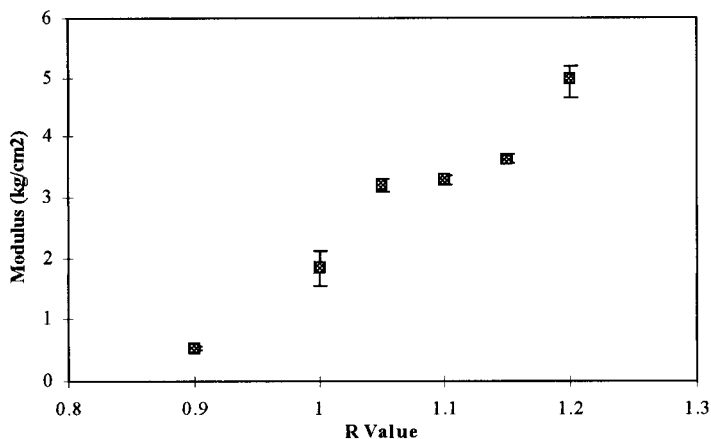


Figure 4 Effect of *R* value on modulus of cured matrix elastomer.

no change in the peak intensity of the C=C stretching at 1640 cm^{-1} throughout the polymerization reaction. Absorptions for the OH stretchings around 3400 cm^{-1} are known to be relatively weak and broad. No noticeable change is observed in this region of the spectrum. The decrease in the characteristic absorption of the NCO stretching at 2255 cm^{-1} and the growth of the band for the CO stretching at 1730 cm^{-1} are indicative of polyurethane (—NHCOO—) formation.¹³ The absorption band at 1515 cm^{-1} is assigned to N—H bending. In a preliminary kinetic study, the change in the intensity of the absorption band at 2255 cm^{-1} was used to estimate the rate of the polyurethane formation reaction starting with a mixture of HTPB and IPDI having an *R* value of 1.00. The rate of the polyurethane formation reaction is

found to be first order with respect to the NCO and OH concentrations. Thus, the reaction overall obeys a second-order kinetics.¹⁴ The evaluation of the kinetic data at different temperatures gives an activation energy of ca. 49.7 kJ/mol for the polyurethane formation reaction between HTPB and IPDI. The results of the undergoing detailed kinetic study will be reported elsewhere.

Effect of Triol/Diol Ratio on Mechanical Properties

In this part of the experiments, the effect of the triol/diol ratio on the mechanical properties was studied by changing the concentration of triethanolamine (TEA) for a typical matrix formulation with a constant *R* value of 1.1 which provides the elastomer with relatively the best mechanical

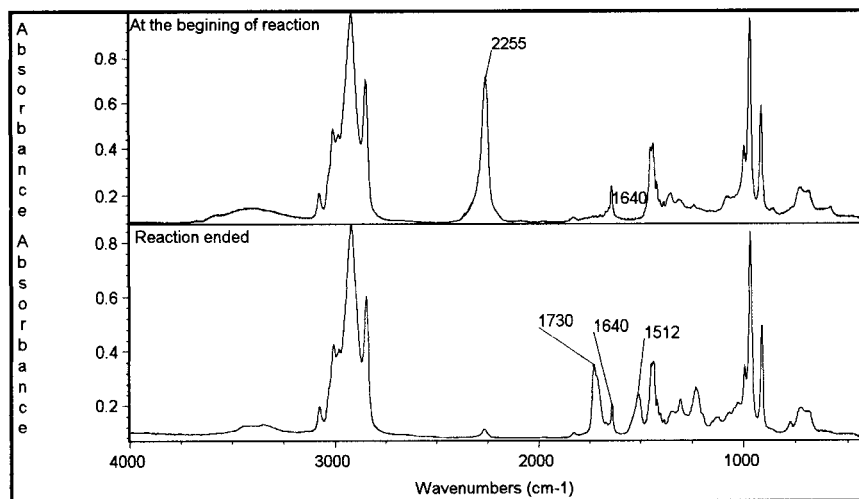


Figure 5 FTIR spectra of a mixture of HTPB and diisocyanate with a NCO/OH ratio of 1.00 (top) before and (bottom) after curing.

