Studies on Urethane–Allophanate Networks Based on Hydroxyl-Terminated Polybutadiene: Modeling of Network Parameters and Correlation to Mechanical Properties

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ABSTRACT: Hydroxyl-terminated polybutadiene (HTPB)-based allophanate–urethane networks were prepared by reacting HTPB with di-isocyanates, such as toluene–di-isocyanate (TDI), isophorone–di-isocyanate (IPDI), and 4,4'-di(socyanatocyclohexyl)methane ($H_{12}MDI$) at stoichiometric ratios (r-values) ranging from 1.0 to 1.5. The networks were characterized for mechanical and swell properties. The network parameters, such as "X," which is the fraction of urethane groups involved in the allophanate formation, and effective chain length (L_x) were calculated from experimental crosslink density values determined from swell data, using α-model equations developed by Marsh. Excellent linear correlations were obtained between mechanical properties and the calculated network parameters. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2986–2994, 2006

Key words: hydroxyl-terminated polybutadiene; toluene–di-isocyanate; isophorone–di-isocyanate; 4,4'-di(isocyanatocyclohexyl)methane; polyurethane; allophanate; network parameters; modeling
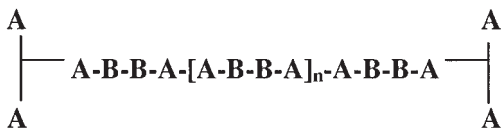
INTRODUCTION

Polyurethane network systems based on hydroxyl-terminated polybutadiene (HTPB) are extensively used as composite solid propellant binders, due to convenient reaction conditions and relative lack of adverse side reactions.[1] The curing process is accompanied either without or with very little shrinkage. A prominent advantage with urethane systems is the ease with which the ultimate properties can be modified with fairly good control by merely adjusting the propellant formulation.[2] For instance, the ultimate mechanical properties of the urethane elastomers can be tailored to a requirement by varying the r-value (equivalents of NCO groups/equivalents of OH groups).[3] Also, the ultimate properties of the gum stock and the propellants depend critically on the nature of the hydroxyl telechelic polymer and the type of isocyanate curative. Therefore, it is desirable to have an understanding on the dependence of the mechanical behaviour of the urethane elastomers on the binder network characteristics, which are, in turn, determined by the formulation chosen.[4]

A good deal of research has been undertaken in developing theoretical models that adequately describe the post-gel structure of condensation (polyurethane) polymer networks.[4–14] Network characteristics, such as concentration of elastically effective chains that is commonly known as crosslink density (v_e), effective chain length (L_x), and sol-gel contents, have been satisfactorily calculated and successfully correlated to mechanical. properties for simple and well-defined systems like polyesters and siloxanes,[10] from the prepolymer data, such as composition, functionality distribution, and the extent of cure reaction. For systems like HTPB, the task is difficult, as it involves the evaluation of complex functionality distribution data and the near impossible task of estimation of the extent of the cure reaction. However, these problems were satisfactorily addressed by us, and we have reported methodologies by which the functionality distribution and the extent of the cure reaction are determined.[11–13]

Carothers,[15] Flory,[16] and Stockmayer[17] introduced certain initial concepts regarding the theoretical modelling of three dimensional step-reaction polymer networks. The simplest crosslinking polycondensation system, which may be represented as (3,2,0/2,0),[4] consists of a trifunctional component (branching component,

$$A{-\!\!-\!\!-}A$$
$$\quad|$$
$$\quad A$$

), a difunctional component (chain extender, A–A), and a difunctional curative (B–B). In

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such a case, the formation of the chains will be of the type:

$$
\begin{array}{c}
\text{A} \qquad\qquad\qquad\qquad\qquad\qquad \text{A} \\
| \qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\
\text{A-B-B-A-[A-B-B-A]}_n\text{-A-B-B-A} \\
| \qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\
\text{A} \qquad\qquad\qquad\qquad\qquad\qquad \text{A}
\end{array}
$$

Theoretical modeling of such networks can be attempted through the α-model approach. The α-model method, developed originally by Flory[16] and improved by Marsh,[4] is based on the determination of the probability that a given branch of the branching component leads to another branching arm exclusively. Such a probability is termed as the branching coefficient (α). The network parameters are calculated from α, using the α-model equations listed in the Appendix. The α-model assumes that (1) the functional groups react independently, (2) no intermolecular or intramolecular side reactions occur, and (3) reactivity of all functional groups of a given type is equal.

Further, in the formulations that contain NCO groups in excess over the stoichiometric requirement, the excess NCO groups, in principle, are likely to undergo the following competing reactions:[18] isocyanate dimerization, biuret formation, and the allophanate formation. As allophanate formation is the most likely to happen under the current reaction conditions, only this is considered in the present treatment.

