

Comparison Between Crosslink Densities Derived from Stress–Strain Data and Theoretically Data Evaluated Through the α -Model Approach for a Polyurethane Network System Based on Hydroxyl Terminated Polybutadiene and Isophorone-Diisocyanate

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ABSTRACT: The crosslink density (CLD) for polyurethane elastomeric networks based on hydroxyl terminated polybutadiene and isophorone-diisocyanate was theoretically calculated with α -model equations the employing the functionality distribution and extent of reaction as input parameters. The theoretical crosslink density (v_t) was compared with the CLD values computed from stress–strain data evaluated at various strain rates. The methods for the calculation of the CLD from stress–strain data were based on the Mooney–Rivlin and Young's modulus approaches. Theoretical stress–strain curves were generated on the basis of v_t conforming to both phantom

and affine model calculations. The experimental stress–strain plots aligned more closely to the affine model line. The deviation of the experimentally derived stress–strain curves from the theoretical affine curve was probably due to the presence of temporarily trapped physical entanglements. From the stress–strain data, the concentrations of true chemical crosslinks and physical entanglements were estimated individually. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 920–925, 2010

Key words: crosslinking; modeling; networks; polybutadiene; polyurethanes

INTRODUCTION

Hydroxyl-terminated polybutadiene (HTPB) is the workhorse solid-propellant binder polymer used for most of the current launch vehicle programs. Toluene-diisocyanate (TDI) is the commonly used curing agent in HTPB binder processing. However, a major drawback associated with TDI is the short pot life for the propellant slurry, which is detrimental to achieving defect-free propellant grains with minimal material wastage. Replacing TDI with isophorone-diisocyanate (IPDI) would address this problem very effectively as IPDI is much less reactive than TDI and thus very useful in enhancing the pot life of propellant slurries.¹ However, in addition to pot life considerations, the characterization of the unfilled binder network (gum stock) is mandatory for optimizing the ultimate propellant characteristics.

The most common method of binder characterization is the evaluation of the mechanical properties.

In addition to the mechanical characteristics, an evaluation of the crosslink density (CLD) is essential as it is the most important property determining mechanical, swelling, and damping characteristics of the binder network.²

Most methods adopted for the determination of CLDs are based on swelling and uniaxial tensile stress (σ)/strain evaluations. Both methods are based on the basic rubber elasticity theory.^{3–8} Experimentally determined CLDs include both true chemical crosslinks arising from step-growth polycondensation reactions and physical chain entanglements. The physical chain entanglements fall into two categories: (1) permanently trapped chain entanglements and (2) temporarily trapped sliding-type physical entanglements. It is impossible to determine the chemical and physical crosslinks individually through experimental techniques. CLDs derived with the swelling method should be the sum of true-type chemical crosslinks and permanent-type chain entanglements (physical crosslinks). On the other hand, the theoretical approach (α -model) may deliver exclusively the chemically manifested true chemical CLDs. A comprehensive mathematical analysis of various approaches may help to resolve the three different types.

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Theoretical modeling of urethane networks

A considerable amount of work has been undertaken to develop theoretical models pertaining to condensation-type polymer networks.^{9–17} Among the models meant to theoretically calculate the network parameters, the α -model, developed by Marsh,⁹ is more suitable for HTPB-based urethane networks. The input parameters required for the α -model are (1) the concentrations of the network-forming components, (2) the equivalent weight of the curing system (w_{eq}), (3) the density, (4) the functionality-type distribution of HTPB, and (5) the extent of the reaction (p) of the components. The first three parameters can be readily obtained from physical and chemical analytical data, but unambiguous methods for determining the last two parameters were not previously available. However, a method for evaluating the functionality-type distribution for HTPB based on the ¹³C-NMR technique was developed by Rama Rao et al.¹⁶ p was determined by the adoption of an approach explained elsewhere.¹⁷

Evaluation of the CLD from the stress–strain data

The most important methodology based on stress–strain characteristics is the Mooney–Rivlin method. The Mooney–Rivlin equation for unswollen elastomers, obtained from the phenomenological theory of rubber elasticity, is shown by the following expression:¹⁸

$$\sigma(\lambda - \lambda^{-1}) = C_1 + C_2\lambda^{-1} \quad (1)$$

where σ is the uniaxial tensile stress, λ is the extension ratio determined as the ratio of the deformed length to the original length when the polymer specimen is pulled uniaxially, and C_1 and C_2 are constants characteristic of the elastomer. The Mooney–Rivlin crosslink density (v_{MR}) can be calculated from the constant C_1 with the following expression:¹⁸

$$v_{MR} = C_1/RT \quad (2)$$

where R is the universal gas constant and T is the temperature in Kelvin scale at which the stress–strain measurements are made. Alternately, the CLD can be determined from the initial modulus [Young's modulus (E)], which is obtained from stress–strain curves with the following relationship:^{6,7,19}

$$E = 3v_E RT \quad (3)$$

where v_E is the crosslink density calculated from Young's modulus. The CLD was also determined from swelling characteristics (v_c) with the Flory–Rehner equation. CLDs obtained by various experi-

mental approaches were compared with the value calculated theoretically, and the differences in the values were explained in terms of the network's fine structure. Furthermore, the experimentally evaluated stress–strain plots were compared with the theoretically generated stress–strain curves adopting phantom and affine model approaches.^{20–22}

