

# Modeling of Polyurethane Networks Based on Hydroxy-Terminated Polybutadiene and Poly(12-hydroxy stearic acid-co-TMP) Ester Polyol: Correlation of Network Parameters with Mechanical Properties

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## SYNOPSIS

The modeling of network properties of copolyurethane systems of varying compositions based on hydroxy-terminated polybutadiene and poly(12-hydroxy stearic acid-co-TMP) ester polyol (PEP), a copolyester polyol derived from 12-hydroxy stearic acid and trimethylol propane, crosslinked by different triols, and cured by various isocyanate compounds, has been carried out by the  $\alpha$ -model developed by Marsh et al. The network parameters such as crosslink density, effective chain length, sol content, and mechanical properties of these systems have been evaluated. The functionality distribution of PEP has been derived from <sup>29</sup>Si nuclear magnetic resonance spectroscopy of the silyl derivative of PEP and chemical analysis. The extent of cure reaction ( $p$ ) has been estimated by the use of an empirical relationship of the type:  $p = a - b(A_3 \times F_s)$ , where  $A_3$  is the mole fraction of the trifunctional component of the OH group and  $F_s$  is the fraction of secondary hydroxyls in the system. A method for evaluating the constants  $a$  and  $b$  is presented. The calculated network parameters by the  $\alpha$ -model are found to be in good agreement with the observed values. Excellent linear correlations between the calculated network parameters and the mechanical properties of the urethane elastomers confirm the utility of the approach presented here in arriving at formulations with desired properties. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polyurethane-based binder systems have been extensively used in composite solid propellants in view of their convenient reaction conditions and relative lack of adverse side reactions.<sup>1</sup> The ease with which the ultimate propellant properties, which are dictated by the structural loads, subjected during combustion, flight, transportation, and other environmental conditions, can be achieved by simply altering their formulations is an added advantage of these systems. An understanding of the dependence of the mechanical behavior of the binder networks on the prepolymer characteristics is, therefore, potentially useful and enables one to design solid propellants

with desired properties using a minimum number of formulation trials.

Considerable work has been carried out in the development of theoretical models describing the network structures of condensation polymers.<sup>2-8</sup> Network characteristics, such as concentration of effective chains or crosslink density ( $\nu_e$ ), effective chain length ( $L_x$ ), and sol-gel contents, have been calculated from the prepolymer data, such as composition, functionality distribution, and the extent of cure reaction ( $p$ ). Excellent agreement is generally observed between the experimental and calculated network parameters for simple and well-defined systems like polyesters and siloxanes.<sup>7</sup> However, the application of these models to complex systems, like hydroxy-terminated polybutadiene (HTPB) and other polyol binders, which contain non-, mono-, di-, tri-, and higher functionalities, is hampered by the

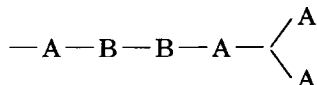
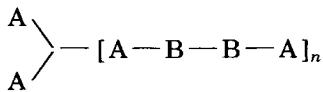
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nonavailability of methods for the determination of functionality distribution and also the extent of cure reaction. Rao et al.<sup>9</sup> have recently reported satisfactory correlations between prepolymer characteristics and network properties for HTPB-based systems using fairly judicious assumptions regarding the functionality distribution of HTPB. However, this work was restricted to simple polyurethane networks based on HTPB. An analysis of copolyurethane networks has not been attempted so far.

In our earlier works,<sup>10,11</sup> we reported the swelling and mechanical properties of the copolyurethane networks based on HTPB and poly(12-hydroxy stearic acid-co-TMP) ester polyol (PEP), called ISRO POLYOL thereat, synthesized from 12-hydroxy stearic acid (THSA) and trimethylolpropane (TMP), crosslinked by triols such as TMP, triethanolamine (TEA), and castor oil, and cured by diisocyanates, such as toluene diisocyanate (TDI), hexamethylene diisocyanate (HMDI), and isophorone diisocyanate (IPDI). The PEP used in these cases is a multifunctional copolymer with unknown functionality distribution. In this article, we present a detailed analysis of these systems, examine the applicability of the  $\alpha$ -model described by Marsh et al.<sup>7,8</sup> in calculating the network properties, which includes the determination of the functionality distribution of PEP and the extent of cure reaction in the copolyurethane networks, and finally, make an attempt to correlate the calculated network parameters with the mechanical properties of the cured systems.

## THEORY

Some of the initial concepts pertaining to the theoretical modeling of three-dimensional step-reaction polymer networks are established by Carothers,<sup>12</sup> Flory,<sup>13</sup> and Stockmayer.<sup>14</sup> The components of the most simple polycondensation system, namely, (3, 2, 0/2, 0) are a single trifunctional component (or branching component),  $\begin{matrix} \text{A} - \text{A} \\ | \\ \text{A} \end{matrix}$ , and two difunctional components, A—A and B—B, and involve the formation of chains of the type:



The modeling of such networks is attempted through two different approaches. (1) The  $\alpha$ -model method was developed by Flory<sup>13</sup> and improved by Marsh.<sup>8</sup> The development of this method was through answering the question, what is the probability that a given branch of the branching component leads to another branch exclusively? Such a probability is termed the branching coefficient ( $\alpha$ ). The other network parameters are calculated from  $\alpha$ . The set of equations that form the  $\alpha$ -model is listed in Appendix. (2) In the  $P_F$  model method, developed by Miller and Macosko,<sup>5,8</sup> the probability that a particular branch unit will lead exclusively to a finite end (or ends) is evaluated. This probability is called "finite chain extension coefficient," and the network properties are calculated subsequently from this probability. Both approaches assume that (1) all functional groups react independently, (2) no intermolecular or intramolecular side reactions occur, and (3) reactivities of all functional groups of a given type are equal.

