

# Mechanical and Swelling Properties of HTPB-Based Copolyurethane Networks

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## SYNOPSIS

Copolyurethanes of hydroxy terminated polybutadiene (HTPB) and ISRO-Polyol (ISPO), an indigenously developed castor-oil based polyol, have been prepared using toluene diisocyanate and hexamethylenediisocyanate. The mechanical strength and swelling characteristics of the copolyurethanes cured with trimethylol propane and triethanolamine have been studied to evolve improved solid propellant binders. By varying the ratios of the two hydroxy pre-polymers, chain extenders, and crosslinkers, copolyurethanes having a wide range of tensile strength and elongation could be obtained. Many of these systems are desirable for their use as propellant binders. The results have been explained in terms of the measured crosslink densities and other swelling properties. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polybutadiene binders have been used extensively in solid composite propellants. Not only do they give higher specific impulse, their elastic nature imparts desirable mechanical strength to the grain. The requirement of mechanical properties of a solid propellant grain is, however, dictated by the structural loads it is subjected to during combustion, flight, and transportation. Different applications thus demand different mechanical property requirements. For example, rocket motors for launch vehicles require low moduli grains, while stiff propellant grains are needed for sounding rockets and missiles. The structural integrity of the propellant is mainly determined by the binder characteristics. In order to tailor the mechanical strength of grain to a particular mission, therefore, the binder characteristics have to be altered suitably. The method commonly used to alter the characteristics involves modification of the polymer backbone. The characteristics of polybutadiene binder, for example, can be modified by using copolymers, such as polybutadiene-acrylic acid (PBAA) and polybutadiene-acrylic acid-acryloni-

trile (PBAN). In fact, PBAA and PBAN have been extensively used for making high solid-loading propellants.

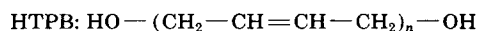
Polyurethane binders based on hydroxy-terminated polybutadiene (HTPB) offer many advantages and have been widely used in modern propellants.<sup>1</sup> These binders not only provide better energetics (higher specific impulse), but the propellants have adequate mechanical strength. In addition the cured systems have excellent low temperature properties. Another hydroxy group terminated binder developed recently by ISRO, India, the ISRO-Polyol (ISPO), is derived from cheaply available castor oil. The urethane based on this polyol has been examined for its use as a binder in solid rockets. Although from the specific impulse point of view, the HTPB-based propellants are marginally superior, ISPO provides better pot life, permits higher solid loadings, and is expected to have better aging characteristics.<sup>2</sup> In view of the advantages offered by the two polymers individually, it is interesting to see if these qualities could be integrated, by making copolymers of these two polymers. Also, since the backbone composition can be varied by altering the ratio of the two polymers, it is envisaged that the required mechanical strength could be achieved simply by changing the ratio. In the present study we report the characterization of the unfilled copolyurethanes

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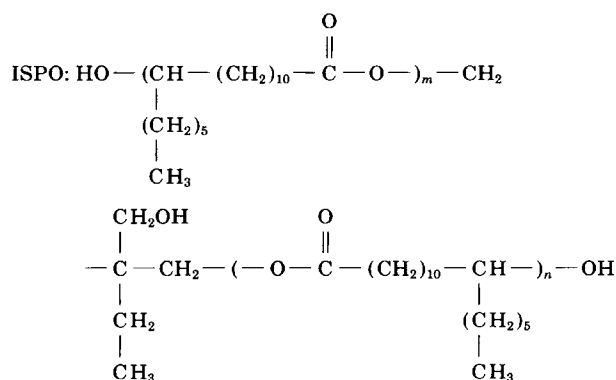
of HTPB and ISPO cured with various isocyanates and cross linkers, in regard to their mechanical and swelling properties.

## EXPERIMENTAL

### Materials



The polymer, synthesized by the free radical polymerization of butadiene gas was supplied by Vikram Sarabhai Space Center (VSSC), India. It had an average number molecular weight ( $M_n$ ),  $\sim 2800$ ; functionality, 2.4; and viscosity, 6500 cp at 30°C.



