Polyurethanes based on hydroxyl terminated polybutadiene: modelling of network parameters and correlation with mechanical properties

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Abstract

Hydroxyl terminated polybutadiene (HTPB) based urethane networks were synthesized by reacting HTPB with toluene diisocyanate (TDI) at various stoichiometric ratios (R) ranging from 1.0 to 1.5. The resulting networks would contain allophanate linkages in addition to urethane groups. The networks were characterized for mechanical and swell characteristics. The parameter X which is the extent of urethane groups involved in the allophanate formation and other network parameters, such as crosslink density (ν_e) and effective chain length (L_X), were calculated using the α-model developed by Marsh with suitable modifications. The value of X showed very good correlation with R-value, and linear correlations were obtained between mechanical properties and the calculated network parameters. Crosslink densities, calculated from stress–strain data were found to be nearly 1.2 times the corresponding values calculated from swell data. Dynamic mechanical studies showed that R value did not influence the glass transition temperature (T_g); however tan δ_{max} was shown to be a linear function of the crosslink density. Activation energy for the variation of storage moduli with temperature decreased with R-value, while that for loss moduli remained nearly unaffected by the R value. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hydroxyl terminated polybutadiene; Toluene diisocyanate; Polyurethane

1. Introduction

Polyurethane-based binder systems are extensively used in composite solid propellants, due to convenient reaction conditions [1] and relative lack of adverse side reactions. A very useful feature associated with urethane binder systems is the ease with which the ultimate properties can be varied with good control by adjusting the formulations [2]. More commonly, the ultimate mechanical properties of the binder can be tailored by varying the R-value (equivalents of NCO groups/equivalents of OH groups) [3]. Thus, an understanding of the dependence of the mechanical behaviour of the propellant grain on the binder network characteristics, which are, in turn, determined by the formulation chosen, is of critical importance [4]. Such an understanding is potentially useful and enables one to design solid propellants with desired properties using a minimum number of formulations.

Considerable amount of work has been carried out in the direction of developing theoretical models, which adequately describe the post-gel structure of condensation (polyurethane) polymer networks [4–12]. Network characteristics, such as concentration of effective chains or crosslink density (ν_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. In the present system, viz. hydroxyl terminated polybutadiene (HTPB), the task is arduous, as it involves understanding of complex functionality distribution and near impossible determination of extent of cure reaction. However, this problem was successfully addressed by Rama Rao et al. [11,12] in their previous publications, in which methods to determine the functionality distribution and the extent of cure reaction were presented.

In our previous works [11–13], we reported modelling 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]. In the present work, we extend it to the modelling of urethane networks based on HTPB containing allophanate linkages. Urethane networks based on HTPB and toluene diisocyanate (TDI) were synthesized at R-values ranging from 1.0 to 1.5, and were characterized for their mechanical and swell characteristics. The

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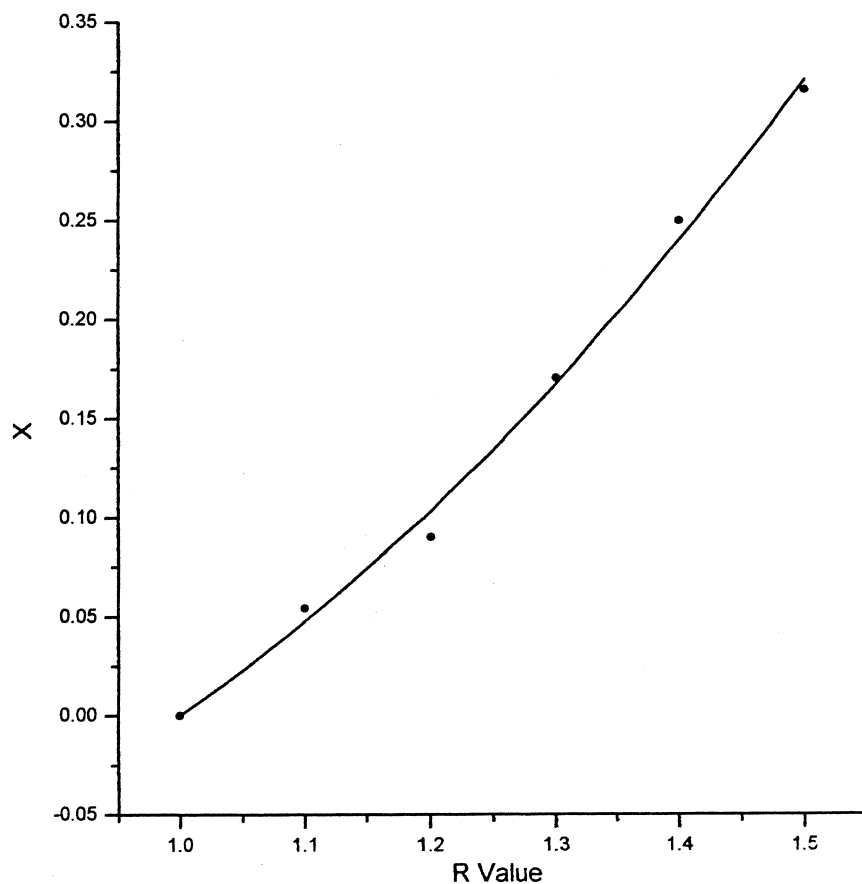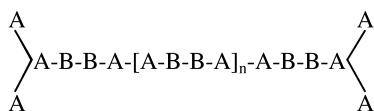
Fig. 1. Effect of *R*-value on *X* for HTPB–TDI systems.

extent of allophanate formation and the network parameters were calculated using the α-model with certain modifications. Stress–strain behaviour of the allophanate-urethane elastomers was analysed. Dynamic mechanical properties were correlated with the calculated network parameters.

1.1. Theory

Some of the initial concepts regarding the theoretical modelling of three-dimensional step-reaction polymer networks were introduced by Carothers [14], Flory [15] and Stockmayer [16]. The simplest crosslinking polycondensation system, which may be represented as (3,2,0/2,0), contains a single trifunctional component (branching component),

$$A\text{—}A$$
$$|$$
$$A$$

a difunctional component (A–A) and a difunctional curative (B–B). In such a case, the formation of the chains will be of the type:

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

Theoretical modelling of such networks can be attempted through two different approaches. (i) The α-model method developed by Flory [15] 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 Appendix. (ii) In the p_F model developed by Miller and Macosko [4,8], the probability that a particular branch unit will lead exclusively to a finite end is evaluated. This probability is called "finite chain extension coefficient" and the network parameters are calculated from this coefficient. Both the models assume that: (i) the functional groups react independently; (ii) no intermolecular or intra molecular side reactions occur; and (iii) reactivities of all functional groups of a given type are equal.