EXPERIMENTAL

Materials

The HTPB $\{[\text{HO}-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n-\text{OH}]\}$ prepolymer used in this study was produced at Propellant Fuel Complex of Vikram Sarabhai Space Centre, Indian Space Research Organization, Thiruvananthapuram, Kerala, India, through H_2O_2 -initiated free-radical polymerization of butadiene in a mixed solvent system composed of propan-2-ol and water.²³ The equivalent weight of HTPB was determined by the acetylation method with a pyridine/acetic anhydride mixture.²⁴ The equivalent weight of the HTPB resin used in the current study was estimated to be 1375 g/equiv. IPDI was procured from M/s. A.G. Bayers and was used as such without further purification after its purity was ascertained. The estimation of the NCO content in the isocyanate compound was undertaken through the reaction of the isocyanate with a known excess of *n*-butyl amine and back-titration of the unreacted amine.²⁵ The assay of IPDI was found to be 99.5%.

Preparation of the urethane elastomers

The urethane elastomer based on HTPB and IPDI was prepared as follows. HTPB was dried at 80–90°C *in vacuo* in a rotary flash evaporator. The dried HTPB was mixed with IPDI at an NCO/OH equivalent ratio of 1. The reaction mixture was degassed *in vacuo* to remove air bubbles, poured into aluminum molds, and cured at 70°C for 48 h. The thickness of the cured elastomers was maintained at 3 mm. The cured elastomers were subjected to mechanical and swelling characterization.

Stress–strain data evaluation

The stress–strain data and mechanical properties of the polyurethane elastomers, such as tensile strength, elongation at break, and initial modulus, were determined with an Instron (Norwood, MA) model 4469 universal testing machine using dumbbell-shaped specimens as per the ASTM D 412 test method. Tensile tests were performed at various crosshead speeds (500, 50, 5, and 0.5 mm/min). The

TABLE I
Input and Output Parameters in the α Modeling of the HTPB-IPDI System

Parameter	Value
t in HTPB	0.5102
d in HTPB	0.4898
A_3	0.6097
A_2	0.3903
p	0.91
v_t (mol/m ³)	53.0

$$A_2 = 2d/(2d + 3t) \quad (9)$$

$$A_3 = 3t/(2d + 3t) \quad (10)$$

The extent of cure reaction (p)

In accordance with the approaches presented in our earlier publications,¹⁷ p between HTPB and IPDI was found to be 0.91 when r was 1.

Calculation of the CLD

The relevant α -model equations developed by Marsh et al.⁹ to calculate the theoretical crosslink density (v_t) for a polycondensation system pertaining to the formation of polyurethane networks between a polyol containing trifunctional, difunctional, and non-functional species and a difunctional curing agent are as follows:

$$\alpha = p^2 A_3 / (r - p^2 A_2) \quad (11)$$

$$v_t = [(2\alpha - 1)/\alpha]^3 A_3 d \times 10^6 / (2W_{eq}) \text{ (mol/m}^3\text{)} \quad (12)$$

The parameter α is known as the branching coefficient, and d is the density of the polymer system (g/cc). v_t for the present system is 53.0 mol/m³. The input and output parameters are listed in Table I.

Evaluation of the CLD from the stress-strain plots

There are two approaches by which the CLD can be evaluated from stress-strain plots. They are (1) the Mooney-Rivlin method and (2) the Young's modulus method. In the former case, eqs. (1) and (2) were used for the calculation of the CLD. Straight line plots were drawn between $\sigma/(\lambda - \lambda^{-1})$ and λ^{-1} , for which C_2 is the slope and C_1 is the y -axis intercept