This binder, prepared by self-polymerization of 12-hydroxy stearic acid in the presence of para toluene sulfonic acid catalyst followed by condensation with trimethylol propane, was obtained from VSSC, India. It had an average  $M_n$ ,  $\sim 2000$ ; functionality 2.0; and viscosity, 2000 cp at 30°C.

The isocyanates used for making the urethanes were toluene diisocyanate (TDI) and hexamethylenediisocyanate (HMDI). A 80 : 20 mixture of 2,4 and 2,6 isomers of TDI, and HMDI were supplied by M/S AG Bayer, and Fluka Co., respectively. The crosslinkers used were 1,1,1-trimethylol propane (TMP) and triethanolamine (TEA). These were supplied by M/S Celanese Corporation and SD Chemicals, respectively.

### Preparation of Copolyurethanes

The copolyurethane elastomers based on HTPB and ISPO were prepared by mixing the two prepolymers in four different equivalent ratios. These were reacted with the two different isocyanates, namely TDI and HMDI. The copolyurethanes thus formed were crosslinked using the triols, TMP, and TEA. The

triol content was kept at 1.2 times the hydroxy equivalents present in the polymer mixtures. For comparison sake, urethanes of HTPB as well as ISPO were also made and crosslinked under identical conditions. In all the cases, the NCO/OH ratio was kept at unity.

In actual practice, calculated amounts of HTPB, ISPO, and the triol crosslinker were mixed thoroughly in a beaker and dried for one hour at 70°C in a vacuum oven. A calculated amount of the isocyanate was then added, followed by the addition of a drop of dibutyltindilaurate catalyst, and mixed thoroughly. The mixture was degassed and poured into aluminum molds and kept at room temperature for 24 h, followed by curing at 70°C for another 24 h. The cured elastomers were subjected to mechanical testing and swelling studies.

### Mechanical Properties

Tensile strength and percentage elongation at break of the cast urethanes were determined using an Instron universal testing machine Model 14202 using dumb-bell shaped specimens as described in ASTM-D412. Moduli of various specimens were measured at 100% elongation. A Frank hardness tester with shore-A durometer was used to measure the hardness of the viscoelastic materials as per the ASTM-D2240-81 procedure.

### Crosslink Density and Average $M_n$ between Crosslinks

Cross-link density, defined as moles of effective network chain per cubic centimeter, was obtained by calculating the volume fraction of the swollen polymer. For this, the swell ratio ( $Q$ ) was obtained experimentally by placing the polymer specimens, measuring  $7 \times 7$  mm, in toluene for 24 h. The specimens were removed from the solvent and weighed after gently wiping off the solvent. Subsequently, the solvent absorbed was driven off by placing the specimen in a vacuum oven for 2 h at 100°C, and the weight of the deswollen specimen was determined. From the weights of the swollen ( $W_s$ ) and deswollen ( $W_{ds}$ ) specimens, the swell ratio is given by

$$Q = W_s/W_{ds} - 1. \quad (1)$$

The weight fraction of the polymer ( $W_2$ ) and the solvent ( $W_1$ ) can then be calculated by the relation,

$$W_2 = 1/(1 + Q) \quad \text{and} \quad W_1 = 1 - W_2. \quad (2)$$

The volume fraction of the polymer ( $V_2$ ) in the swollen specimen is given by

$$V_2 = \frac{W_2/\rho_2}{W_2/\rho_2 + W_1/\rho_1} \quad (3)$$

where  $\rho_1$  and  $\rho_2$  are the densities of the solvent and the polymer, respectively.