Table III Mechanical Properties of the Elastomer Matrices with Various Triol/Diol Ratios

Triol/Diol	Tensile Strength (kg/cm ²)	Elongation at Break (%)	Initial Modulus (kg/cm ²)	Hardness (Shore A)
0.000	8.9 ± 1.2	300 ± 50	2.9 ± 0.8	32
0.031	6.1 ± 1.6	330 ± 40	1.6 ± 0.7	34
0.054	6.9 ± 0.7	230 ± 30	3.3 ± 0.1	36
0.130	6.5 ± 0.4	165 ± 20	4.3 ± 0.2	38
0.388	8.0 ± 1.2	200 ± 50	4.5 ± 2.5	47
0.500	9.4 ± 2.5	190 ± 6	5.6 ± 2.6	48

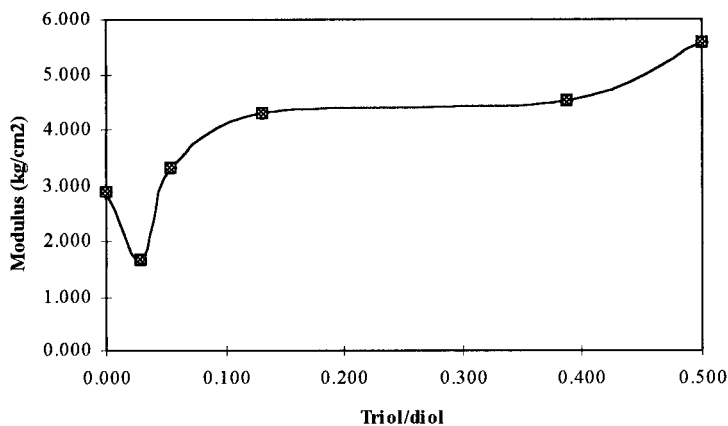
properties. Elastomeric matrix samples were characterized in terms of their tensile properties and their hardness. The results of this set of experiments are given in Table III. The experiments were carried out by varying the triol/diol ratio in the range of 0.0–0.5. Introduction of chemical crosslinks is expected to modify the overall behavior of these polymers. Chemical crosslinking can be introduced into a polyurethane matrix either by the use of a short polyol having a functionality greater than 2 as the chain extender or by the use of triols. The latter was chosen in our experiments.

As the crosslink density in the elastomeric polyurethane matrix increases, several systematic changes occur in the tensile properties: The modulus of the matrix decreases initially and starts to increase as shown in Figure 6. An initial decrease in the modulus reflects the acquirement of a rubbery character with the inclusion of crosslinks into the system coupled with a decrease in the average molecular weight, since three HTPB molecules are replaced by approximately two

small TEA molecules. As the number of crosslinks increases above a critical level, which can be related to the formation of infinite network structure, the material becomes more rigid.

Maximum tensile stress values also increase with the triol concentration in the system (Fig. 7). In the absence of triol, the elastomeric matrix material shows a high tensile strength value (≈ 9 kg/cm²), due to the high average molecular weight. When a small amount of triol is introduced into the system, the average molecular weight is decreased, which cannot be counterbalanced by the small number of the crosslinks formed. This is thought to be responsible for the decrease in the tensile strength.

An observation which supplements the variation in the modulus (Fig. 6) is the change in the maximum elongation with the triol/diol ratio (Fig. 8). The elongation at break increases first with the increasing concentration of triol, and after reaching a maximum at the triol/diol ratio of 0.031, it starts to decrease. The observation of this maximum is indicative of the acquirement of

**Figure 6** Effect of triol concentration on modulus of the HTPB-based polyurethane elastomer.

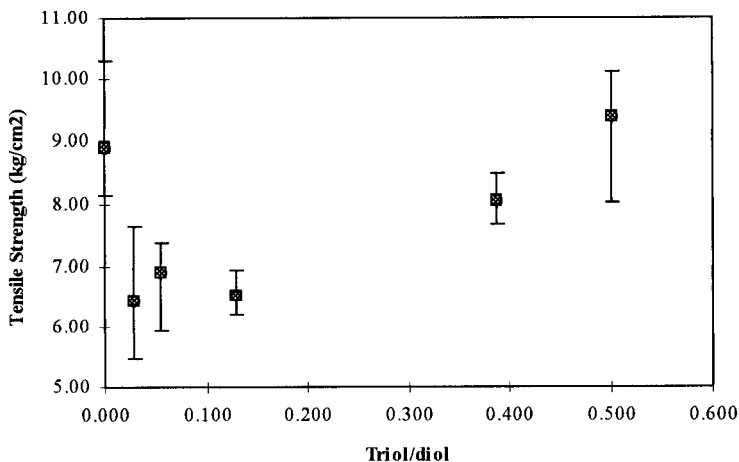


Figure 7 Effect of triol concentration on tensile strength of the HTPB-based polyurethane elastomer.

a rubbery character followed by increased rigidity with an increase in triol/diol ratio.