The main reaction during the curing of urethane propellant binders is,

$$\text{R—N} {=\!=} \text{C} {=\!=} \text{O}$$

$$+\ \text{R}'\ \text{OH} \rightarrow \text{R—NH—CO—OR}'\ \text{(urethane formation)}$$

When excess isocyanate is used, the excess isocyante will react with urethane groups and form allophanate linkages

$$\text{R—NH—CO—OR}' + \text{RN}{=\!=}\text{C}{=\!=}\text{O} \rightarrow \text{R—N—CO—OR}'$$
$$|$$
$$\text{CO—NH—R (allophanate formation)}$$
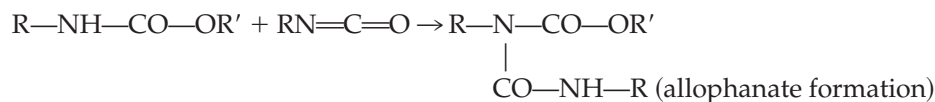
It can be noted that each new allophanate unit becomes a new branch point and a potential crosslink.

The extents of reaction in OH (p_{OH}) and NCO(p_{NCO}) are represented by the probabilities,-

$$p_{OH} = \text{OH reacted/OH total} \qquad (1)$$

$$p_{NCO} = \text{NCO reacted/NCO total} \qquad (2)$$

The extent of urethane groups(p_U) reacted during the allophanate formation can be expressed as,

$$p_U = U_{reacted}/U_{total} \qquad (3)$$

At equilibrium, the fraction of urethane groups (X) involved in the allophanate formation can be given as

$$X = p_U/p_{OH} \qquad (4)$$

For calculation purpose, the formulation should be expressed in terms of the various network forming components. The following parameters represent the relative contents of the functional moieties in the case of the (3,2,1/2,1) system. A_3 = mol fraction of the OH groups contributed by trifunctional components. A_2 = mol fraction of the OH groups contributed by di-functional components A_1 = mol fraction of the OH groups contributed by monofunctional components

By definition,

$$A_3 + A_2 + A_1 = 1. \qquad (5)$$

The branching coefficient "α" can be calculated using the expression[14]

$$\alpha = p_{OH}^2(A_3 + p_{OH}X)/(r\text{-}p_{OH}^2 A_2) \qquad (6)$$

Other network parameters can be calculated from "α" using the equations listed in the Appendix.

In our previous publications,[11–13] we reported the modeling of copolyurethane networks based on hydroxyl-terminated polybutadiene (HTPB) and poly(12-hydroxy stearic acid-co-TMP) ester polyol (PEP) using the α-model developed by Marsh.[4] The α-modeling approach has been extended to more complex allophanate–urethane networks based on HTPB and toluene–di-isocyanate (TDI).[14] In the present work we extend the theoretical evaluation of the network parameters to other isocyanates, such as isophorone–di-isocyanate (IPDI) and 4,4'-di(isocyanatocyclohexyl)methane (H$_{12}$MDI). Network parameters have been theoretically calculated, and the calculated network parameters are correlated to the mechanical properties and the influence of isocyanate type on such correlations is studied.

EXPERIMENTAL

Materials

HTPB, HO—$(CH_2$—CH=CH—$CH_2)_n$—OH:

HTPB prepolymer was prepared by H_2O_2-initiated free radical polymerization of butadiene in a 2-propanol–water solvent system.[19] Equivalent weight of HTPB was determined by the acetylation method using a pyridine–acetic anhydride mixture.[20] Toluene–di-isocyanate (TDI) was procured from M/s. A.G. Bayers and isophorone–di-isocyanate (IPDI) and 4,4′-di(isocyanatocyclohexyl)methane (H_{12}MDI) were procured from M/s. Sigma-Aldrich Ltd., and were used as such without further purification after ascertaining their purity. The estimation of NCO content in the isocyanate compounds involved reacting the isocyanate with an excess of *n*-butyl amine and back titrating the unreacted amine.[21]

Preparation of urethane–allophanate elastomers:

The urethane networks containing allophanate linkages based on HTPB and isocyanate curatives, such as TDI, IPDI, and H_{12}MDI, at various *r*-values ranging from 1.0 to 1.5, were prepared as follows: HTPB was dried at 80–90°C under vacuum using rotary flash evaporator. The dried HTPB was mixed with calculated amounts of the di-isocyanates, degassed under vacuum to remove air bubbles, poured into aluminium molds, and cured at 70°C for 168 hs. The thickness of the cured elastomers was 3 mm. The cured elastomers were subjected to mechanical and swelling evaluations.

Mechanical properties

The mechanical properties, such as tensile strength, stress at 100% elongation, and elongation at break were determined with an Instron Universal Testing Machine (Model 4202) using dumbbell-shaped specimens as per the ASTM-D412 test method. Relaxation moduli values were determined by subjecting dumbbell specimens to a constant strain of 100%. The strain was maintained at the same level by adjusting the load over a period of time. The load required to maintain the strain at 100% at various time intervals was monitored and the load would eventually reach a stable value (equilibrium). Relaxation modulus was calculated from the equilibrium load values.