From the volume fraction data under equilibrium swollen condition, the cross-link density ( $\nu_e$ ) and molecular weight between crosslink points ( $M_c$ ) were calculated by the Flory–Rhener relation,<sup>3</sup>

$$\nu_e = \frac{-[\ln(1 - V_2) + V_2 + \chi V_2^2]}{V_s(V_2^{1/3} - V_2/2)} = \frac{\rho_2}{M_c} \quad (4)$$

where  $V_s$  is the molar volume of the solvent, and  $\chi$  is the polymer–solvent interaction parameter, which is related to the solubility parameters<sup>4</sup> of the polymer ( $\delta_p$ ) and the solvent ( $\delta_s$ ), as,

$$\chi = 0.34 + V_s/RT (\delta_p - \delta_s)^2 \quad (5)$$

where  $R$  is the gas constant and  $T$  is the absolute temperature. The solubility parameter could be equated<sup>5</sup> to the square root of the cohesive energy density ( $E_{coh}$ ) by the relation

$$\chi = (E_{coh}/V)^{1/2}. \quad (6)$$

The cohesive energy (Van Krevelen–Hoflyzer)<sup>5</sup> and molar volume ( $V$ ) parameters<sup>5a</sup> could be estimated by the group additivity method.

#### Sample Calculation of the Solubility and Polymer Solvent Interaction Parameters for HTPB and ISPO

The repeating unit in HTPB being ( $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$ ), the calculated value for this unit will represent the value for the polymer molecule. The  $E_{coh}$  values for this unit may be written as follows

$$\begin{aligned} E_{coh} &= \Sigma E_{icoh} = E_{icoh}(\text{CH}=\text{CH}) + 2E_{icoh}(\text{CH}_2) \\ &= 10200 + 2 \times 4190 = 18590 \text{ J/mole.} \end{aligned}$$

Similarly molar volume is given by

$$\begin{aligned} V &= \Sigma V_i = V_i(\text{CH}=\text{CH}) + 2V_i(\text{CH}_2) \\ &= 60.65 \text{ cm}^3/\text{mole.} \end{aligned}$$

Hence,

$$\delta_{\text{HTPB}} = 17.5 \text{ J}^{1/2}/\text{cm}^{3/2}.$$

Similarly for ISPO,

$$\begin{aligned} E_{coh} &= 15E_{icoh}(\text{CH}_2) + E_{icoh}(\text{CH}_3) + E_{icoh}(\text{COO}) \\ &\quad + E_{icoh}(-\text{C}-\text{H}) \\ &= 86320 \text{ J/mole.} \end{aligned}$$

and

$$V = 304 \text{ cm}^3/\text{mole.}$$

Hence,

$$\delta_{\text{ISPO}} = 16.85 \text{ J}^{1/2}/\text{cm}^{3/2}.$$

Assuming,

$$\delta = 18.1 \text{ J}^{1/2}/\text{cm}^{3/2} \text{ and } V_s = 106.3 \text{ cm}^3,$$

for toluene,<sup>5</sup> the interaction parameters for HTPB and ISPO can be calculated using eq. (5)

$$\chi_{\text{HTPB}} = 0.355 \quad \text{and} \quad \chi_{\text{ISPO}} = 0.406.$$

The  $\chi$  values for different mixtures of HTPB and ISPO were calculated as the weighted average of the individual values. By substituting the  $V_2$  and  $V_s$  values in eq. (4), the cross-link density and molecular weight between the crosslinks of the various compositions were calculated. These parameters are listed in Table I.

## RESULTS

The mechanical strength data of the urethanes and copolyurethanes, presented in Figures 1–4, reveal vividly the effect of various chemical processing parameters. The non-triol crosslinked polyurethane of HTPB show considerably higher mechanical strength in contrast to that based on ISPO. In fact, the ISPO polyurethane, having no triol curative is so soft that it has no measurable mechanical strength. As a result, a common feature of the polyurethanes having no crosslinking agent is that the tensile strength, modulus at 100% elongation ( $E_{100}$ ), and the hardness decrease with an increase in the ISPO content in the composition. The elongation on the other hand increases and the polymer be-