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 [17]: isocyanate dimerization, biuret formation and the allophanate formation. As allophanate formation is the most likely to happen under the current reaction conditions, this alone is considered in the present treatment.
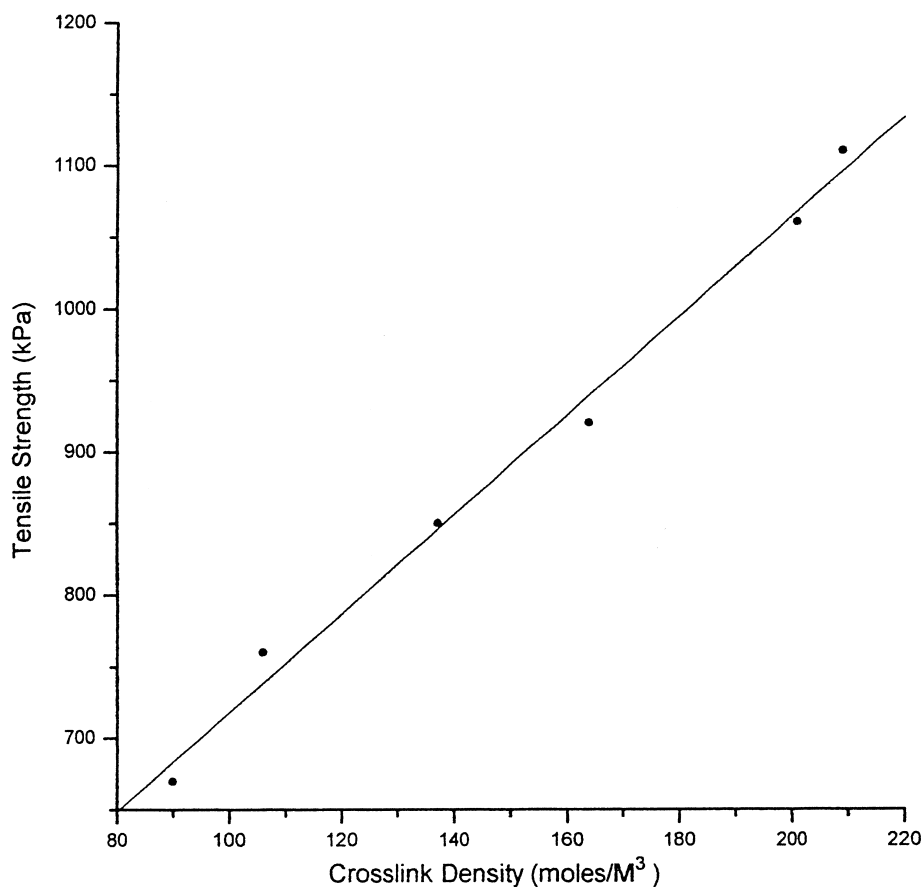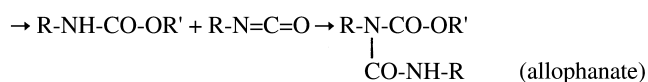
Fig. 2. Dependence of tensile strength on crosslink density for HTPB–TDI systems.

The main reaction during the curing of urethane binders is

$$R-N{=}C{=}O + R'OH \rightarrow R-NH-CO-OR' \qquad \text{(urethane)}$$

Once the urethane is formed, it can further react with excess NCO groups but to a lesser extent.

$$\rightarrow R\text{-NH-CO-OR'} + R\text{-N}{=}C{=}O \rightarrow R\text{-N-CO-OR'}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad CO\text{-NH-R} \qquad \text{(allophanate)}$$

It can be noted that each new allophanate unit becomes a new branch point, a potential crosslink.

In the present work, the network parameters were calculated for the allophanate–urethane systems based on HTPB and TDI, with R-values ranging from 1.0 to 1.5. The input parameters required are composition, functionality distribution in HTPB and the extent of cure reaction. The method to determine the functionality distribution and the extent of cure were discussed in detail in our previous publications [11–13].

The extent 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 (3,2,1/2,1) system.

A_3 = mole fraction of OH groups contributed by trifunctional components.

A_2 = mole fraction of OH groups contributed by difunctional components

A_1 = mole fraction of 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
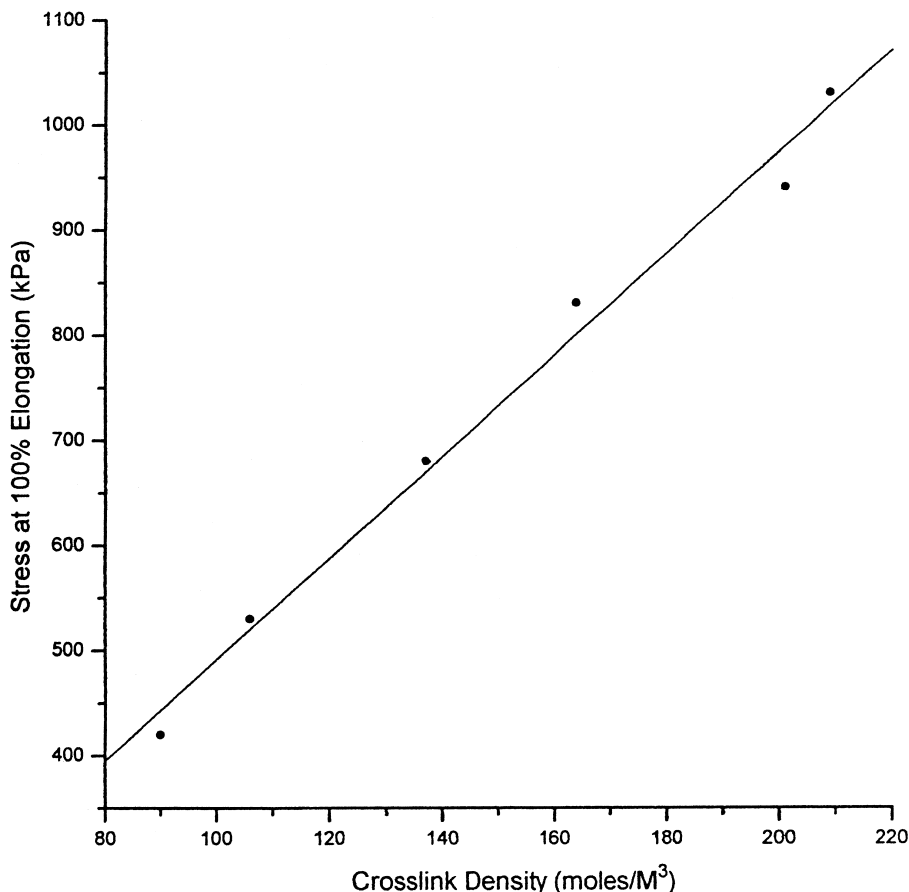
Fig. 3. Effect of crosslink density on stress at 100% elongation for HTPB–TDI systems.

expression:

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

The other network parameters can be calculated from α using the equations listed in Appendix.

2. Experimental

2.1. Materials

HTPB, $HO-(CH_2-CH = CH-CH2)n-OH$

HTPB prepolymer was prepared at Propellant Fuel Complex, Vikram Sarabhai Space Centre (VSSC), Thiru-vananthapuram, India, by H_2O_2 initiated free radical polymerization of butadiene in a 2-propanol–water solvent system [18].

Toluene diisocyanate (TDI) was supplied by A.G. Bayer, Germany and was used as received.