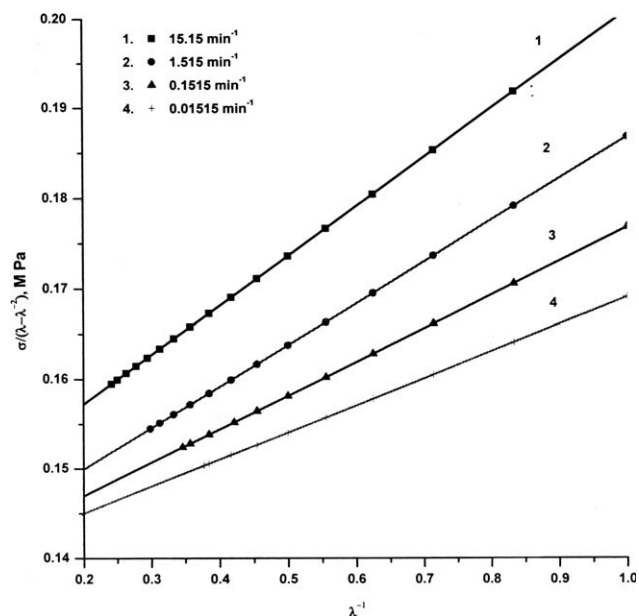


Figure 1 Mooney-Rivlin plots at various strain rates for the HTPB-IPDI system.

(Fig. 1). v_{MR} can be calculated from C_1 with eq. (2). Alternately, the CLD can be calculated from Young's modulus (E) with eq. (3). CLD values were obtained with both approaches at different strain rates (i.e., 15.15, 1.515, 0.1515, and 0.01515 min⁻¹). The CLD values obtained at various strain rates are listed in Table II.

Comparison of the v_t and experimental CLD values

It can be observed from Table II that the CLD values obtained with the Mooney-Rivlin (v_{MR}), E (v_E), and swelling methods (v_e) are higher than v_t (Table I) calculated with the α -model equations. Furthermore, the v_E approach posts a higher value than the corresponding values obtained with other methods. Table II and Figure 2 show that values determined by the Mooney-Rivlin and Young's modulus methods increase nominally with the crosshead speed from 0.5 to 50 mm/min but increase sharply at higher strain rates. The different values from different approaches may be due to the inherent nature of these methodologies. However, if we consider v_t to be the base value for which the contribution comes from only chemical crosslinks, the difference between the theoretical and other experimental

TABLE II
CLD for the HTPB-IPDI System Evaluated from the Stress-Strain Plots

No.	Strain rate (min ⁻¹)	C_1 (MPa)	C_2 (MPa)	v_{MR} (mol/m ³)	v_E (mol/m ³)	v_e (mol/m ³)
1	15.15	0.1463	0.05455	59.1	76.3	59.7
2	1.515	0.1407	0.04603	56.8	67.5	
3	0.1515	0.1396	0.03724	56.3	66.1	
4	0.01515	0.1390	0.03009	56.1	66.5	

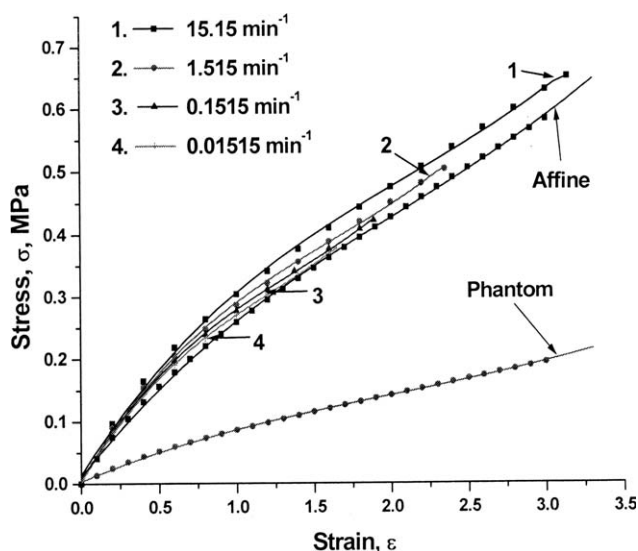


Figure 2 Plots of the CLD versus the logarithm of the strain rate for the HTPB-IPDI system.

approaches can be mainly due to the contribution from physical chain entanglements.

As mentioned earlier, the physical chain entanglements fall under two categories: permanent-type chain entanglements and temporarily trapped chain entanglements (temporary type). The permanent-type chain entanglements, in principle, behave very similarly to chemical crosslinks. The sliding or temporary-type physical entanglements respond to applied stress in an entirely different manner. At small extensions, the contribution to the modulus by sliding-type physical entanglements is quite significant, and the same decreases with λ ; at larger extensions, the chemical crosslinks outweigh the temporary-type physical entanglements in determining the modulus. Thus, v_E can be expected to be the sum of contributions from all three types of crosslinks, whereas the CLD from the Mooney-Rivlin treatment is a combination of true chemical crosslinks and permanent-type physical entanglements. Thus, from the values of v_t , v_{MR} , and v_E , it may be possible to resolve the overall CLD into chemical crosslinks and the two types of physical entanglement components. Probable figures for the three types of crosslinks—the true chemical crosslinks, permanent nonsliding-type physical entanglements, and sliding-type temporary physical entanglements—are 53.0, 3.0, and 10–11 mol/m³, respectively, as per this exercise. These figures are tentative and indicative and may not represent the actual values for these entries because of the approximations used in arriving at the theoretical model and other methodologies. It is to be noted that the concentration of sliding-type temporary physical entanglements is sensitive to the strain rate chosen. Its content increases with the strain rate.