**Table I** Swelling Properties of Copolyurethanes

System/Property	HTPB : ISPO Ratio					
	1.0 : 0.0	0.8 : 0.2	0.6 : 0.4	0.4 : 0.6	0.2 : 0.8	0.0 : 1.0
<b>HTPB-ISPO-TDI</b>						
$Q$	4.085	5.095	6.845	11.211	20.861	—
$V_2$	0.185	0.155	0.118	0.075	0.042	—
$\nu_e (\times 10^4)$	1.433	0.915	0.507	0.196	0.06	—
$M_c$	6514	10271	18556	48235	159700	—
<b>HTPB-ISPO-TDI-TMP</b>						
$Q$	2.145	2.295	2.482	2.710	3.060	3.516
$V_2$	0.296	0.282	0.265	0.246	0.223	0.199
$\nu_e (\times 10^4)$	4.250	3.660	3.012	2.435	1.841	1.330
$M_c$	2263	2628	3229	4020	5359	7425
<b>HTPB-ISPO-TDI-TEA</b>						
$Q$	3.385	3.75	3.975	4.315	4.735	5.101
$V_2$	0.210	0.193	0.183	0.170	0.157	0.146
$\nu_e (\times 10^4)$	1.884	1.503	1.267	1.038	0.822	0.668
$M_c$	5129	6451	7712	9457	12001	14869
<b>HTPB-ISPO-HMDI</b>						
$Q$	4.312	5.591	7.565	12.988	22.833	—
$V_2$	0.177	0.146	0.108	0.066	0.038	—
$\nu_e (\times 10^4)$	1.297	0.827	0.423	0.151	0.051	—
$M_c$	7211	11367	22279	62952	187451	—
<b>HTPB-ISPO-HMDI-TMP</b>						
$Q$	2.768	2.679	3.199	3.553	4.338	5.66
$V_2$	0.292	0.249	0.216	0.198	0.156	0.133
$\nu_e (\times 10^4)$	4.108	2.721	1.854	1.462	0.815	0.547
$M_c$	2362	3580	5312	6760	12142	18208
<b>HTPB-ISPO-HMDI-TEA</b>						
$Q$	3.107	4.414	5.224	6.066	7.94	10.47
$V_2$	0.223	0.167	0.144	0.126	0.099	0.0767
$\nu_e (\times 10^4)$	2.158	1.104	0.762	0.550	0.314	0.175
$M_c$	4579	8856	12932	17975	31611	57005

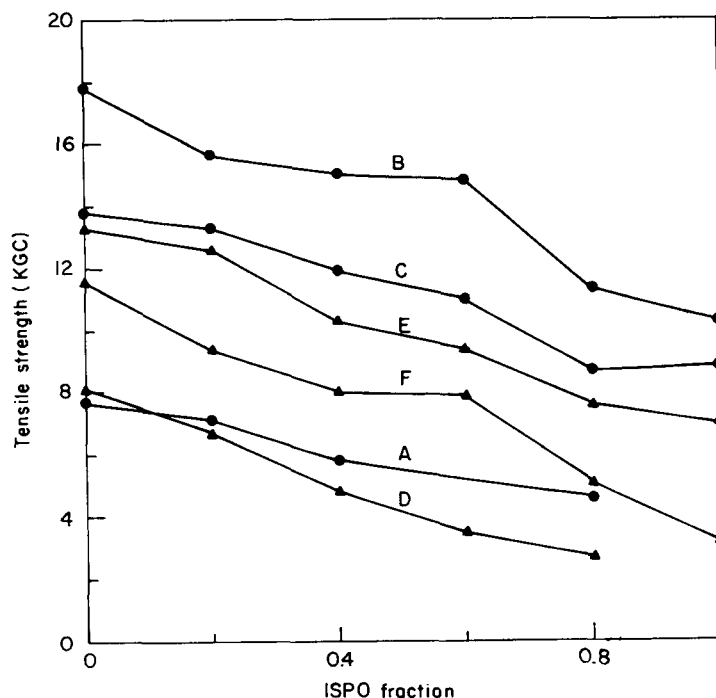
comes soft on increasing the ISPO content. This feature is irrespective of the chain extenders, TDI or HMDI, used. Addition of the crosslinking agents, as expected, improves the tensile strength, modulus, and hardness significantly and decreases the elongation. Variation of these properties with the increase in the ISPO content, however, follows the same trend as observed in the case of the uncrosslinked copolyurethanes.

The tensile strength data of the crosslinked copolyurethanes presented in Figure 1, show an overall decreasing strength with the increase in the ISPO content. The plots, however, do not conform to a linear pattern. The typical plots of percent elongation and hardness vs. the composition shown in Figures 2 and 3, respectively, indicate that while the elongation increases the hardness decreases with the ISPO content. It is also apparent that the percent elongation of HTPB polyurethane is relatively less

affected by the types of crosslinker or chain extender used than that based on ISPO.