Crosslink density

Crosslink density, defined as mole of elastically effective chains per cubic metre, was obtained from volume fraction of the swollen polymer when swollen in a solvent. The polymer specimens measuring 7×7

$\times$ 3 mm were placed in toluene for 48 h. The swollen specimens were then 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 at 100°C for 2 h, 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 (Q) was calculated as given below:

$$Q = (w_s/w_{ds}) - 1 \qquad (7)$$

The weight fraction of the polymer (w_2) and that of solvent (w_1) in the swollen specimen are given by the relation:

$$w_2 = 1/(1 + Q) \text{ and } w_1 = 1 - w_2 \qquad (8)$$

Now the volume fraction of the polymer (v_2) in the swollen specimen can be expressed as:

$$v_2 = (w_2/d_2)/\{(w_2/d_2) + (w_1/d_1)\}, \qquad (9)$$

where, d_1 and d_2 are the densities of solvent and the polymer, respectively. Crosslink density values are obtained from v_2 using the Flory-Rhener equation,[2,22]

$$v_e = - [\ln(1 - v_2) + v_2 + \chi v_2^2]/V_s(v_2^{1/3} - v_2/2) \qquad (10)$$

where V_s is the molar volume of the solvent and χ is the polymer–solvent interaction parameter. A detailed account on the determination of χ is given elsewhere.[2,23]

RESULTS AND DISCUSSION

Polymer networks are generally characterized by three important parameters namely, gel-sol contents, density of elastically effective chains or crosslink density (v_e), and effective chain length (L_x). These parameters can be theoretically calculated using the α-model developed by Marsh,[4] using input parameters, such as composition, extent of cure reaction, and functionality distribution in the prepolymers. When the isocyanate used is more than the stoichiometric requirement, the excess isocyanate will be utilized for further reaction with urethane groups to form allophanate linkages. Each allophanate linkage is a potential crosslink point. Thus, the crosslink density increases with *r*-value beyond 1.0 (see Table I), which confirms that additional crosslinks are formed due to allophanate linkages. This is further supported by modulus data (Table II).

The extent of allophanate formation in the urethane networks is described by another important parameter, *X*, which is the fraction of urethane groups in-

TABLE I
Network Parameters of Urethane–Allophanate Networks: HTPB–TDI, IPDI, H$_{12}$MDI Systems

System	r-value	Crosslink density by swell method (v_e), mol/m^3 [a]	X	Effective chain length (L_x)
HTPB–TDI	1.0	90	0	524
	1.1	106	0.054	421
	1.2	137	0.09	347
	1.3	164	0.17	276
	1.4	201	0.249	226
	1.5	209	0.315	205
HTPB–IPDI	1.0	75	0	553
	1.1	85	0.037	488
	1.2	103	0.068	415
	1.3	115	0.133	347
	1.4	124	0.2	298
	1.5	139	0.268	262
HTPB–H$_{12}$MDI	1.0	82	0	560
	1.1	100	0.0485	489
	1.2	120	0.0975	414
	1.3	139	0.153	353
	1.4	152	0.22	316
	1.5	162	0.289	269

volved in the allophanate formation.[14] As there is no unambiguous experimental method to determine X, X was calculated using the α-model equations from the experimentally determined crosslink density values, and the effective chain length (L_x) was calculated from X values thus obtained.[14]

Input parameters for the α-model

The input parameters for the model were evaluated as described below.

Stoichiometric ratio (r-value)

The ratio of the equivalents of NCO groups to OH groups taken in the curing mixture is denoted as on r-value.

$r = (NCO)/(OH) = E_{Di-isocyanate}/E_{HTPB}$, $E_{Di-isocyanate}$, and E_{HTPB} are the number of equivalents of the di-isocyanate and HTPB, respectively. For the present studies the r-value was varied from 1.0 to 1.5.

Equivalent weight of the curing system (W$_{eq}$)

Equivalent weight W_{eq} of the curing system can be obtained using the expression,

$$W_{eq} = (56100/\text{hydroxyl value of HTPB}) + \text{equivalent weight of the isocyanate} \times r \quad (11)$$

where the hydroxyl value of HTPB is expressed in terms of mg of KOH/g of HTPB.

Functionality distribution

Invoking certain judicious assumptions, a method to evaluate the functionality distribution of HTPB based on[13] C-NMR spectral data has been developed.[11–14] This method is based on the following considerations: (1) it has been observed that mono- and higher than tri-functionals in HTPB are in negligible amounts, and hence, HTPB can be approximated to contain only di-and tri-functionals. (2) HTPB contains three types of hydroxyls namely, H, V, and G types with the structures:[24–26] H, HOCH$_2$—CH=CH—CH$_2$-; V, HO—CH$_2$—CH(CH=CH$_2$)— and G, >C=CH—

TABLE II
Mechanical Properties of the Urethane–Allophanate Networks; HTPB–TDI, IPDI, H$_{12}$MDI Systems