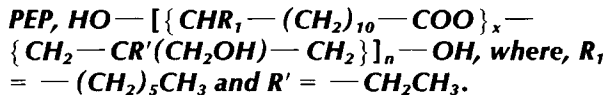
In this work, the network-parameter calculations applicable to copolyurethanes have been made using the  $\alpha$ -model, for the first time. The input parameters for the model are as follows: (1) composition of the network-forming components, (2) functionality distribution of the prepolymer binders, and (3) extent of cure reaction ( $p$ ). The latter two parameters, namely, the functionality distribution and  $p$ , were evaluated in this work. The methods adopted for the evaluation are presented in detail in the analytical section.

## EXPERIMENTAL

### Materials



HTPB prepolymer was prepared at the Vikram Sarabhai Space Centre (VSSC), Thiruvananthapuram, India, by  $\text{H}_2\text{O}_2$ -initiated free radical polymerization of butadiene in a 2-propanol-water solvent system.<sup>15</sup>



PEP was prepared in two stages. In the first stage, self-condensation of THSA,  $[\text{HOOC} - (\text{CH}_2)_{10} - \text{CHR}_1\text{OH}]$ , was conducted in the presence of an acid catalyst, followed by copolyesterification with TMP in the second stage, according to details given elsewhere.<sup>16</sup>

The triol crosslinkers used in this work, viz., TMP [ $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{OH})_3$ ], TEA [ $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ ], and castor oil [ $\text{R}_2\text{CH}(\text{CH}_2\text{R}_2)_2$ ], where  $\text{R}_2 = \text{HOR}_1\text{HC}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COO}-$ , were obtained from M/s Celanese Corporation, SD Chemicals, and IVP Ltd., respectively. The di-isocyanate compounds, namely, TDI, HMDI, and IPDI, were supplied by M/s. A.G. Bayer and M/s Fluka Co., and were used as received.

### Preparation of Copolyurethane Networks

Copolyurethane networks between HTPB and PEP at various equivalent ratios with different triols and isocyanates were synthesized as per the procedure cited elsewhere.<sup>10,11</sup> The triol content was kept at 1.2 equivalent times of the hydroxy equivalents present in the polymer mixture. Dibutyltindilaurate (DBTDL) was used as the curing catalyst.

### Mechanical Properties

Tensile strength, modulus (stress at 100% elongation), and the elongation at break (%Eb) of the copolyurethane networks were determined with an Instron Universal Testing Machine Model 4202, conforming to the test method ASTM-D412. A Frank hardness tester with a shore A durometer was used to measure the hardness as per ASTM-D2240-81 procedure.

### Sol Content and Crosslink Density

Sol contents were determined by use of the Soxhlet extraction method with toluene as the solvent. Crosslink density was obtained by the swelling methods,<sup>17</sup> as detailed in our earlier work.<sup>10,11</sup>

### <sup>13</sup>C and <sup>29</sup>Si Nuclear Magnetic Resonance Spectra

Proton noise-decoupled <sup>13</sup>C nuclear magnetic resonance (NMR) spectra of HTPB polymers were recorded at 22.5 MHz in  $\text{CDCl}_3$  solutions (10% wt/vol), with tetramethylsilane (TMS) as internal standard, on a JEOL FX 90Q NMR spectrometer. The <sup>29</sup>Si-NMR spectrum of trimethyl silylated PEP was recorded at 79.5 MHz in  $\text{CDCl}_3$  solvent. Gated decoupling was used to suppress the negative nuclear overhauser effect (NOE), and ferric acetylacetonate was used as the relaxation agent. For this, the silylated PEP was prepared by reacting PEP with an excess of trimethylchlorosilane in pyridine medium at 60°C for about 3 h. The excess trimethylchlorosilane and pyr-

idine were removed under a vacuum. The infrared spectrum of the silylated derivative contained no OH vibrations, indicating complete conversion.

## ANALYSIS, RESULTS, AND DISCUSSION

### Evaluation of the Functionality Distribution of PEP

Since PEP contains both the primary and the secondary hydroxyls, its functionality distribution has to be quantified in terms of the ratio of the primary to the secondary hydroxyls, ( $k = [\text{pri-OH}]/[\text{sec-OH}]$ ), as well as to the relative concentrations of non-, mono-, di-, and trifunctional species. These parameters were evaluated on the basis of the following considerations.

### Analysis of THSA

The acid value and the hydroxyl value of THSA are found to be 175 (theoretical, 187) and 160 mg of KOH/g, respectively, indicating that THSA contains some nonfunctional species, as well as some free stearic acid. The average equivalent weight of the carboxyl functionals works to be 292, and correspondingly, the purity of acid functionals was found to be 90%. The remaining 10% is assumed to be nonfunctional species.

### Esterification of THSA

The self-condensation of THSA (250 g, 0.780 equivalents of COOH and 0.713 equivalents of OH functionalities) was carried out to the extent of nearly 75% completion. The amounts of COOH and OH equivalents in the resulting poly-THSA, as estimated by chemical analysis, were found to be 0.203 and 0.136 equivalents, respectively. The amount of water collected was as expected by the stoichiometry, suggesting that no dehydration had taken place during this stage of the reaction.