Of the two crosslinkers used, TMP appears to be more effective in imparting high tensile strength and hardness. The type of isocyanate used also plays a major role. In general, the TDI-cured polyurethanes give higher tensile strength and lower elongations. The effect of the isocyanate type and crosslinker on the modulus ( $E_{100}$ ) is shown in Figure 4. Almost linear plots are obtained when  $E_{100}$  values are plotted against the composition of the polyurethanes. Significant differences in  $E_{100}$  are observed, however, when crosslinkers TMP and TEA are used. Overall, the TDI appears to be superior to HMDI in imparting the mechanical strength.

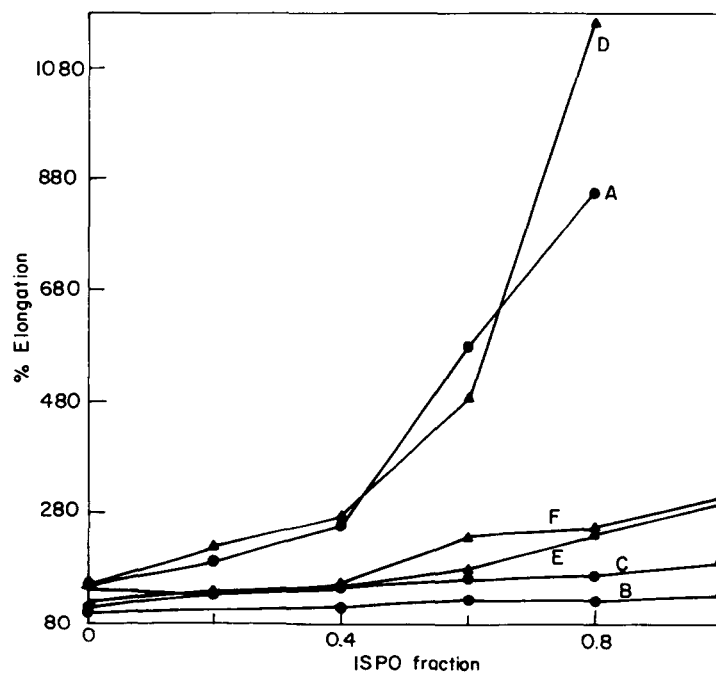
The swelling properties of the polyurethanes and copolyurethanes listed in Table I show that the swell ratio ( $Q$ ) of HTPB-TDI system is significantly lower than that of ISPO-TDI system in the absence



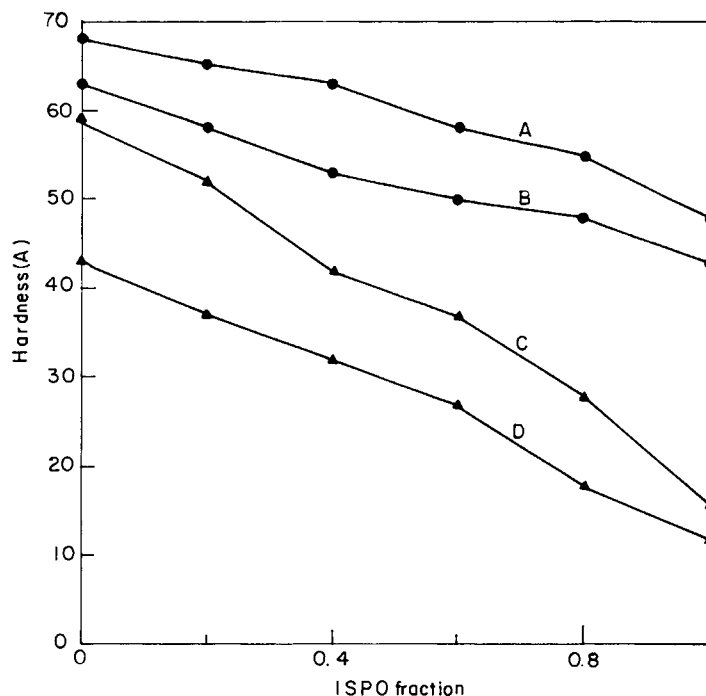
**Figure 1** Tensile strength vs. copolyurethane (HTPB-ISPO) composition having, (A) TDI, (B) TDI-TMP, (C) TDI-TEA, (D) HMDI, (E) HMDI-TMP, (F) HMDI-TEA.