2.2. Preparation of urethane–allophanate elastomers

The urethane networks containing allophanate linkages based on HTPB and TDI 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 TDI and degassed under vacuum to remove air bubbles, poured into aluminium moulds and cured at 70°C for 168 h. The cured elastomers were subjected to mechanical and swelling evaluations.

2.3. Mechanical properties

Tensile strength, modulus at 100% elongation and elongation at break were determined with an Instron Universal testing machine (Model 1121) using the dumbbell shaped specimens as per the ASTMD412 test method.

2.4. Crosslink density

Crosslink density, defined as moles of 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 mm^2 were placed in toluene for 48 h. The specimens were then removed from the solvent and weighed after gently wiping out the solvent. Subse-quently, the solvent absorbed was driven off by placing the specimen in a vacuum oven at 100°C for 2 h and the
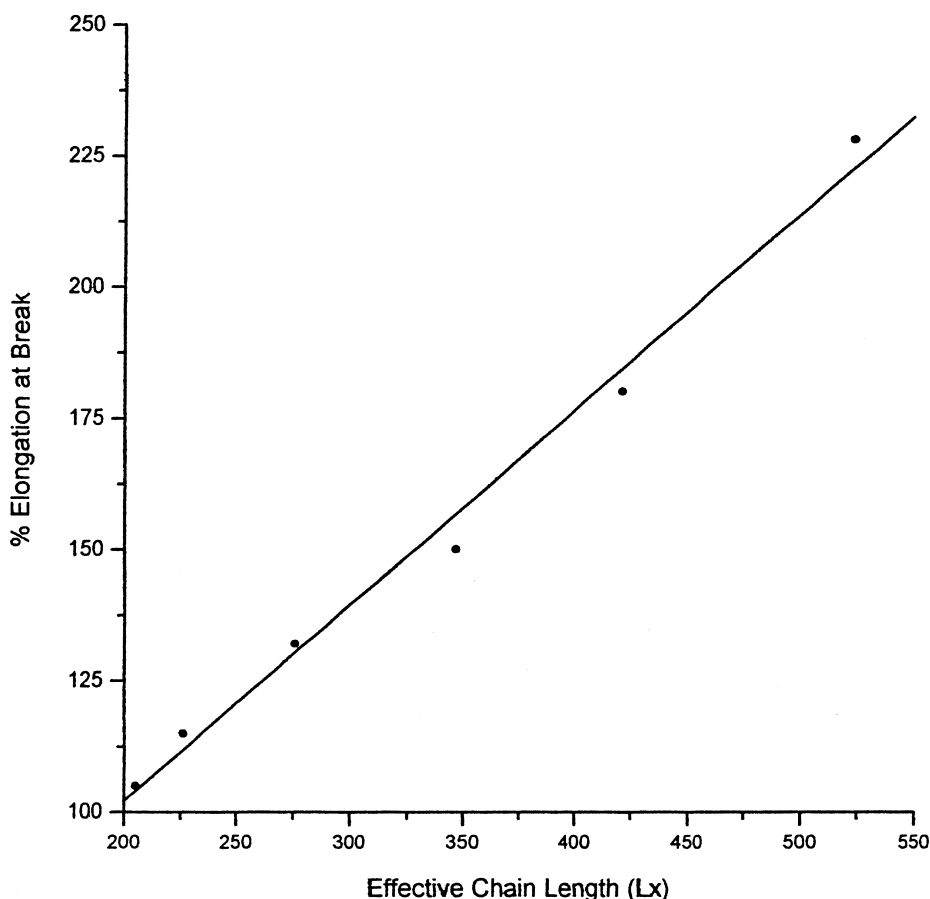
Fig. 4. Dependence of elongation on effective chain length for HTPB–TDI systems.

weight of the deswollen specimen was determined. From the weights of the swollen (ws) and deswollen (wds) specimens, the swell ratio (Q) was calculated as given below:

$$Q = (ws/wds) - 1 \tag{7}$$

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

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

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

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

where, d_1 and d_2 are the densities of solvent and the polymer, respectively. Crosslink density values are obtained from v_2 using Flory–Rhener equation [19]

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

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 [20].

2.5. Dynamic mechanical analysis

The viscoelastic properties of the allophanate group containing urethanes were evaluated using Rheovibron Viscoelastometer Model DDV-III-C at a frequency of 35 Hz over a temperature range of -100 to $50°C$. Specimens measuring $50 \times 10 \times 2 \text{ mm}^3$ were used for the purpose. The loss tangent (tan δ) is directly read by the instrument while the storage (E') and loss (E'') moduli were calculated using the following equations [21]:

$$E^* = L/(8ADW\text{Th}) \times 10^{12} \text{ dyn/cm}^2 \tag{11}$$

$$E' = E^* \cos \delta \tag{12}$$

$$E'' = E^* \sin \delta \tag{13}$$

where, E^* is the complex modulus, L the length of the specimen in cm, A an instrument parameter, D the dynamic force reading, W the width of the specimen in cm, Th the thickness in cm, and δ the phase difference.

2.6. ^{13}C NMR spectra

Proton noise decoupled ^{13}C NMR spectra of HTPB was
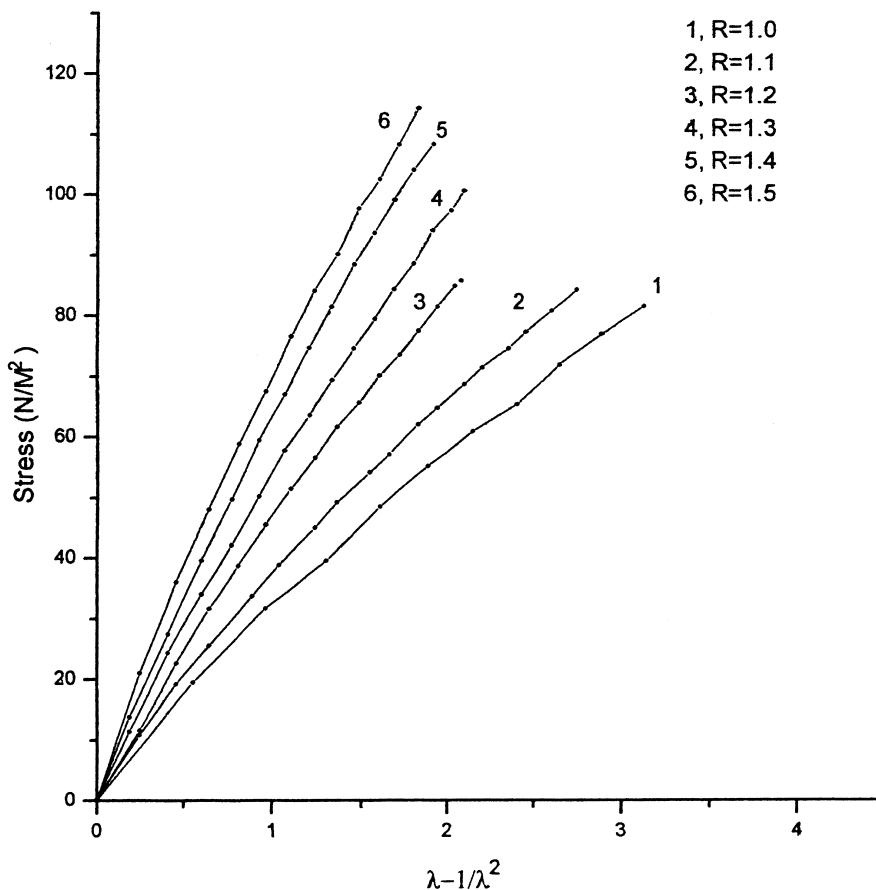
Fig. 5. Plots of stress versus strain function for HTPB–TDI systems.

recorded at 300 MHz on an ~10% (w/v) solution in CDCl$_3$ with TMS as the internal standard. Other relevant operating parameters were the following: sweep width 21929.824 Hz, acquisition time 15.58 s, number of scans ~2000.