### Copolymerization of Poly-THSA with TMP

TMP (0.323 Eq) was added to the esterification reaction mixture, and polymerization was continued until the acid value was nearly zero. In view of the much greater reactivity of primary OH groups from TMP, compared with secondary OH groups of poly-THSA, it is reasonable to expect that primary hydroxyls exclusively react with COOH groups and that the secondary OH groups do not participate in the esterification reaction. Therefore, at the end of

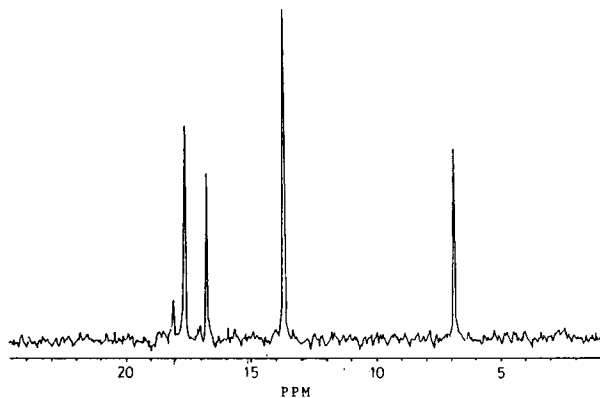
polymerization, the product PEP contains both primary and secondary OH groups and the content of primary OH groups will be equal to  $(0.323 - 0.203 = 0.120)$  Eq. The total hydroxyl content of PEP was found to be 0.223 Eq by chemical analysis. Consequently, the content of the secondary hydroxyls would be  $(0.223 - 0.120 = 0.103)$  Eq. Since before the addition of TMP, poly-THSA had 0.136 Eq of secondary OH groups, the lower value observed indicates that the dehydration of secondary hydroxyls occurs during the polymerization reaction, which is consistent with the observation that a larger than stoichiometric amount of water was collected during this step. It is apparent, therefore, that (1) the ratio of primary to secondary hydroxyl groups ( $k$ ), is equal to  $0.120/0.103 = 1.17$  in PEP, and (2) in poly-THSA, the species containing both COOH and OH groups (0.103 Eq) is nearly equal to the species containing COOH functionals (0.100 Eq) alone.

### Characterization of PEP

The mode of synthesis of PEP suggests that the polymer may contain non-, mono-, di-, and tri-functional hydroxyl species. The polymer is completely soluble in  $\text{CHCl}_3$  and  $\text{CCl}_4$ , while TMP is not soluble in these solvents. This suggests that PEP does not contain any unreacted TMP and that at least one OH group of each TMP molecule is esterified. Therefore, the possible species present in PEP are I, II, and III: (I)  $\text{ROCH}_2\text{CR}'(\text{CH}_2\text{OH})_2$ , (II)  $\text{HOCH}_2\text{CR}'(\text{CH}_2\text{OR})_2$ , and (III)  $\text{CR}'(\text{CH}_2\text{OR})_3$ , where R = poly-THSA unit and  $\text{R}' = -\text{CH}_2\text{CH}_3$ , in which one, two, and three hydroxyl groups of TMP are esterified by poly-THSA (R) units. The relative concentrations of I, II, and III can be obtained from statistical consideration in which 0.120 Eq of free OH groups (as discussed above) and 0.096  $(0.203 - 0.323/3 = 0.096)$  Eq of COOH groups are to be distributed to arrive at species I, II, and III. Assuming equal reactivity of OH groups of TMP, irrespective of the substitution, the relative amounts of the various species would be given by I : II : III =  $(0.120 \times 0.120) : (2 \times 0.096 \times 0.120) : (0.096 \times 0.096) = 0.309 : 0.494 : 0.197$ . These results were further confirmed from  $^{29}\text{Si}$ -NMR data.

### $^{29}\text{Si}$ -NMR Studies

$^{29}\text{Si}$ -NMR of the trimethylsilyl derivative of PEP in  $\text{CDCl}_3$  is shown in Figure 1. On the basis of the observed chemical shifts of trimethylsilyl derivatives of TMP,<sup>18</sup> the resonance peak at  $\delta = 17.65$  ppm was



**Figure 1**  $^{29}\text{Si}$ -NMR spectrum of trimethylsilyl derivative of PEP.

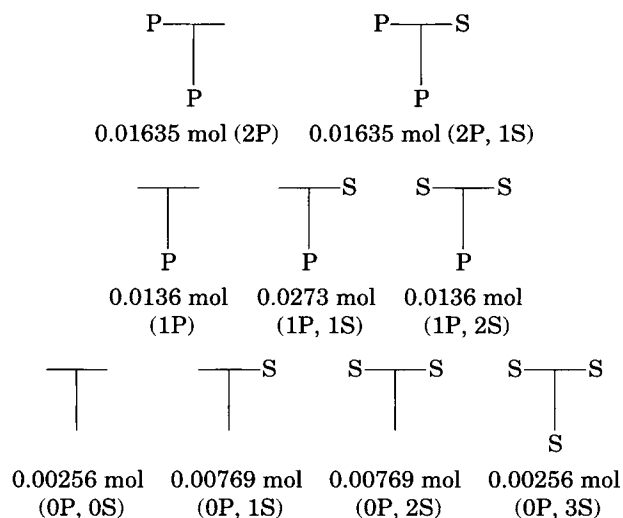
assigned to the structure Ia and the peak at  $\delta = 16.76$  ppm was assigned to the structure IIa. Peak 3 at  $\delta = 13.69$  ppm was assigned to the silyl derivative of the secondary hydroxyl in R(poly-THSA) units: Peak 1,  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{OSi}(\text{Me})_3)_2\text{CH}_2\text{OR}$  ( $\delta = 17.65$  ppm,  $I_p = 7.2$ ) Ia; Peak 2,  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{OR})_2\text{CH}_2\text{OSi}(\text{Me})_3$  ( $\delta = 16.76$  ppm,  $I_p = 6.0$ ) IIa; Peak 3,  $\text{CH}-\text{OSi}(\text{Me})_3$ , ( $\delta = 13.69$  ppm,  $I_p = 11.4$ ).