System	r-value	Tensile strength (MPa)	Stress at 100% elongation (MPa)	Elongation at break (%)	Equilibrium relaxation modulus (MPa)
HTPB–TDI	1.0	0.71	0.44	228	0.41
	1.1	0.80	0.58	180	0.43
	1.2	0.90	0.71	150	0.62
	1.3	0.98	0.86	132	0.74
	1.4	1.13	0.98	115	0.84
	1.5	1.18	1.07	105	0.92
HTPB–IPDI	1.0	0.70	0.39	260	0.34
	1.1	0.76	0.48	240	0.39
	1.2	0.84	0.54	220	0.49
	1.3	0.89	0.60	205	0.51
	1.4	0.94	0.66	190	0.56
	1.5	1.01	0.70	180	0.60
HTPB–H$_{12}$MDI	1.0	0.71	0.47	240	0.36
	1.1	0.78	0.56	220	0.45
	1.2	0.87	0.66	200	0.51
	1.3	0.96	0.78	180	0.59
	1.4	1.03	0.83	174	0.64
	1.5	1.08	0.88	164	0.68

CH$_2$OH. G-type hydroxyls represent the tri-functional (branching) components. The fraction of di- and tri-functional species can be readily calculated from the relative amounts of H, V, and G-type hydroxyls obtained from[13] C-NMR spectra, and the method is described in detail elsewhere.[11–14]

The relative contents of di- and tri-functional moieties in the HTPB used in the current study were found to be di (d) = 0.5757 and tri (t) = 0.4243. From the relative contents of di-and tri-functional species in HTPB, A_2 and A_3 were computed using the following equations,

$$A_2 = 2d/(2d + 3t) \tag{12}$$

$$A_3 = 3t/(2d + 3t) \tag{13}$$

Extent of cure reaction

By the argument put forth in our earlier publications,[12,13] the extent of the cure reaction in OH (p_{OH}) was estimated to be 0.9556 when r = 1.0. At r-values greater than 1, p_{OH} can be conveniently assumed to be 1.0. Because NCO is in excess over OH groups, it is quite reasonable to assume that all the OH groups would be completely consumed during the cure reaction.

Calculation of the network parameters

Using the input parameters obtained by the methods discussed in the previous sections and employing the α-model equations (see Appendix), the network parameters X and effective chain length (L_x) were calculated. The parameter X is a vital requirement in the allophanate modeling, and X values for various systems were calculated from the experimentally determined crosslink density values. Using the calculated X values, effective chain length (L_x) was calculated. The calculated network parameters are listed in Table I.

Effect of r-value on network parameters

Effect of r-value on crosslink density

Crosslink density of the allophanate–urethane networks was determined using equilibrium swelling method. Crosslink density increases with r-value for all the isocyanates used in the present study and reaches a plateau level at higher r-values (Fig. 1). The plateau is not clearly observed for IPDI system. Based on the magnitudes of v_e (Table I) the di-isocyanates can be arranged in the order, TDI > H$_{12}$MDI > IPDI. Being an aromatic isocyanate TDI is more reactive than the other aliphatic isocyanates, namely IPDI and H$_{12}$MDI, thereby realizing a higher extent of reaction on the NCO groups and causing a higher magnitude
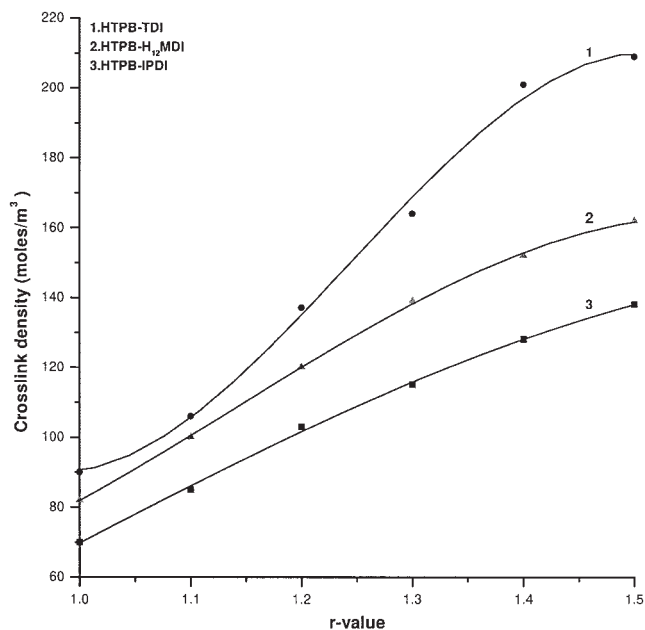

Figure 1 Effect of r-value on crosslink density; HTPB–TDI, H$_{12}$MDI, and IPDI systems.

for crosslink density.[18] H$_{12}$ MDI is expected to be less reactive than IPDI, as one of the two isocyanate groups in IPDI is secondary while both the isocyanate groups in H$_{12}$MDI are secondary. However, the v_e values obtained for H$_{12}$MDI are higher than the corresponding values for IPDI systems. The probable reason for the above observation could be due to the symmetric nature of the H$_{12}$MDI molecule as opposed to IPDI, because of which the urethane–allophanate networks derived from the former may be able to have more ordered crystallite domains compared to IPDI systems.[27] The orderliness in the network can be expected to manifest in the form of apparently enhanced crosslink density values for H$_{12}$MDI systems.