of a crosslinker. The difference in  $Q$  is narrowed down when a crosslinker is used. The swell ratio increases with increase in the ISPO content in the

copolyurethanes. This aspect is further reflected in other swell properties. Thus, while the volume fraction of the polymer and crosslink density decrease



**Figure 2** Percent elongation vs. copolyurethane (HTPB-ISPO) composition having (A) TDI, (B) TDI-TMP, (C) TDI-TEA, (D) HMDI, (E) HMDI-TMP, (F) HMDI-TEA.

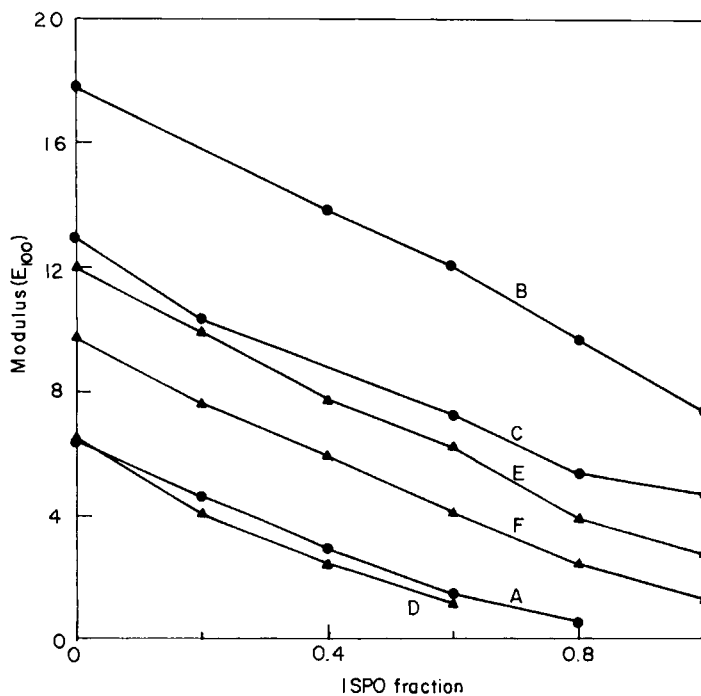


**Figure 3** Hardness (shore A) vs. copolyurethane (HTPB-ISPO) composition having, (A) TDI-TMP, (B) TDI-TEA, (C) HMDI-TMP, (D) HMDI-TEA.

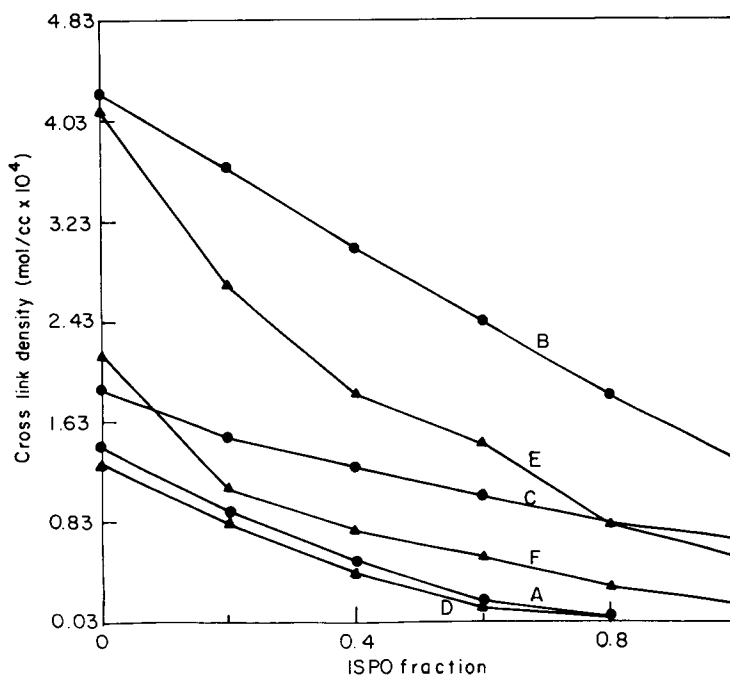
with the increase in the ISPO content, the molecular weight between the crosslinks increases.