Thus, the ratio of the primary to the secondary hydroxyls can be obtained from their peak intensities ( $I_p$ ) using the relation  $k = (I_{p1} + I_{p2})/I_{p3}$  and was found to be 1.16, which is in good agreement with the value obtained from the chemical analysis described above. Also, the relative amounts of species Ia and IIa can be obtained from the ratio of intensity of peak 2 to half the intensity of peak 1 and was found to be 1.667. Now, if  $x$ ,  $y$ , and  $z$  represent the amounts of the species I, II, and III of the polymer PEP, then  $x + y + z = 0.323/3$  (number of moles of TMP taken),  $x + 2y + 3z = 0.203$  (amount of TMP hydroxyls reacted), and  $y/x = 1.667$  (from  $^{29}\text{Si}$ -NMR). Solving these equations, we get  $x = 0.0327$ ,  $y = 0.0545$ , and  $z = 0.0205$ . Thus, the relative amounts of the three species are given by I : II : III = 0.304 : 0.506 : 0.190. This is in good agreement with the distribution derived from statistical considerations alone, as discussed earlier.

### Functionality Distribution

Poly-THSA (R) moieties consist of species which contain both COOH and OH groups and also species which contain COOH groups alone, as discussed earlier. The next step is to distribute the two poly-THSA units in the species I, II, and III. It is very reasonable to assume that the reactivity of COOH

groups in poly-THSA is independent of the presence or absence of OH groups in the molecule. Since the units containing COOH and OH groups are nearly equal to the units containing COOH groups alone, the distribution of these units in species I, II, and III is dictated purely by statistical considerations. This leads to the following distribution of various ( $P$  = primary OH;  $S$  = secondary OH) species present in 0.1077 mol of PEP.



The above statistical treatment leads to the following distribution of various functional species: Non- ( $n$ ) = 0.0241, Mono- ( $m$ ) = 0.1968, Di- ( $d$ ) = 0.4763 and Tri- ( $t$ ) = 0.3018.

### Evaluation of Functionality Distribution of HTPB

A method to arrive at the functionality distribution of HTPB was reported by Sastri et al.,<sup>19</sup> which gave good correlation between functionality distribution and mechanical properties. The same method has been used to determine the functionality of HTPB used in this work. It is based on the following observations: (1) The sol of the urethane cured at  $r = 1$  (NCO/OH equivalent ratio) contains predominantly nonfunctionals. In the case presented here, the sol content is approximately 8%, and hence, the fraction of nonfunctionals can be assumed to be 8%. (2) HTPB can be approximated to be containing only non-, di-, and trifunctional chains.<sup>19</sup> (3) HTPB contains three types of hydroxyls,  $H$ ,  $V$ , and  $G$ , with the following structures<sup>20,21</sup>:  $H$ ,  $\text{HOCH}_2\text{CH}=\text{CH}-\text{CH}_2-$ ;  $V$ ,  $\text{HOCH}_2\text{CH}(\text{CH}=\text{CH}_2)-$ , and  $G$ ,  $\text{C}(=\text{CHCH}_2\text{OH})$ .  $G$ -type hydroxyls represent the trifunctional (branching) component. (4) The

fractions of di- and trifunctional species can be readily calculated from the relative amounts of  $H$ -,  $V$ -, and  $G$ -type hydroxyls obtained from <sup>13</sup>C-NMR spectra<sup>19</sup> by the following reasoning.

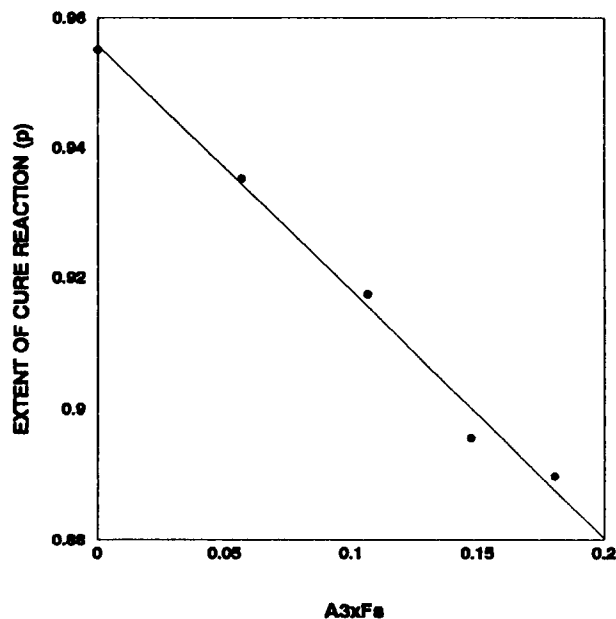
If  $f$  is the fraction of  $G$ -type hydroxyls, then the total number of chains in the polymer is proportional to half the chain ends,  $(H + V)/2$ , and is equal to  $[(1 - f)/2]$ . Hence, the fraction of trifunctional moieties ( $t$ ) will be equal to  $2f/(1 - f)$  and the difunctional component ( $d$ ) is represented by the quantity  $(1 - 3f)/(1 - f)$ . With this logic, the relative amounts of the di- and trifunctional species in HTPB used in this work were found to be di- ( $d$ ) = 0.4437 and tri- ( $t$ ) = 0.5563.