3. Results and discussion

Polymer networks are generally characterized by three important parameters namely, sol content, density of effective chains or crosslink density and effective chain length (L_X). These parameters can be theoretically calculated by the α-model developed by Marsh, using input parameters, such as composition, extent of cure reaction and functionality distribution in the prepolymers. When isocyanate is used 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 up to 1.5 (see Table 1) which confirms that additional crosslinks are formed due to allophanate linkages. This is further supported by modulus data (Table 2).

Now, allophanate forming urethane networks should be described by another important parameter, X, which is the

fraction of urethane groups involved in the allophanate formation. In the absence of unambiguous experimental methods to determine X, in the present case, X was calculated using the α-model from the experimentally determined crosslink density values and further used to calculate the effective chain length (L_X).

3.1. Input parameters

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

3.1.1. Stoichiometric ratio (R-value)

R-value is the ratio of the equivalents of NCO groups to OH groups taken in the curing mixture, $R = (NCO)/(OH) = E_{TDI}/E_{HTPB}$; E_{TDI} and E_{HTPB} are the number of equivalents of TDI and HTPB, respectively. For the current studies R-value was varied from 1.0 to 1.5.

3.1.2. Equivalent weight of the curing system (w$_{eq}$)

Equivalent weight of the curing system can be obtained using the expression

$$w_{eq} = (56\,100/\text{hydroxyl value of HTPB}) + 87 \times R \qquad (14)$$

Table 1
Calculated network parameters for HTPB–TDI polyurethanes using the α-model

Sl no.	R	X	Crosslink density (mol/M^3)	Effective chain length L_X	Branching coefficient α
1	1.0	0	90	524	0.8467
2	1.1	0.054	106	421	0.8319
3	1.2	0.090	137	347	0.8480
4	1.3	0.166	164	276	0.8373
5	1.4	0.249	201	226	0.8365
6	1.5	0.315	209	205	0.8195

3.1.3. Functionality distribution

A method to arrive at the functionality distribution of HTPB was reported by Rama Rao et al. [11]. This method is based on the following considerations: (i) HTPB can be approximated to contain only non-, di- and tri-functional moieties [11]; (ii) HTPB contains three types of hydroxyls namely H, V and G types with the structures [22,23]: H, $HOCH_2$–CH=CH–CH_2–; V, HO–CH_2–CH (CH=CH_2) and G, C=CH–CH_2OH. G type hydroxyls represent the trifunctional (branching) components. The fraction of di- and trifunctional species can be readily calculated from the relative amounts of H, V and G type hydroxyls obtained from ^{13}C NMR spectra [11] by the following reasoning: If

Table 2
Mechanical properties of HTPB–TDI based urethane–allophanate networks at various R values

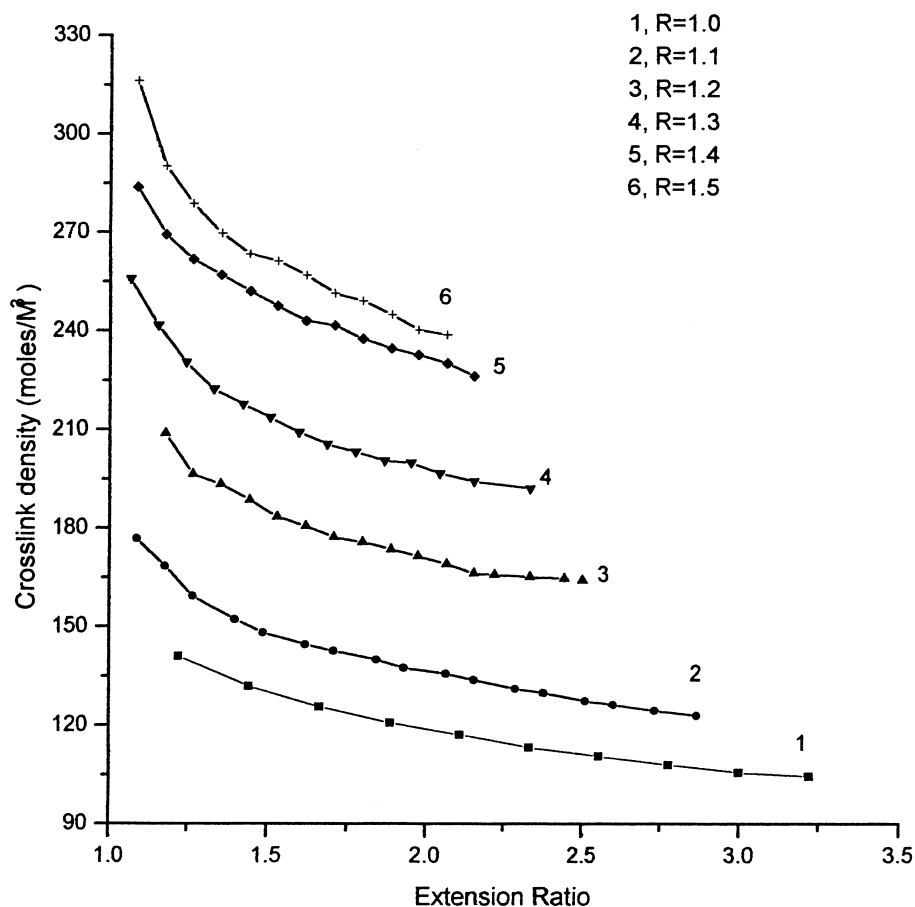| Sl no.	R value	Tensile strength (kPa)	Elongation at break (%)	Modulus at 100% elongation (kPa)
1	1.0	670	228	420
2	1.1	760	180	530
3	1.2	850	150	680
4	1.3	920	132	830
5	1.4	1060	115	940
6	1.5	1110	105	1030