The effect of the isocyanate type and crosslinker

on the crosslink density is shown in Figure 5. It is seen that the use of TDI gives slightly better crosslink density than HMDI, in the absence of a triol



**Figure 4** Modulus ( $E_{100}$ ) vs. copolyurethane (HTPB-ISPO) composition having, (A) TDI, (B) TDI-TMP, (C) TDI-TEA, (D) HMDI, (E) HMDI-TMP, (F) HMDI-TEA.



**Figure 5** Crosslink density vs. copolyurethane (HTPB-ISPO) composition having, (A) TDI, (B) TDI-TMP, (C) TDI-TEA, (D) HMDI, (E) HMDI-TMP, (F) HMDI-TEA.

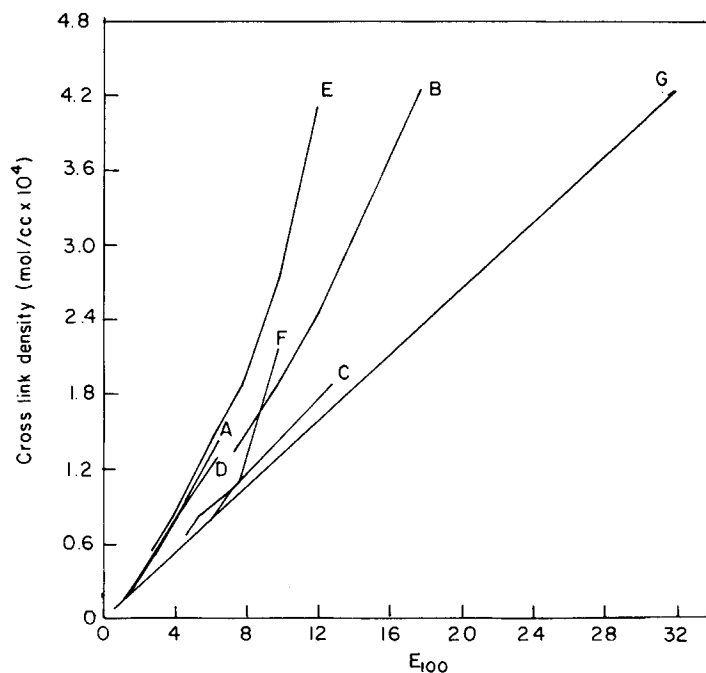
crosslinker. A relatively high crosslink density is obtained with HTPB-TDI system while no crosslink density value could be obtained for the ISPO-TDI or ISPO-HMDI system. The crosslink density of the various compositions of the copolyurethanes having varied amounts of HTPB and ISPO thus increase with the increase of the HTPB content. A similar trend is seen in the crosslinked samples. The HTPB-TDI-TMP system gives highest crosslink density. The plot of the crosslink density vs. the composition of the HTPB-ISPO copolyurethanes with TDI having TMP crosslinker (Fig. 5) is almost linear; the crosslink density being maximum at 1.0 : 0. (HTPB : ISPO) composition. Samples cured with TEA crosslinker, generally result in a low value of crosslink density than those obtained with TMP. Here, the relation between crosslink density and the composition of copolyurethanes show considerable deviation from the linear relationship, especially at higher concentrations of HTPB. The molecular weight between crosslinks being inversely proportional to crosslink density, increases (Table I) as the concentration of ISPO is increased, as expected.