### Computation of the Input Parameters $A_1$ , $A_2$ , and $A_3$

After calculating the relative amounts of mono-, di-, and trifunctional species from the functionality distribution data of the prepolymers and the composition, the input parameters  $A_1$ ,  $A_2$ , and  $A_3$  were calculated. In doing so, it is assumed that the triols, such as TMP and TEA, contribute only trifunctional

**Table I** Input Parameters of Prepolymers

(HTPB/PEP) (Eq Ratio)	$A_2$	$A_3$	$F_s$
<b>HTPB-PEP-No Triol System</b>			
100/0	0.3471	0.6529	0.0000
80/20	0.3670	0.6165	0.0922
60/40	0.3885	0.5776	0.1843
40/60	0.4115	0.5355	0.2765
20/80	0.4365	0.4900	0.3686
0/100	0.4636	0.4406	0.4608
<b>HTPB-PEP-TMP/TEA System</b>			
100/0	0.1441	0.8559	0.0000
80/20	0.1493	0.8440	0.0419
60/40	0.1544	0.8320	0.0838
40/60	0.1599	0.8196	0.1257
20/80	0.1655	0.8067	0.1676
0/100	0.1712	0.7934	0.2095
<b>HTPB-PEP-Castor Oil System</b>			
100/0	0.2773	0.7227	0.5445
80/20	0.2848	0.7081	0.5874
60/40	0.2926	0.6930	0.6292
40/60	0.3006	0.6775	0.6711
20/80	0.3088	0.6615	0.7130
0/100	0.3174	0.6449	0.7549



**Figure 2** Plot of  $A_3xF_s$  vs. extent of cure reaction ( $p$ ); HTPB-PEP-TDI-No Triol system.

species and castor oil contains both di- and trifunctional moieties in the relative ratio of 0.3 : 0.7. The equations relating to these parameters can be written as:  $A_1 = m/(m + 2d + 3t)$ ,  $A_2 = 2d/(m + 2d + 3t)$ , and  $A_3 = 3t/(m + 2d + 3t)$ , where  $m$ ,  $d$ , and  $t$  represent the relative amounts of mono-, di-, and trifunctional species in the prepolymer mixtures. The input parameters  $A_2$  and  $A_3$  for various triol

**Table II** Values of Empirical Constants  $a$  and  $b$

Triol	$a$	$b$
HTPB-PEP-TDI System		
None	0.9556	0.3707
TMP	0.9556	0.4420
TEA	0.8676	0.1732
Castor Oil	1.0190	0.2850
HTPB-PEP-HMDI System		
None	0.9500	0.3700
TMP	0.9500	0.6490
TEA	0.8581	0.3556
Castor Oil	1.1800	0.6700
HTPB-PEP-IPDI System		
None	0.9500	0.3457
TMP	0.9340	0.4022
TEA	0.8924	0.4120
Castor Oil	1.2106	0.7739

systems are listed in Table I, along with the fraction of secondary hydroxyl ( $F_s$ ) groups present in the system.

### Estimation of the Extent of Cure Reaction ( $p$ )

Apart from the functionality distribution, the extent of cure reaction ( $p$ ) is a very important input parameter for the  $\alpha$ -model. So far, no unambiguous method for a satisfactory estimation of  $p$  has been reported. Hence, the following procedure was adopted in this work to evaluate  $p$ . From the observed crosslink densities, the values of  $p$  were calculated initially for the copolyurethane networks containing no triol crosslinker and cured by TDI alone, by appropriately rearranging equations (2) and (4) listed in Appendix 1. That is to say, when  $r = 1$ ,  $p_A = p_B = p$ , where  $p_A$  and  $p_B$  are the extents of reactions in the OH and NCO groups, respectively. Equation (2) then reduces to  $\alpha = p^2 A_3 / (1 - p^2 A_2)$ . Thus,  $p$  can be calculated, given the values of  $A_3$ ,  $A_2$ , and  $\alpha$ . From this set of values (listed in Table III along with other parameters), it is seen

**Table III** Extent of Cure Reaction Data

(HTPB/PEP) (Eq Ratio)	No Triol	TMP	TEA	Castor Oil
HTPB-PEP-TDI System				
100/0	0.9556 <sup>a</sup>	0.9556	0.8676	0.9066
80/20	0.9345 <sup>a</sup>	0.9474	0.8614	0.9004
60/40	0.9161 <sup>a</sup>	0.9298	0.8555	0.8947
40/60	0.9009 <sup>a</sup>	0.9174	0.8498	0.8894
20/80	0.8886 <sup>a</sup>	0.9055	0.8442	0.8845
0/100	0.8803 <sup>a</sup>	0.8939	0.8388	0.8802
HTPB-PEP-HMDI System				
100/0	0.9500	0.9500	0.8707	0.9158
80/20	0.9289	0.9272	0.8581	0.9014
60/40	0.9106	0.9050	0.8459	0.8879
40/60	0.8954	0.8836	0.8341	0.8754
20/80	0.8832	0.8628	0.8226	0.8640
0/100	0.8749	0.8428	0.8116	0.8538
HTPB-PEP-IPDI System				
100/0	0.9500	0.9340	0.8924	0.9055
80/20	0.9304	0.9198	0.8778	0.8888
60/40	0.9132	0.9060	0.8638	0.8731
40/60	0.8990	0.8926	0.8500	0.8587
20/80	0.8875	0.8796	0.8368	0.8456
0/100	0.8798	0.8671	0.8240	0.8338

<sup>a</sup> Calculated from observed crosslink density values.

**Table IV Comparison of Calculated and Observed Sol Content**

(HTPB/PEP) (Eq Ratio)	Sol Content (%) <sup>a</sup>							
	No Triol		TMP		TEA		Castor Oil	
	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
HTPB-PEP-TDI System								
100/0	6	10	3	8	5	12	7	12
80/20	14	11	4	9	7	14	9	13
60/40	20	16	6	10	8	17	10	15
40/60	30	27	7	11	11	20	14	17
20/80	45	43	10	13	13	23	18	20
0/100	—	—	14	16	19	27	26	23
HTPB-PEP-HMDI System								
100/0	8	10	4	8	4	12	7	11
80/20	12	12	5	9	7	15	11	13
60/40	20	18	8	11	10	19	12	16
40/60	32	30	10	14	15	25	22	19
20/80	46	46	15	19	21	32	31	27
0/100	—	—	20	27	29	43	39	33
HTPB-PEP-IPDI System								
100/0	9	10	2	13	5	8	13	12
80/20	14	12	4	15	8	12	15	15
60/40	19	16	6	11	12	15	20	20
40/60	30	25	10	13	17	20	24	27
20/80	47	47	13	16	23	26	29	37
0/100	—	—	17	19	33	35	41	50