Application of the stress-strain data to the phantom and affine models

The ideal stress-strain curve has a Gaussian pattern, and the Gaussian behavior is mathematically represented by two theoretical models, the phantom and affine models.^{20–22} According to phantom theory, the network junctions are assumed to be freely fluctuating in space. In the affine theory, the network junctions are assumed to move affinely with macroscopic deformation. The mathematical representations of the models are as follows:

$$\begin{aligned} \sigma_{\text{red}} &= [\sigma/(\lambda - \lambda^{-2})] \\ &= [(\phi - 2)/\phi]vRT(\text{phantom model}) \end{aligned} \quad (13)$$

$$\sigma_{\text{red}} = [\sigma/(\lambda - \lambda^{-2})] = vRT(\text{affine model}) \quad (14)$$

where σ_{red} is the reduced stress, ϕ is the functionality of the network system (for this system, $\phi = 3$), and v is crosslink density.

According to both theories, $\sigma_{\text{red}} \{ \sigma_{\text{red}} = [\sigma/(\lambda - \lambda^{-2})] \}$ is independent of the strain and, therefore, the strain rate. The two models, however, lead to different values for the modulus. A comparison of the experimental stress-strain curves and the theoretical affine and phantom curves is depicted in Figure 3. The theoretical curves were generated on the basis of the CLD values obtained with the theoretical α -model approach. It can be seen clearly in the figure that the experimentally evaluated curves align very closely to the affine model curve, and this indicates that the stress-strain behavior of this system is

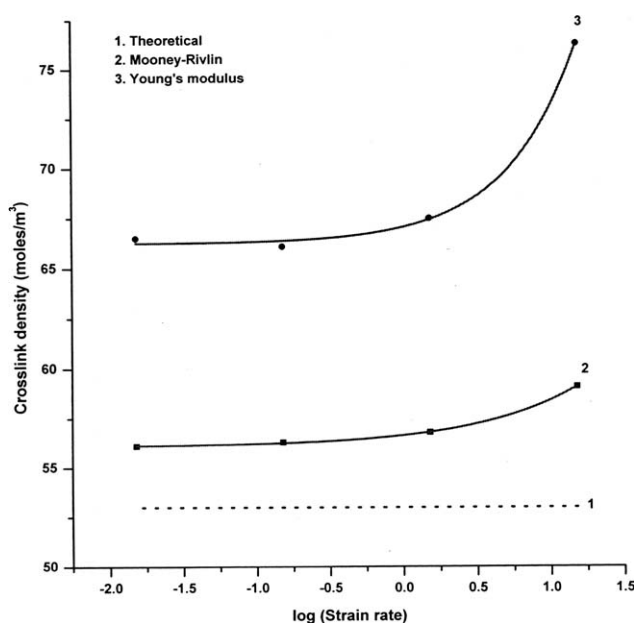


Figure 3 Experimental stress-strain plots at various strain rates and comparison with theoretically generated stress-strain plots for the HTPB-IPDI system.

affine-like; the smaller the strain rate is, the closer the stress–strain curve is to the theoretical affine line. The chief reason for the deviation from the theoretical stress–strain line is the existence of sliding-type and nonsliding-type temporary physical entanglements.

CONCLUSIONS

From the study, the following conclusion can be drawn:

1. v_t calculated with the α -model represents the true chemical crosslinks formed through a step-growth polycondensation chemical reaction.
2. The CLDs calculated with the equilibrium swelling and Mooney–Rivlin approaches represent the true chemical crosslinks and permanently trapped physical entanglements together.
3. v_E is the result of chemical crosslinks and permanently trapped and temporarily trapped physical entanglements all put together.
4. From the knowledge of the CLD calculated with the α -model and the CLDs calculated with the swelling, Mooney–Rivlin, and Young's modulus approaches, it may be possible to arrive at individual estimations of the three types of crosslinks (i.e., the chemical, permanent, and temporary-type physical entanglements).
5. The stress–strain behavior at the various strain rates adopted in this study conforms to affine behavior.

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