## DISCUSSION

From the results, it is obvious that a variety of copolyurethanes differing widely in mechanical

strength could be obtained by using different proportions of ISPO and HTPB, the isocyanates and the crosslinkers. In general, the mechanical properties like tensile strength, modulus, and hardness decrease while the elongation increases on increasing the ISPO content. This is mainly caused by the lower functionality of ISPO, which is slightly less than 2.0, while that of HTPB is 2.3 to 2.4. Prepolymers having functionality higher than 2 are capable of participating in crosslinking with the bi-functional chain extenders. Indeed, HTPB undergoes curing with di-isocyanates even without a trifunctional crosslinker as seen by the tensile strength data (Fig. 1). Thus, as the ISPO content in the copolyurethane increases the average functionality of the prepolymer mixture decreases and as a result, the degree of crosslinking decreases. The measured crosslink density plotted against the composition of copolyurethanes (Fig. 5) having no triol crosslinker substantiates this point amply. A decrease in the crosslink density with an increase in the ISPO content is observed. The polyurethane of ISPO alone has neither measurable mechanical strength (Fig. 1) nor crosslink density (Fig. 5). As expected, a lowering in the crosslink density results indeed in lowering of the tensile strength, modulus, hardness, and an increase in the ultimate elongation.

A possible reason for the poor mechanical properties of the ISPO-based copolyurethanes, is also



**Figure 6** Crosslink density vs.  $E_{100}$  of copolyurethanes having, (A) TDI, (B) TDI-TMP, (C) TDI-TEA, (D) HMDI, (E) HMDI-TMP, (F) HMDI-TEA, (G) calculated.

the presence of a pendant hexyl group<sup>6,7</sup> in the backbone of the polymer. The hexyl group may cause poor packing of the chains in the network making them move apart, which in turn may cause irregularity in the network. A similar effect was noticed when 1,2 propane diol was used in place of 1,3 propane diol to chain extend the HTPB based polyurethanes.<sup>7</sup> In addition to causing irregularity in the chain packing the pendant hexyl group in ISPO may act as an internal plasticizer.<sup>8</sup> Lower reactivity of the secondary hydroxyl groups in ISPO could be yet another reason for the reduction in mechanical properties. The reactivity of the aliphatic secondary hydroxy group towards isocyanate groups is about a third of the primary hydroxy group.<sup>9</sup> The difference in the relative rates could lead to a defective network formation as a result of incomplete cure reaction.<sup>6</sup>

The mechanical strength, however, increases on the addition of crosslinkers. Of the two triols used, TMP-based networks possess better mechanical properties than the TEA-cured elastomers. This observation conforms to the fact that softer networks with low modulus are generally produced by the use of tertiary amines crosslinkers.<sup>10</sup> In regard to the chain extenders, TDI promises to give better mechanical strength. This could be related to the presence of an aromatic ring in the isocyanate chain. The aromatic ring offers stiffness by causing resis-

tance to chain rotation. Lack of such stiffening in the aliphatic isocyanate, such as HMDI, makes the chain flexible resulting in lower moduli.

The tensile modulus at small strains, where the Hooke's law is valid, is related to the crosslink density by the equation<sup>11,12</sup>

$$E = 3\nu_e KT \quad (7)$$

where  $K$  is the Boltzman constant and  $T$ , the absolute temperature. A plot of the modulus ( $E_{100}$ ) versus crosslink density for various systems is shown in Fig. 6. It is clearly seen that the experimental moduli of the copolyurethanes deviate significantly from the linear calculated plot, meaning thereby that at high elongations the relation is not valid. Although it may be argued that the relationship could be valid only at low elongation moduli i.e.,  $< E_{100}$ , it is well known that for rubber-like materials, the stress is a complex function of elongation.<sup>11</sup> The rather straight-line plot observed for the TMP-TDI cured system indicate that the crosslink density varies linearly with the modulus. However, for all systems, there is a large deviation from the calculated values. Surprisingly, the moduli values of the TDI-TEA cured system are closest to the calculated moduli values although this system does not yield the best mechanical strength.



## CONCLUSIONS

The mechanical strength of the copolyurethanes based on HTPB and ISPO are largely determined by the HTPB : ISPO ratio, the nature of the cross-linker, and the isocyanate chain extenders. By varying these parameters it is possible to produce a variety of copolyurethanes having a wide range of mechanical properties.

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