<sup>a</sup> Cal, calculated; Exp, experimental.

that the  $p$  values decrease as the copolyurethanes become richer in PEP. Two factors, namely, the mole fraction of the trifunctional components ( $A_3$ ) and the fraction of secondary hydroxyls ( $F_s$ ), are expected to influence the extent of cure reaction. If  $A_3$  increases, incipient gelation will occur at an early stage of conversion. After gelation, the mobility of the growing polymer chains and, thereby, the fluidity of the polymer will be greatly reduced. Consequently, the probability of the reacting groups coming proximate to each other will be reduced, and thereby, the extent of cure reaction will be reduced. Second, in view of the lower reactivity of the secondary OH groups,<sup>22,23</sup> the extent of reaction is expected to decrease as the fraction of secondary OH groups increases. Therefore, the extent of cure reaction can be correlated to the two parameters  $A_3$  and  $F_s$  by an empirical equation of the type:

$$p = a - b(A_3 \times F_s) \quad (1)$$

where  $a$  and  $b$  are empirical constants. This was indeed found to be the case, as shown by the linearity of the plot of calculated values of  $p$  and the product of  $A_3$  and  $F_s$  (Fig. 2), which leads to the equation for the system containing no triol and cured by TDI alone,

$$p = 0.9556 - 0.3707(A_3 \times F_s). \quad (2)$$

The values of  $a$  and  $b$  for various crosslinked systems were evaluated by the following considerations. The  $p$  values were derived from the crosslink densities observed for individual urethane systems HTPB-TMP-TDI and PEP-TMP-TDI systems. In the former system, no secondary hydroxyls exist and the value of constant  $a$  is equal to  $p$ , which as stated earlier, can be calculated from the  $\alpha$ -model equations using the observed  $v_e$  values. The value of constant  $b$  can then be obtained by knowing the value of  $a$  and substituting in the equations relating to  $p$  of the PEP-TMP-TDI system. The extents of cure for

**Table V Comparison of Calculated and Observed Crosslink Densities**

(HTPB/PEP) (Eq Ratio)	Crosslink Density (mol/M <sup>3</sup> ) <sup>a</sup>					
	TMP		TEA		Castor Oil	
	Exp	Cal	Exp	Cal	Exp	Cal
HTPB-PEP-TDI System						
100/0	425	417	138	138	138	139
80/20	366	351	110	118	110	117
60/40	301	290	95	98	96	97
40/60	244	233	78	80	78	79
20/80	184	181	64	63	64	63
0/100	134	134	48	48	48	49
HTPB-PEP-HMDI System						
100/0	411	397	216	146	159	160
80/20	272	308	110	110	109	120
60/40	185	227	76	79	83	85
40/60	146	157	55	53	56	57
20/80	82	99	31	32	33	36
0/100	55	55	18	18	19	20
HTPB-PEP-IPDI System						
100/0	327	326	235	197	159	160
80/20	288	272	155	151	109	120
60/40	215	221	109	111	83	85
40/60	165	174	75	77	56	57
20/80	108	132	49	49	33	36
0/100	96	96	30	28	19	20

<sup>a</sup> Cal, calculated; Exp, experimental.

other in-between compositions were then calculated with the values of  $a$  and  $b$  thus obtained. The same procedure was adopted for calculating the constants  $a$  and  $b$  for the other systems, as shown in Table II. As expected, the values of  $a$  and  $b$  are found to be dependent on the nature of the system. The  $p$  values calculated from constants  $a$  and  $b$  for various systems are listed in Table III.

It can be observed from Table III that the value of  $p$  decreases as HTPB becomes lean in the recipe. This is consistent with the fact that the reactivity of primary OH groups is significantly higher than that of secondary OH groups, as stated earlier. As PEP content increases in the composition, the amount of secondary OH groups increases. For the same reason, the elastomers containing castor oil as crosslinker record a lower extent of reaction compared with TMP crosslinked systems, since castor oil contains only secondary OH groups. It is interesting to observe that the  $p$  values obtained for TEA

crosslinked systems are significantly lower than both TMP and castor oil systems, even though the OH groups in TEA are primary in nature. This could probably be due to the loss of a portion of NCO groups during amine-catalyzed side reactions, which are subsequently not available for network building. In general, the aliphatic isocyanates HMDI and IPDI cause a lower degree of cure extent than do TDI and this difference is significant when the system is richer in secondary OH content.

### Equivalent Weight of the Curing System

The equivalent weight of the system is given by  $W_{Eq} = [ \{ (f_{HTPB} \times W_{Eq\ HTPB}) + (f_{PEP} \times W_{Eq\ PEP}) + (1.2 \times W_{Eq\ triol}) \} / \text{total no. of hydroxy equivalents} ] + Eq\ wt\ of\ the\ diisocyanate$ , where  $f_{HTPB}$  and  $f_{PEP}$  are fractions of HTPB and PEP in the prepolymer mixture, and  $W_{Eq\ HTPB}$ ,  $W_{Eq\ PEP}$ , and  $W_{Eq\ triol}$  are the equivalent weights of HTPB, PEP, and the triol, respectively.