Effect of r-value on parameter X

As stated earlier, because there is no unambiguous method to estimate the parameter X directly, it was calculated from experimentally determined crosslink density values using α-model equations. It can be seen from Figure 2 and Table I, that the values of X increase with the r-value for all the three isocyanates. The increase in X with r can be explained as follows: it can be visualized that the degree of crosslinking at the hypothetical point of completion of urethane formation (just before the allophanate formation starts to take place) decreases with the r-value.[14] A lower degree of crosslinking ensures a greater degree of freedom for segmental motion that will favor allophanate formation, as a major portion of allophanate formation is expected to take place during the postgelation stage.
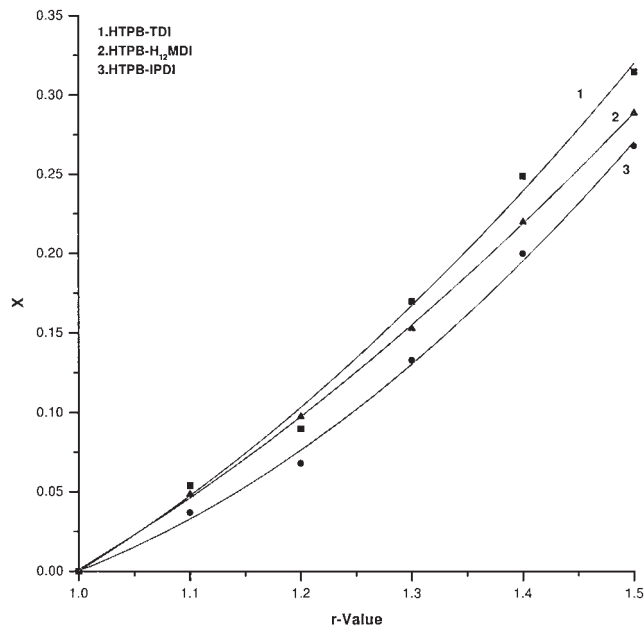
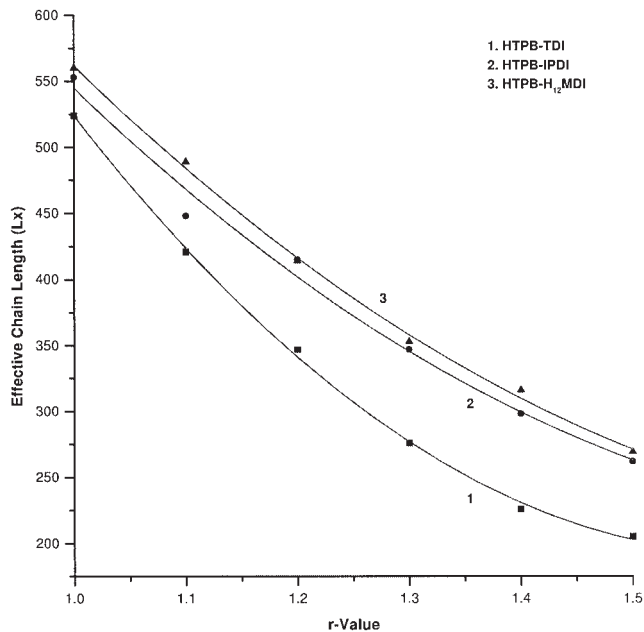**Figure 2** Effect of r-value on parameter X; HTPB–TDI, H_{12}MDI, and IPDI systems.

Figure 3 Effect of r-value on effective chain length; HTPB–TDI, H_{12}MDI, and IPDI systems.

According to X values, the isocyante compounds can be arranged in the order TDI > H_{12}MDI > IPDI. But it was expected that X values for H_{12}MDI would be less than those obtained for IPDI, as it should be less reactive than IPDI for the reasons explained earlier. But higher values for H_{12}MDI than IPDI arise because X values in the present study were calculated from experimentally determined crosslink densities and so the order in crosslink density values gets reflected in the case of X values as well.

Effect of r-value on effective chain length

Effective chain length (L_x) decreases with r-value (Fig. 3 and Table I). According to the L_x values, the order of the isocyanates is H_{12}MDI > IPDI > TDI. The two important network parameters v_e and L_x seem to approach a limiting value with the increase in the r-value.
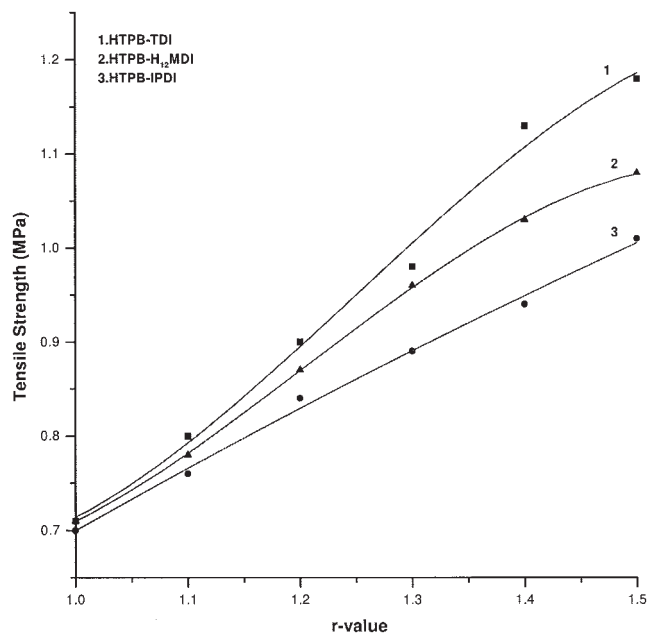
Effect of r-value on mechanical properties