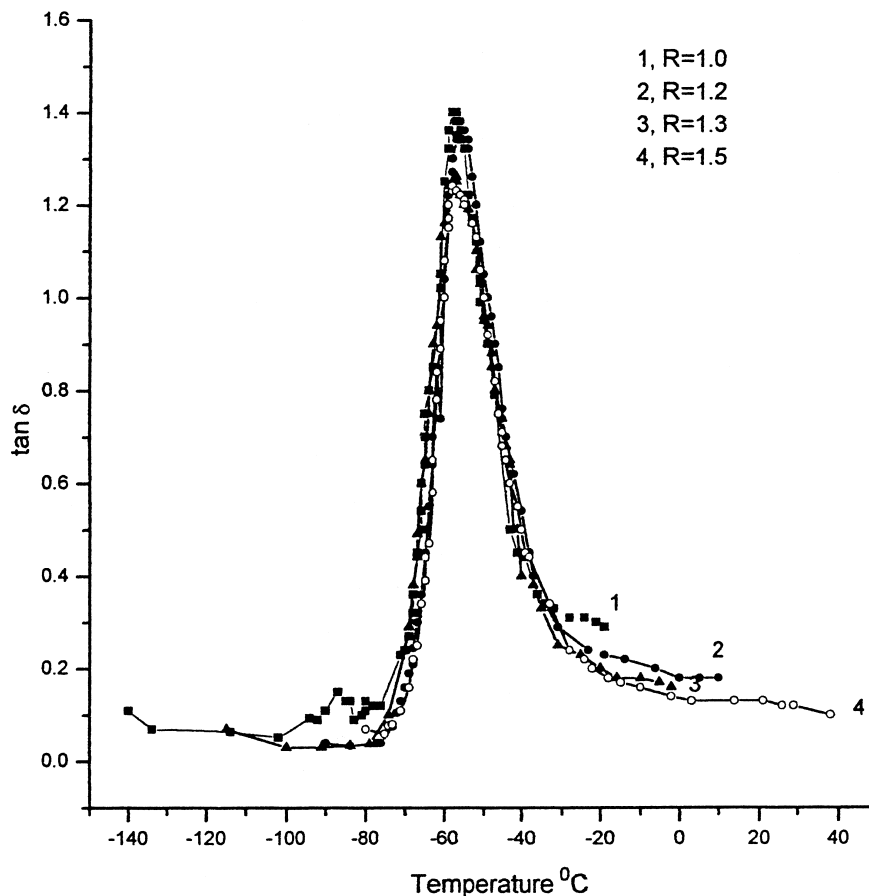Fig. 6. Variation of crosslink density with extension ratio for HTPB–TDI systems.

Fig. 7. Dependence of loss tangent on temperature for HTPB–TDI systems.

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 $(13 - f)/(1 - f)$. Using this logic, the relative amounts of the di- and trifunctional species in HTPB were determined. The relative contents of di- and trifunctional 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 trifunctional species in HTPB, A_2 and A_3 were computed using the following equations:

$$A_2 = 2d/(2d + 3t) \tag{15}$$

$$A_3 = 3t/(2d + 3t). \tag{16}$$

3.1.4. Extent of cure reaction

By the argument given in our earlier publication [12], the extent of 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. Since NCO is in excess over OH groups, it can be expected that all the OH groups would be completely consumed during the cure reaction.

3.2. 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, such as the crosslink density and effective chain length were calculated. The parameter X is a vital requirement in the allophanate modelling and the same was calculated using the experimentally determined crosslink density values. The calculated network parameters are listed in Table 1. It can be seen from Fig. 1, that the values of X increase with R-value and the variation can be represented by the following second-order regression equation:

$$X = 0.4143R^2 - 0.3957R - 0.0184. \tag{17}$$

The increase in X with R can be explained as follows: Hypothetical α values when $X = 0$, i.e. when urethane formation is just complete and no allophanate linkages are formed, at $R = 1.0, 1.1, 1.2, 1.3, 1.4$ and 1.5 are 0.8467, 0.7329, 0.6985, 0.6071, 0.5368 and 0.4811, respectively. It may be noted that α is a measure of degree of
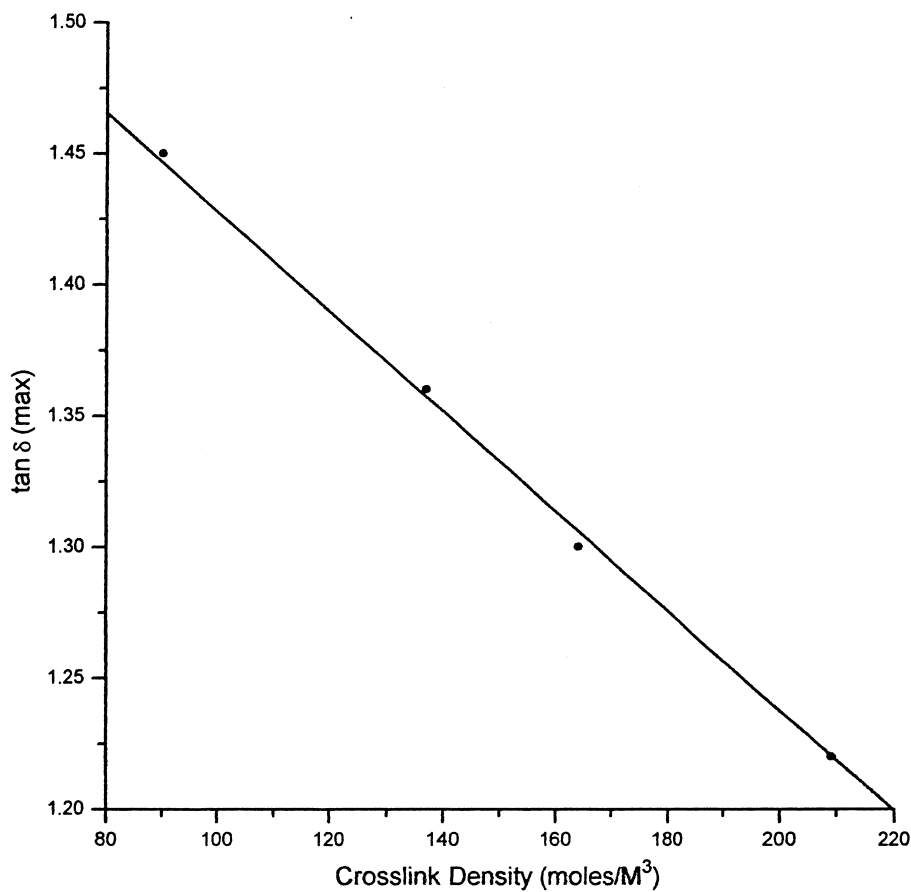
Fig. 8. Tan δ (max) as a function of crosslink density for HTPB–TDI systems.

crosslinking, and at gel point $\alpha = 0.5$. Thus, the degree of crosslinking, at the hypothetical point of completion of urethane formation, decreases steadily with R-value. Lower degree of crosslinking ensures greater degree of freedom for segmental motion, which is essential for allophanate formation. Interestingly, the two important network parameters ν_e and L_X seem to approach a limiting value with the increase in R-value.

3.3. Mechanical properties of the allophanate networks

The mechanical properties of the allophanate networks with R-values ranging from 1 to 1.5 are listed in Table 2. It can be seen that tensile strength, modulus values increase with R-value while per cent elongation decreases, reaching a plateau level eventually. Similar behaviour was reported elsewhere [3].