Hardness, in general, varies with the concentration of the polyurethane units formed and the number of crosslinks. In this set of experiments, the number of polyurethane linkages formed is kept constant at $R = 1.1$. With an increase in the triol/diol ratio, the number of hard segments per unit volume increases. Therefore, the increase in hardness (Fig. 9) can be directly attributed to the number of crosslinks formed and to the increase in the hard-segment density.

CONCLUSION

A liner elastomer with a proper balance of mechanical and adhesive properties is developed,

and in this study, the effect of NCO/OH ratio (R value) and the triol/diol ratio on the mechanical properties were investigated. In the study that follows, the adhesional characteristics of the same system toward a more rigid filled polyurethane matrix will be discussed. The conclusions emerged from this study can be summarized as follows:

- At an R value of 1.15, the elastomer shows the maximum tensile strength and an elongation of 200% at break. The hardness, elongation, and the tensile strength reach a steady value around the same R value.
- For the elastomers having a triol/diol ratio less than 0.03, a decrease in the tensile strength and modulus with a concomitant increase in elongation is observed. Over a triol/

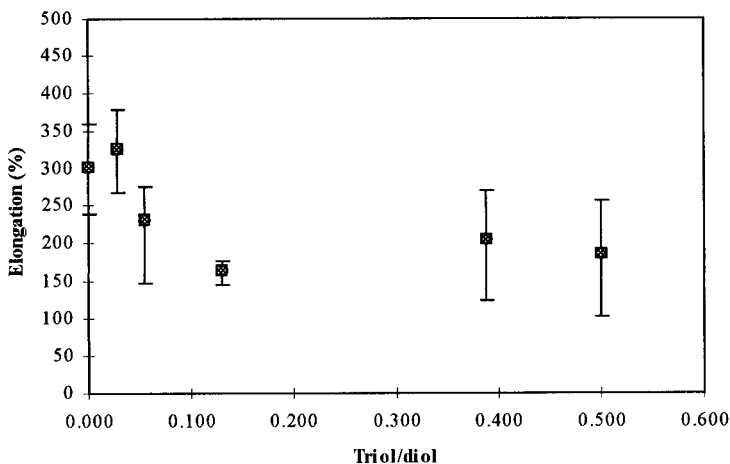


Figure 8 Effect of triol concentration on elongation at break of the HTPB-based polyurethane elastomer.

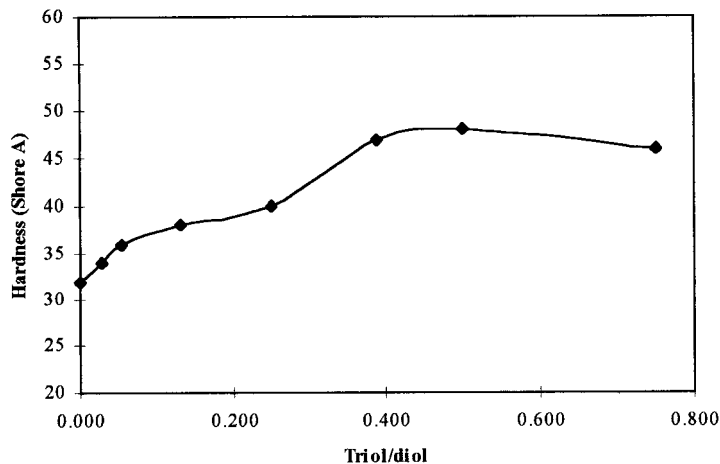


Figure 9 Effect of triol concentration on hardness of the HTPB-based polyurethane elastomer matrix.

diol ratio of 0.05, the tensile strength increases to about the same value for the liner composition without any triol component. The elongation reaches a steady level at a triol/diol ratio of 0.10 and one observes a steady increase in hardness up to about 0.5. The modulus for the compositions having a triol/diol ratio greater than 0.1 is about 50% higher than that for the composition without triol.

The mechanical properties outlined are to be considered together with the elastomer metal–liner–propellant matrix adhesion to achieve an optimum composition toward the end use which gives the shock-absorption capacity, compressibility, and the thermal behavior.

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