The mechanical properties such as tensile strength, stress at 100% elongation, elongation at break, and equilibrium relaxation modulus of the urethane networks based on HTPB and various di-isocyanate compounds, with the r-values varying from 1.0 to 1.5, are listed in Table II. The variation of the above properties with r-values are graphically depicted in Figures 4–7. The results indicate that tensile strength, stress at 100% elongation, equilibrium relaxation modulus increase, and elongation decreases with the r-value for

all the three isocyanates used in the present study, with each of them eventually reaching plateau level. A similar behavior has been reported elsewhere.[3] However, the plateau level is not well stated for IPDI systems. Because the crosslink density is one of the chief parameters, which determines the mechanical properties of the elastomers, the pattern of crosslink density variation with the r-value is expected to be
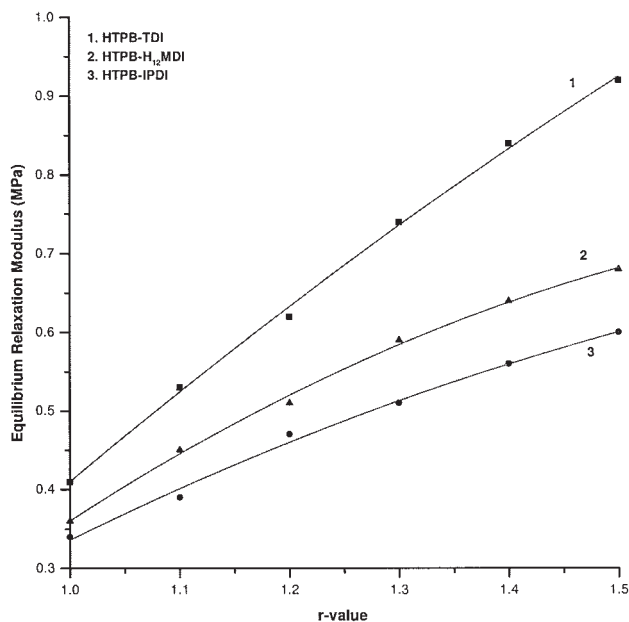

Figure 4 Effect of r-value on tensile strength; HTPB–TDI, H_{12}MDI, and IPDI systems.
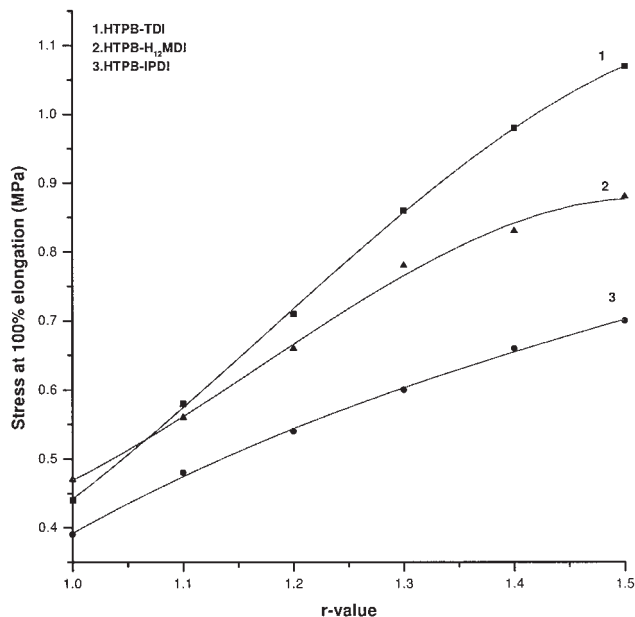
Figure 5 Effect of *r*-value on stress at 100% elongation; HTPB–TDI, H$_{12}$MDI, and IPDI systems.

reflected in the mechanical properties. This explains the occurrence of plateau level in the mechanical property dependence on the *r*-value. It can further be observed that the properties corresponding to various isocyanates at the same *r*-value are distinctly different, which suggests that the isocyanate type plays a crucial role in dictating the network properties. According to the magnitude of tensile strength and stress at 100% elongation, the isocyanates can be arranged in the