3.4. 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 by the following relationship [24]:

$$\sigma = \nu_e R_g T(\lambda - 1/\lambda^2) \tag{18}$$

where σ is the tensile stress based on original cross-sectional area of the tensile specimen, λ the extension ratio, R_g the universal gas constant and T the temperature in absolute scale. Thus, ν_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) [4,11,12]. As expected, straight line plots are obtained between ν_e and tensile strength and modulus and between L_X and %Eb (Figs. 2–4) with fairly good correlation coefficients, in spite of wide variation in R-values. It can also be observed from Table 1 that as R-values increases, ν_e increases while L_X decreases and both reach a near plateau level at higher R-values. Similar trend is seen in the case of mechanical properties also.

Earlier, Boyer and Miller [25] studied correlations between Mooney Rivlin constant C2 and number of chain atoms between physical entanglements. A detailed study
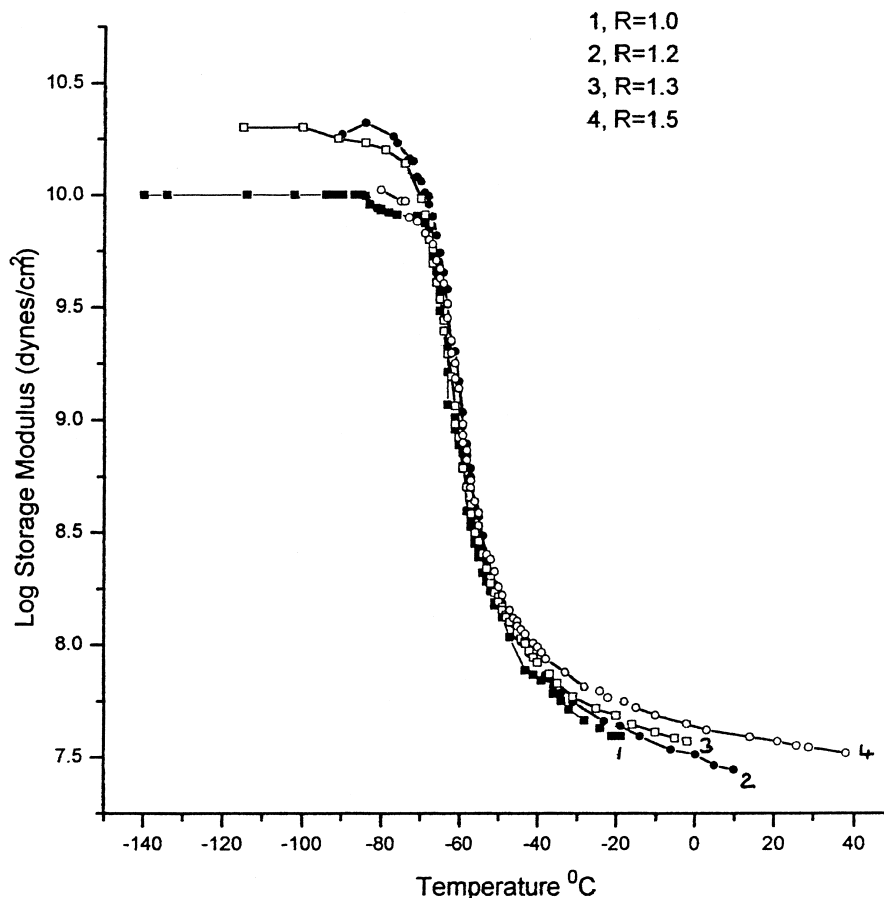
Fig. 9. Storage modulus as a function of temperature for HTPB–TDI systems.

correlating α and the Mooney–Rivlin constants for HTPB–TDI allophanate urethane networks is proposed in our future work on similar lines.

3.5. Crosslink density from stress–strain data

Crosslink densities can be computed from the tensile stress using Eq. (18) [19,24,26,27]. A typical plot of $\lambda - 1/\lambda^2$ against tensile stress is shown in Fig. 5. The plot obtained is a curve with reducing slope and as a result the crosslink density value (ν_{Mech}) calculated from the equation decreases with the extension ratio. However, the values just before rupture tend to converge to a constant value (Fig. 6), and therefore, the average of last few values is taken for consideration. Crosslink densities (ν_{Mech}) obtained in this manner for various R-values are tabulated in Table 3 and compared with the corresponding values obtained using the swell method (ν_{swell}).

The values obtained by the two methods maintain nearly the same ratio between them for all R-values ($\nu_{mech}/\nu_{swell} = 1.16–1.2$), indicating that the cause for variation between the two sets of values is the same for all R-values. Basically,

Eq. (18) was derived based on thermodynamic considerations without involving the time dependence factor, whereas the stress–strain relationship is strongly time dependant and the crosslink density values obtained by this method require a correction. However, since the deviation from the values obtained by standard methods is nearly constant, this method can be used for comparison and quick determination of crosslink density data. Further, it can be expected that the ratio (ν_{mech}/ν_{swell}) may shift to lower values at reduced strain rates.

Table 3
Crosslink density from stress–strain data for HTPB–TDI system

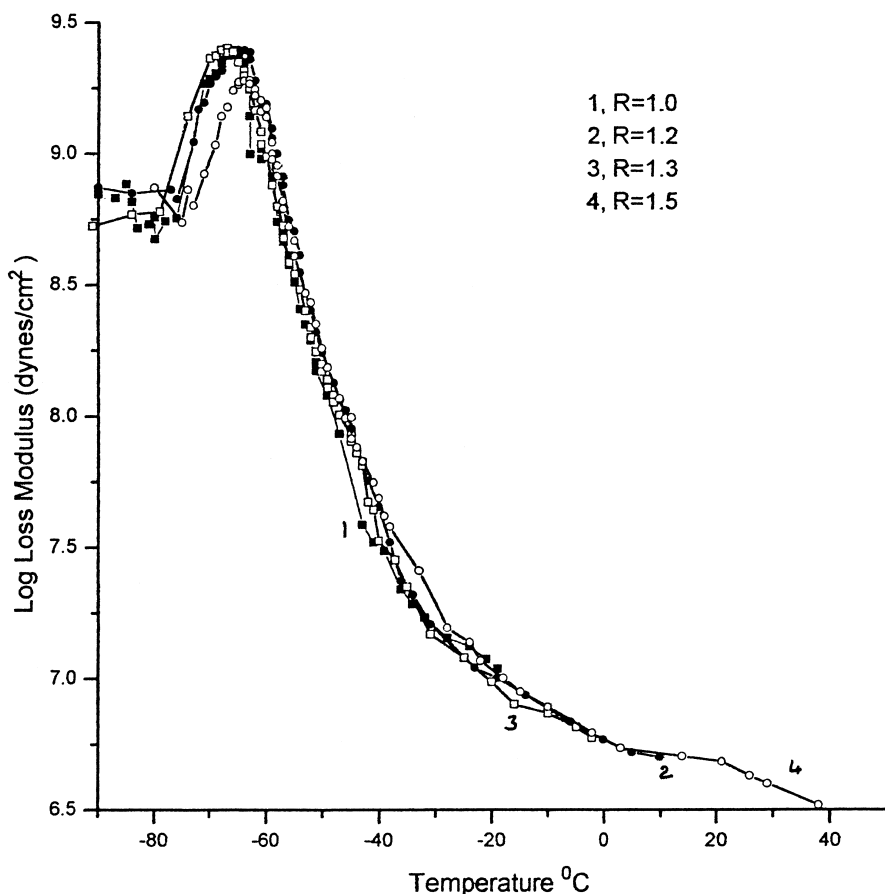| Sl no.	Crosslink density by swell method ν_e (mol/M^3)	Crosslink density by stress–strain method ν_{Mech} (mol/M^3)	ν_{Mech}/ν_e
1	90	104	1.16
2	106	123	1.16
3	137	164	1.20
4	164	192	1.17
5	201	226	1.13
6	209	245	1.17

Fig. 10. Dependence of loss modulus on temperature for HTPB–TDI systems.