### Calculation of Network Parameters

Using the input parameters obtained by the methods explained in the previous sections, the network parameters such as branching coefficient ( $\alpha$ ), sol content,  $v_e$ , and  $L_x$  were calculated with the  $\alpha$ -model equations (Appendix) and are listed in Tables IV–VI. Experimentally determined sol contents and crosslink densities have been compared with the corresponding calculated values (Tables IV and V). Here, the calculated sol contents include the contribution from the nonfunctionals derived from the functionality distribution models developed for HTPB and PEP. A close agreement between the observed and calculated values, especially in the crosslink data, may be because variations in the reactivities of various isocyanates and hydroxyl groups are inherently considered while calculating the values of  $a$  and  $b$  from the observed crosslink densities corresponding to the extreme compositions. The overall excellent agreement between observed and calculated properties validates the theoretical model as well as the methods by which the estimation of functionality distribution and extent of cure were arrived.

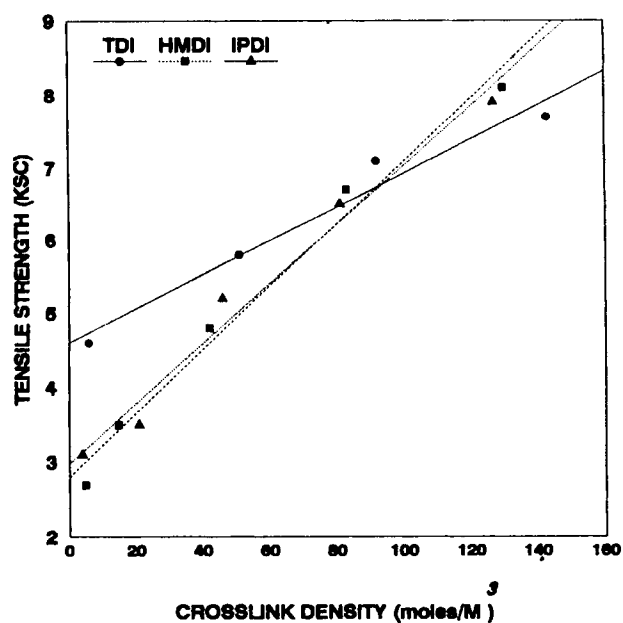
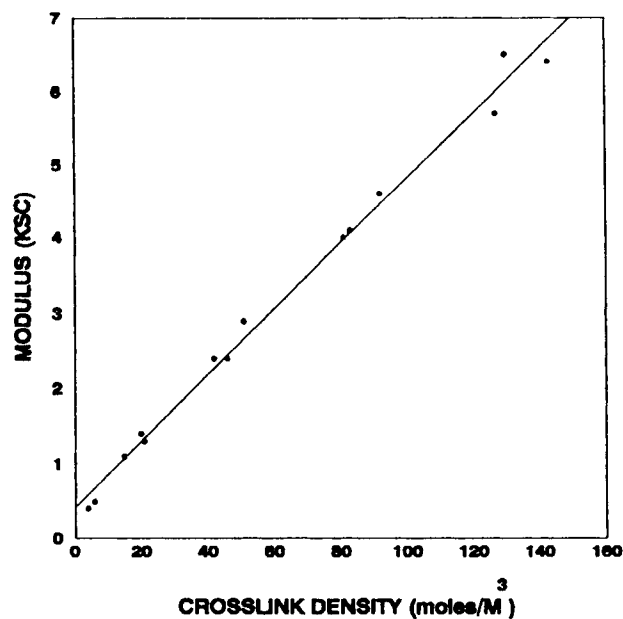
### Correlation of Network Characteristics with the Mechanical Properties

Crosslink density and effective chain length are the most important post-gel network properties. The kinetic theory of rubber elasticity<sup>17,24</sup> predicts that



**Table VI Branching Coefficient ( $\alpha$ ) and Effective Chain Length ( $L_x$ )**

(HTPB/PEP) (Eq Ratio)	No Triol		TMP		TEA		Castor Oil	
	$\alpha$	$L_x$	$\alpha$	$L_x$	$\alpha$	$L_x$	$\alpha$	$L_x$
<b>HTPB-PEP-TDI System</b>								
100/0	0.8715	348	0.9000	129	0.7227	205	0.7694	254
80/20	0.7942	432	0.8590	139	0.7051	220	0.7466	276
60/40	0.7224	575	0.8198	152	0.6865	240	0.7244	303
40/60	0.6475	889	0.7824	167	0.6691	263	0.7032	335
20/80	0.6475	1496	0.7465	188	0.6517	292	0.6825	374
0/100	—	—	0.7123	214	0.6346	328	0.6626	422
<b>HTPB-PEP-HMDI System</b>								
100/0	0.8504	362	0.8879	131	0.7284	199	0.7899	238
80/20	0.7787	451	0.8324	146	0.6982	226	0.7484	274
60/40	0.7038	620	0.7802	167	0.6692	262	0.7099	320
40/60	0.6316	988	0.7311	197	0.6416	309	0.6745	383
20/80	0.5869	1590	0.6849	241	0.6147	380	0.6417	471
0/100	—	—	0.6414	310	0.5890	487	0.6117	601
<b>HTPB-PEP-IPDI System</b>								
100/0	0.8501	370	0.8541	146	0.7700	180	0.7669	264
80/20	0.7795	459	0.8172	158	0.7348	202	0.7217	312
60/40	0.7131	608	0.7820	174	0.7017	232	0.6800	380
40/60	0.6538	872	0.7483	193	0.6695	273	0.6419	481
20/80	0.5823	1715	0.7158	219	0.6389	330	0.6070	639
0/100	—	—	0.6847	253	0.6096	416	0.5754	914