Figure 6 Effect of *r*-value on equilibrium relaxation modulus; HTPB–TDI, H$_{12}$MDI, and IPDI systems.
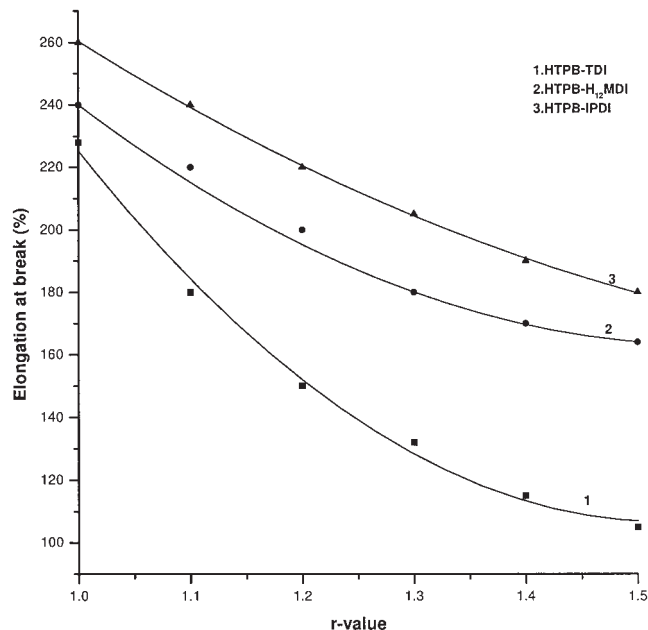
Figure 7 Effect of *r*-value on % elongation at break; HTPB–TDI, H$_{12}$MDI, and IPDI systems.

order, namely, TDI > H$_{12}$ MDI > IPDI, and this order is reversed for elongation values.

## Correlation between the network parameters and the mechanical properties of the elastomers

According to kinetic theory of rubber elasticity the tensile stress can be related to crosslink density as follows:[28,29]

$$\sigma = v_e R_g T(\lambda - 1/\lambda^2) \qquad (14)$$

where σ is the tensile stress based on original cross sectional area of the tensile specimen, λ is the extension ratio, R_g is the universal gas constant, and T is the temperature in the absolute scale. Thus, v_e can be linearly correlated to tensile strength and modulus. L_x, which is a measure of the length of elastically effective chain between the crosslink points, can be correlated to the elongation at break (%Eb).[4,11–14] As expected, straight-line plots were obtained between v_e and tensile strength, stress at 100% elongation and equilibrium relaxation modulus, and between L_x and %Eb (Figs. 8–11)[91011] with fairly good correlation coefficients, despite a wide variation in the *r*-values.

CONCLUSION

The important conclusions that can be drawn are as follows:
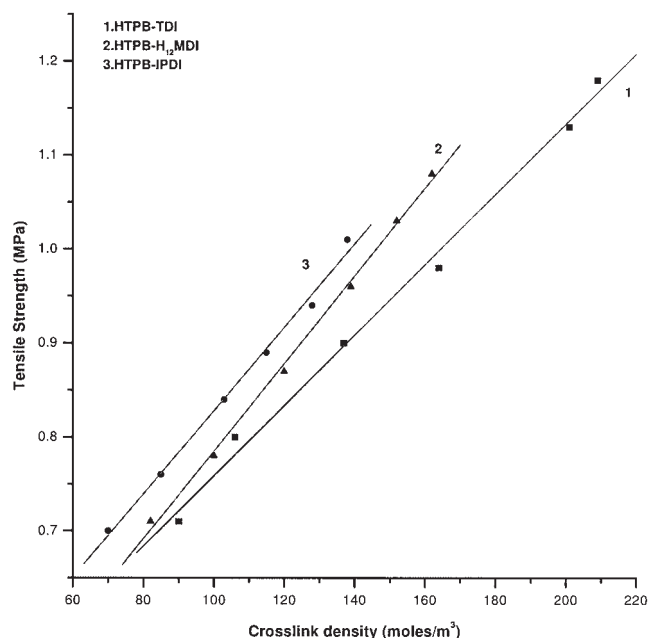
Figure 8 Dependence of tensile strength on crosslink density; HTPB–TDI, H_{12}MDI, and IPDI systems.
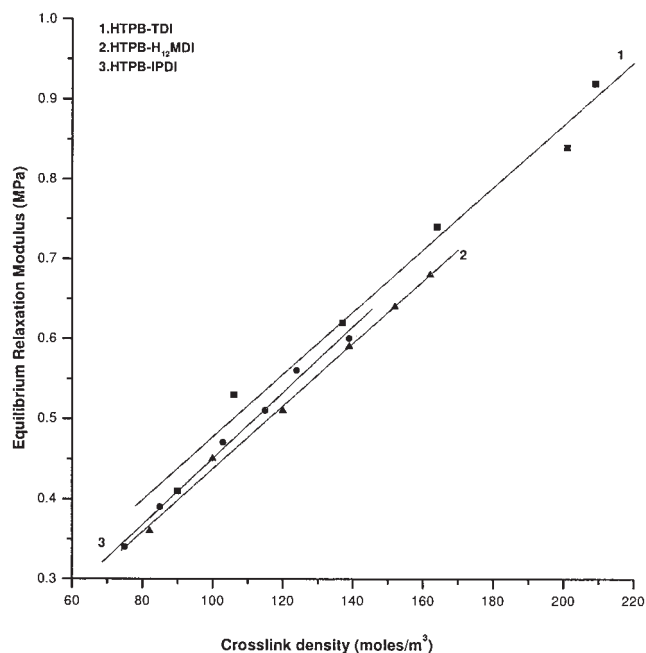

Figure 10 Dependence of equilibrium relaxation modulus on crosslink density; HTPB–TDI, H_{12}MDI, and IPDI systems.