3.6. Dynamic mechanical properties

The variation of loss tangent (tan δ) with temperature, for various allophanate containing urethanes is shown in Fig. 7. The loss tangent exhibits a maximum near the glass transition temperature (T_g). The maximum in tan δ occurs at about -55°C for all the urethane networks irrespective of the R-value. Thus, R-value has very little influence over the glass transition temperature, which may be due to the fact that for elastomers, glass transition temperature is dependant more on the segmental motion of the polymer chains rather than on the concentration of crosslink points. However, the magnitude of tan δ(max) shows dependence on R-value. The magnitude of tan δ(max) (which is approximately proportional to the area under the transition peak) at glass transition shows linear correlation (Fig. 8) with the crosslink density. The variation of storage and loss moduli with temperature are shown in Figs. 9 and 10, respectively. Both storage and loss moduli are affected by temperature, and at glass transition the fall is very steep for storage modulus while loss modulus shows a maximum at glass tran-

sition. It can be seen from Fig. 9 that at any given temperature after glass transition, the storage modulus increases with R-value which is an indication of increased elastic component at higher R-values. Loss modulus is nearly the same at any given temperature after glass transition for various R-values.

In Figs. 11 and 12, log of storage modulus and loss modulus are plotted against $1/T$ (K). Straight lines are obtained, and from the slopes of which activation energies for the variation of storage and loss moduli with temperature are calculated. The results are given in Table 4. It can be seen

Table 4
Activation energies for storage and loss moduli variation with temperature for HTPB–TDI system

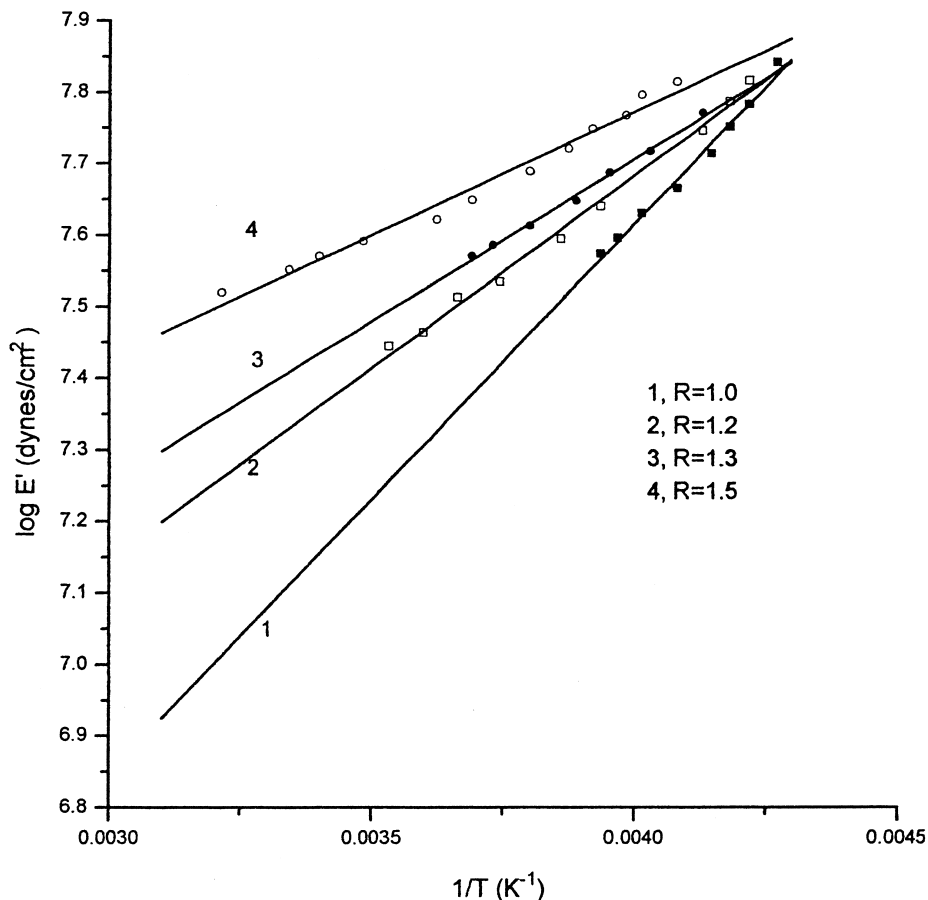| Sl no.	R-value	Activation energy (kJ/mol)	
		Storage modulus	Loss modulus
1	1.0	40.0	52.6
2	1.2	28.0	–
3	1.3	23.6	46.0
4	1.5	17.9	52.1

Fig. 11. Activation energy for storage modulus variation with temperature for HTPB–TDI systems.

that while the activation energy for storage modulus is strongly dependent on R-value, that for loss modulus is not much sensitive to R-value. The activation energy for storage modulus can be visualized as the activation energy for elastic relaxation process while that for loss modulus can be visualized as viscous relaxation. As mentioned earlier, the viscous portion is grossly determined by the backbone structure of the polymer chain and not much altered by the crosslink density. But the elastic portion is significantly dependent on the crosslink density. Table 4 suggests that the activation energy for storage modulus decreases with R-value. Also the activation energy when plotted with crosslink density gives rise to a straight line fit (Fig. 13).

The above observation may be rationalized as follows. Strain on an elastically effective chain can be expected to be higher at high crosslink density levels. More strained chains are expected to relax faster compared to less strained ones. Therefore, at higher R-values, the chains in the elastomer which are more strained due to high crosslink density may relax faster, resulting in lower activation energy when compared to the elastomers prepared at low R-values.