**Figure 3** Tensile strength [ $\text{kg}/\text{cm}^2$  (KSC)] vs. crosslink density; HTPB-PEP-No Triol system.

**Figure 4** Modulus [ $\text{kg}/\text{cm}^2$  (KSC)] vs. crosslink density; HTPB-PEP-No Triol system.

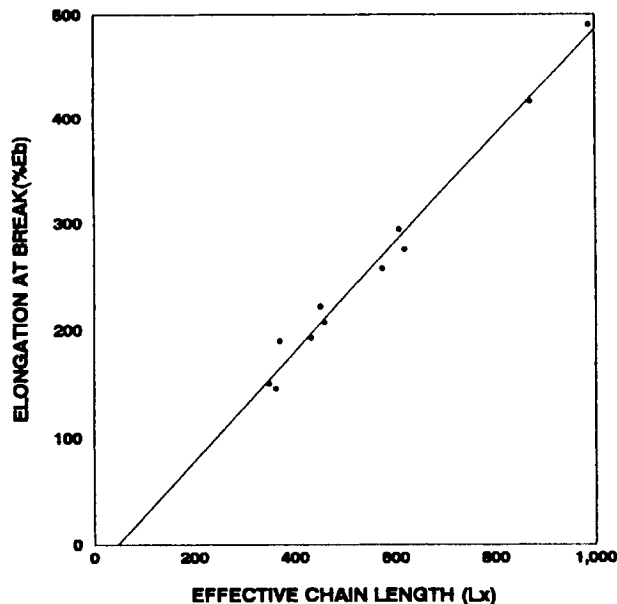


Figure 5 %Elongation vs. effective chain length; HTPB-PEP-no triol system.

the tensile stress-strain relationship is given by the equation:

$$S = \nu_e R_g T / (L - 1/L^2) \quad (3)$$

where  $S$  is the stress based on the original cross-sectional area of the tensile specimen,  $L$  is the extensibility,  $R_g$  is the gas constant, and  $T$  is the absolute temperature. Thus,  $\nu_e$  can be correlated with tensile strength and modulus.  $L_x$ , which is a measure of the length of elastically effective chains between two crosslink points, can be correlated with percent elongation at break. The calculated  $\nu_e$  and  $L_x$  were, therefore, plotted against the experimentally determined mechanical properties, such as tensile strength, modulus at 100% elongation, and percent elongation at break, taken from our earlier work.<sup>10,11</sup> The typical correlation plots for systems having no triol crosslinkers are shown in Figures 3–5.

From the plots, it is obvious that excellent linear correlations with correlation coefficients nearing 0.99 exist in all cases, in spite of wide variation in the structural aspects and functionality type distribution in the prepolymers and isocyanate compounds. Furthermore, even the networks cured with triol crosslinkers such as TMP, TEA, and castor oil show excellent linear correlations (not given here) between the property vs. network parameters. The only major deviation from the linear correlation was

observed in the tensile strength versus  $\nu_e$  plot of the HTPB-PEP-IPDI copolyurethane system cured with TMP.

It is noticed from Figures 4 and 5 that the moduli and elongations at break of the no-triol networks show the same mathematical dependence on the network parameters  $\nu_e$  and  $L_x$  respectively, for all of the isocyanates studied in this case. In the presence of a triol crosslinker, the property vs. network parameter relationship is no doubt linear, but is dependent on the nature of the crosslinker used as indicated by the different slopes of the plots. Some of the probable reasons for such behavior may include (1) the difference in the reactivity of the triol toward the various isocyanates and (2) the presence of hard segments, the nature of which is dependent on the choice of the crosslinker and the isocyanate. These aspects, however, are not considered in arriving at this model. Nevertheless, these studies promise a potential predictive capability, which will be useful in the designing of crosslinked urethane polymers.

## CONCLUSION

The network properties of copolyurethanes could be derived by using the  $\alpha$ -model, developed by Marsh et al. The model adequately describes the post-gel structure of the copolyurethane networks. Very good agreement between the predicted and observed network properties validates the approaches adopted in estimating the various input parameters. The mechanical properties of the copolyurethanes could be predicted from the network parameters. Excellent linear correlations between the calculated network parameters and the observed mechanical properties indicate the predictive potential of this model.

## APPENDIX

The following equations for the  $\alpha$ -model, derived by Marsh et al., are applicable to the formation of polyurethanes from a polyol (component  $A$ ) containing tri-, di-, and monofunctional species and difunctional curing agent (component  $B$ ):

$$r = [B]/[A] = p_A/p_B \quad (1)$$

$$\alpha = p_A p_B A_3 / (1 - p_A p_B A_2) \quad (2)$$

$$W_s = [(1 - \alpha)/\alpha]^3 \quad (3)$$

$$v_e = [(2\alpha - 1)/\alpha]^3 (dA_3/2W_{Eq}) \times 10^6 \quad (4)$$

$$L_0 = W_G W_{Eq} L_{sp} \alpha^3 / A_3 (2\alpha - 1) \quad (5)$$

$$R_n = (1 - \alpha)/\alpha \quad (6)$$

$$X_n = 1/(R_n + 1/R_n) \quad (7)$$

$$R_{n+1} = R_n^2 \quad (8)$$

$$L_n = L_0(1 + 2X_1)(1 + 2X_2) \cdots (1 + 2X_n) \quad (9)$$

$$L = L_n, \quad \text{for } X_n \rightarrow 0 \quad (10)$$

$$L_x = 2L \quad (11)$$

where,  $\alpha$  is the branching coefficient,  $A_3$  is the mole fraction of hydroxyls on trifunctional components of A,  $A_2$  is the mole fraction of hydroxyls on difunctional components of A,  $p_i$  is the fraction of the component  $i$  reacted,  $W_s$  is the weight fraction of sol,  $W_G = 1 - W_s$  is the weight fraction of the gel,  $L_{sp}$  is the number of chain atoms per gram,  $d$  is the density of the polyurethane ( $\text{g cm}^{-3}$ ),  $v_e$  is the cross-link density (moles  $\text{M}^{-3}$ ),  $L_x$  is the effective chain length.

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