1. The α-model developed by Marsh can be extended to allophanate containing urethane systems.
2. The parameter X, which is the extent of urethane groups involved in the allophanate formation, can be calculated using the allophanate model, and it is found to increases with the r-value.

3. The calculated network parameters using the modified α-model show very good linear correlation with the mechanical properties of the networks indicating the predictive potential of the present model.
4. The isocyanate type has a strong influence in determining the network and mechanical characteristics
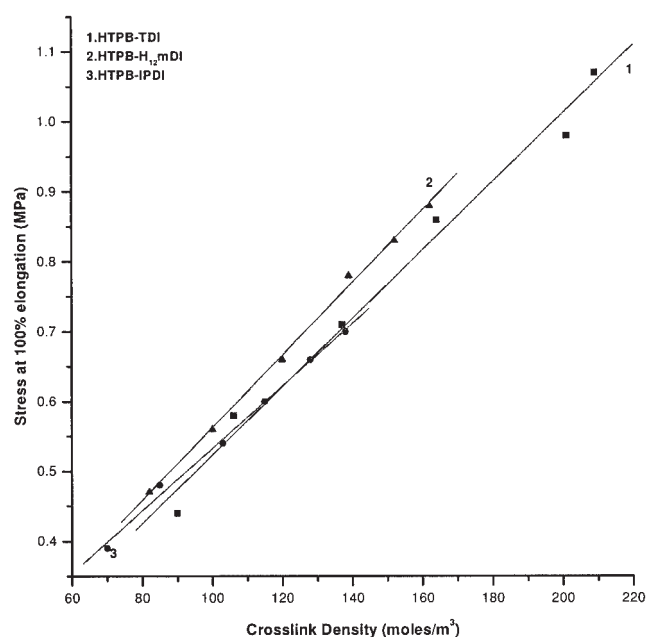
Figure 9 Dependence of stress at 100% elongation on crosslink density; HTPB–TDI, H_{12}MDI, and IPDI systems.
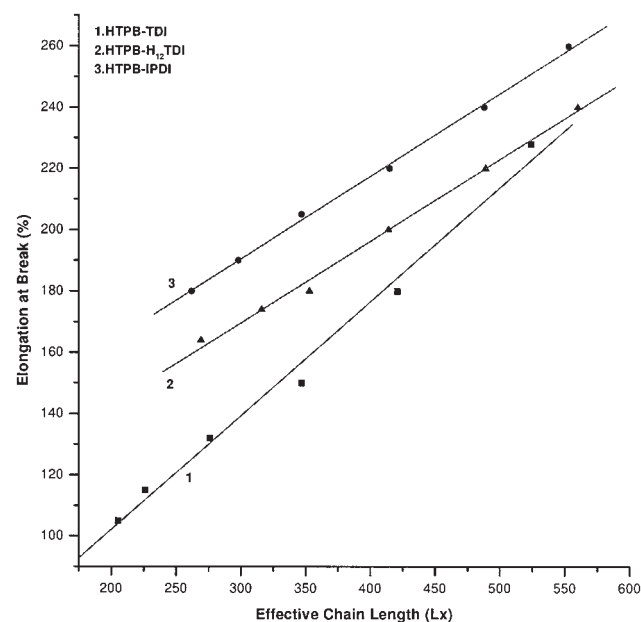
Figure 11 Dependence of elongation at break on effective chain length; HTPB–TDI, H_{12}MDI, and IPDI systems.

APPENDIX

The following equations for the modified α-model, are applicable to the formation of polyurethanes containing allophanate linkages from a polyol (component A) containing tri-, di-, and monofunctional species and difunctional curing agent (component B):

$$r = [NCO]/[OH] \tag{1}$$

$$\alpha = p_{OH}^2(A_3 + p_{OH}X)/(r\text{-}p_{OH}^2A_2) \tag{2}$$

$$W_s = [(1 - \alpha)/\alpha]^3 \tag{3}$$

$$v_e = 3\{(2\alpha - 1/\alpha)\}^3 \{A_3/3 + Xp_{OH}^2\}d*\,10^6 \tag{4}$$

$$W_G = 1 - W_s \tag{5}$$

$$L_o = W_G W_{eq} L_{SP} \alpha^3/(2\alpha - 1)*(A_3 + 3Xp_{OH}^2) \tag{6}$$

$$R_n = (1 - \alpha)/\alpha \tag{7}$$

$$X_n = 1/(R_n + 1/R_n) \tag{8}$$

$$R_{n+1} = R_n^2 \tag{9}$$

$$L_n = L_o(1 + 2X_1)(1 + 2X_2)(1 + 2X_3)...(1 + 2X_n) \tag{10}$$

$$L = L_n, \quad \text{for} \quad X_n \to 0 \tag{11}$$

$$L_x = 2L \tag{12}$$

where, α 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, X is the fraction of urethane groups involved in the allophanate formation, p_{OH} is the extent of reaction in OH, W_s is the weight fraction of sol, W_G is the weight fraction of the gel, L_{SP} is the number of chain atoms per gram of the polymer, d is the density in g cm^{-3}, v_e is the crosslink density in mol/m^3, and L_x is the effective chain length.

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