4. Conclusion

The important conclusions that can be drawn are as follows:

(i) The α-model developed by Marsh can be extended to allophanate containing urethane systems with suitable modifications.
(ii) 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 increase with R-value. 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.
(iii) Crosslink densities of the networks can be evaluated from stress–strain data, which are nearly 1.2 times that of the values obtained by swelling methods.
(iv) Dynamic mechanical studies reveal that the glass transition temperature of the allophanate networks does not change with R-value. Tan δ(max) is shown to be a simple linear function of the crosslink density of the
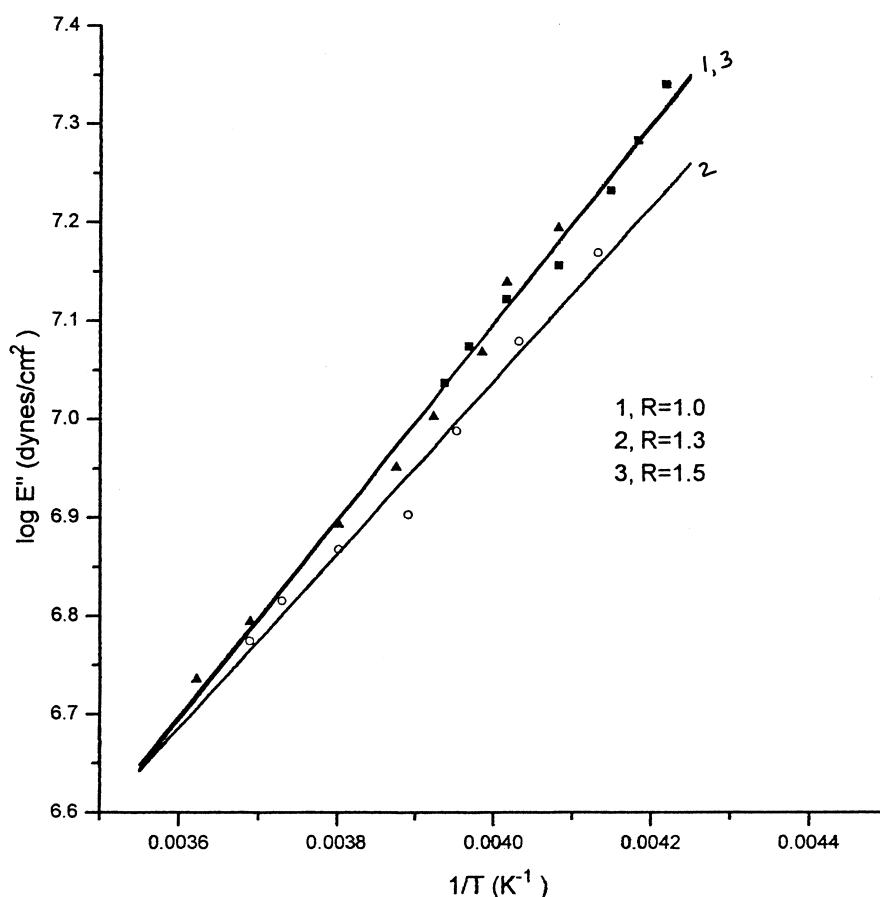
Fig. 12. Activation energy for loss modulus variation with temperature for HTPB–TDI systems.

networks. Activation energies for the variation of storage and loss moduli with temperature, evaluated from the dynamic mechanical data, decrease with R-value for storage modulus, while that for loss modulus remains nearly the same for various R-values.

Appendix A

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):

$$R = [NCO]/[OH] \tag{A1}$$

$$\alpha = p_{OH}^2(A_3 + p_{OH}X)/(R - p_{OH}^2 A_2) \tag{A2}$$

$$W_s = [(1 - \alpha)/\alpha]^3 \tag{A3}$$

$$\nu_e = 3\{(2\alpha - 1)/\alpha)\}^3\{A_3/3 + Xp_{OH}^2\}D \times 10^6 2W_{eq} \tag{A4}$$

$$W_G = 1 - W_s \tag{A5}$$

$$L_0 = W_G W_{eq} L_{SP} \alpha^3/\{(2\alpha - 1)(A_3 + 3Xp_{OH}^2)\} \tag{A6}$$

$$R_n = (1 - \alpha)/\alpha \tag{A7}$$

$$X_n = 1/(R_n + 1/R_n) \tag{A8}$$

$$R_{n+1} = R_2^n \tag{A9}$$

$$L_n = L_0(1 + 2X_1)(1 + 2X_2)(1 + 2X_3)...(1 + 2X_n) \tag{A10}$$

$$L = L_n, \text{ for } X_n - 0 \tag{A11}$$

$$L_x = 2L \tag{A12}$$

where α is the branching coefficient, A_3 the mole fraction of hydroxyls on trifunctional components of A, A_2 the mole fraction of hydroxyls on difunctional components of A, X the fraction of urethane groups involved in the allophanate formation, p_{OH} the extent of reaction in OH, W_s the weight fraction of sol, W_G the weight fraction of the gel, L_{SP} the number of chain atoms per gram of the polymer, D the density in g cm^{-3}, ν_e the crosslink density in mol/M^3 and L_X the effective chain length.
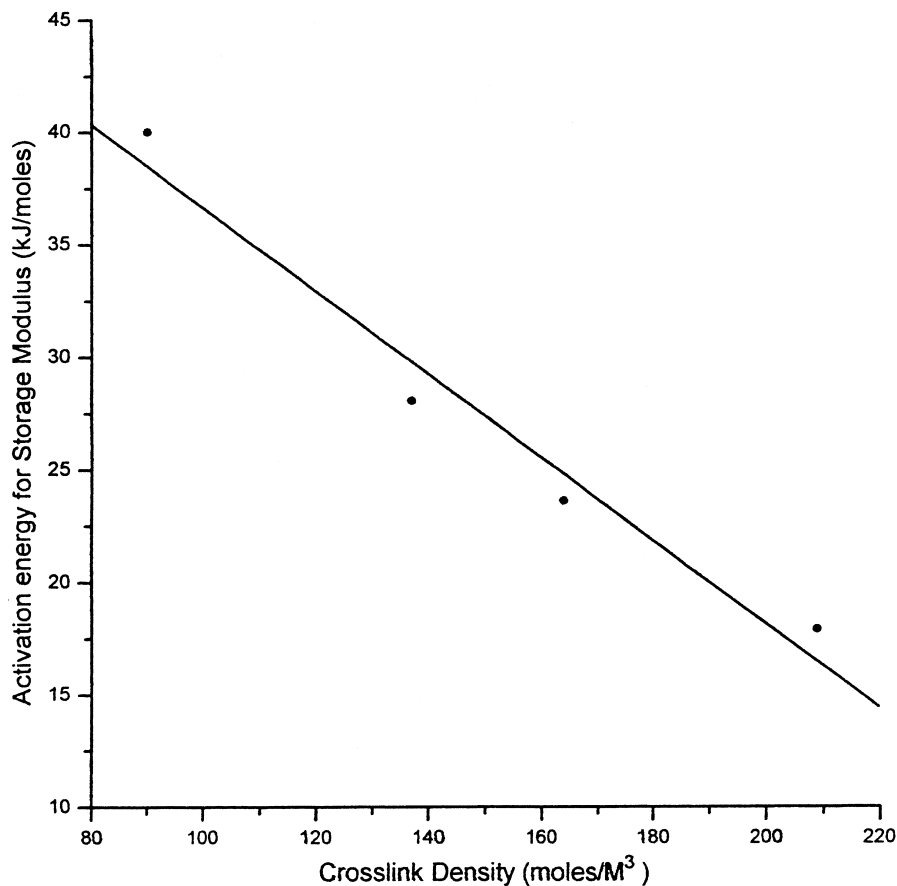
Fig. 13. Dependence of activation energy for storage modulus on crosslink density for HTPB–TDI systems.

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