Evaluation by Various Experimental Approaches of the Crosslink Density of Urethane Networks Based on Hydroxyl-Terminated Polybutadiene

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ABSTRACT: Crosslink density (CLD) is an important characteristic for elastomeric polymer networks. The mechanical and viscoelastic properties of the elastomers are critically dependant on the CLD. Several methods have been adopted for its determination, but swelling and stress–strain methods continue to be more popular because of the convenience associated with these techniques. In this article, the determination of CLD of allophanate–urethane networks based on hydroxyl-terminated polybutadiene and toluene diisocyanate with swelling and stress–strain methods is reported. The Flory–Rhener relationship was applied to calculate CLD from the swelling data. CLDs were also calculated from the initial slope of the stress–strain curve (Young's modulus), Mooney–Rivlin plots, equilibrium relaxation moduli, and dynamic mechanical properties. A comparison was drawn among the values obtained with the various methods. Although the CLD values obtained from Mooney–Rivlin plots were slightly lower than those obtained from swelling data, the values obtained with Young's modulus and storage modulus were considerably higher. The values obtained with swelling and equilibrium relaxation moduli data were very close to each other. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3129–3133, 2007

Key words: crosslinking; elastomers; polybutadiene; polyurethanes; swelling

INTRODUCTION

The concentration of elastically effective chains (ν_e), known as crosslink density (CLD), is one of the most important characteristics of crosslinked elastomeric networks. The properties of elastomers, such as modulus, ultimate tensile strength, maximum extensibility, dynamic mechanical properties, and degree of swelling, critically depend on the degree of crosslinking.[1] Thus the determination of CLD is an essential feature in elastomeric characterization. Of many techniques, two are frequently used to evaluate CLD,[2–4] namely, the (1) measurement of the degree of equilibrium swelling in a good solvent[2] and (2) evaluation of stress–strain characteristics.[3,4] Both methods are based on rubber elasticity theory.[5–7] In addition, recently several methods have been reported, which include small-angle neutron scattering[8–10] and atomic force microscopy.[11] Methodologies that are based on NMR,[12–17] freezing-point depression,[18] and gas chromatographic[19] techniques have also been applied to evaluate CLD for different kind of rubbers. However, the swelling and stress–strain methods still continue to be popular because of the ease with which these measurements are made. For this study, CLDs for poly(allophanate–urethane) networks based on hydroxyl-terminated polybutadiene (HTPB) and toluene diisocyanate (TDI) were determined from swelling and stress–strain data. The values obtained from various methods were compared, and the comparison is discussed in this article.

EXPERIMENTAL

Materials

HTPB [HO—(CH$_2$—CH=CH—CH$_2$)$_n$—OH]

HTPB was prepared at Vikram Sarabhai Space Centre (Trivandrum, India) by H$_2$O$_2$-initiated free-radical polymerization of butadiene in a propan-2-ol–water cosolvent system.[20] The equivalent weight of HTPB was determined by an acetylation method with a pyridine–acetic anhydride mixture (1 : 8 v/v) as the acetylating agent.[21] TDI was procured from M/s. A. G. Bayers (Germany) and was used as such without further purification after the isocyanate content was estimated. The isocyanate content was determined by the reaction of TDI with a known excess of n-butyl amine in 1,4-dioxane solvent. The excess amine was backtitrated with standard HCl. From the amounts of n-butyl amine consumed by the isocyanate compound, the isocyanate content was calculated.[22]

Urethane–allophanate elastomers

Urethane–allophanate networks based on HTPB and the curing agent TDI were synthesized at various ratios of equivalents of isocyanate to equivalents of hydroxyl (r's), ranging from 1.0 to 1.5 as follows. HTPB was dried at 80–90°C *in vacuo* with a rotary flash evaporator. The dried HTPB was mixed with calculated amounts of TDI and degassed *in vacuo* to remove the entrapped air bubbles and was then poured into aluminum molds and cured at 70°C for 168 h. The average thickness of the cured elastomers was 3 mm. The cured elastomers were subjected to mechanical and swelling evaluations.

CLD as evaluated by the swelling method

CLD, expressed as moles of elastically effective chains per cubic meter, was obtained from volume fraction of the polymer (v_2) when swollen in a good solvent. Polymer specimens measuring $7 \times 7 \times 3$ mm were placed in toluene for 48 h. The swollen specimens were then removed from the solvent and weighed after the solvent was gently wiped off. Subsequently, the absorbed solvent was driven off by placing the specimen in a vacuum oven at 100°C for 2 h, and the weight of the deswollen specimen (w_{ds}) was determined. From the weight of the swollen specimen (w_s) and w_{ds}, the swelling ratio (Q) was calculated as follows:

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

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

$$w_2 = 1/(1 + Q) \qquad (2)$$

and

$$w_1 = 1 - w_2 \qquad (3)$$

v_2 in the swollen specimen can be expressed as

$$v_2 = (w_2/d_2)/[(w_2/d_2) + (w_1/d_1)] \qquad (4)$$

where d_1 and d_2 are the densities of the solvent and the polymer, respectively. CLD values were obtained from v_2 with the Flory–Rhener equation:[23–26]

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

where V_s is the molar volume of the solvent and χ is the polymer–solvent interaction parameter. χ for the HTPB–toluene system was 0.355. A detailed account on the determination of χ is presented elsewhere.[23,27]

Stress–strain evaluation

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) (Instron Corp., Norwood, MA) with dumbbell-shaped specimens as per ASTM D 412 test method. We determined relaxation moduli values by subjecting the dumbbell specimens to a constant strain of 100%. The strain was maintained at the same level by the adjustment of 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 eventually reached a stable value (equilibrium). The relaxation modulus was calculated from the equilibrium load values. All of the mechanical characterizations were undertaken at ambient temperature (20°C).

Dynamic mechanical analysis

The dynamic mechanical properties of the allophanate–urethane networks were evaluated with a Rheovibron viscoelastometer (model DDV-III-C) (IMASS Inc., Hingham, MA) at a frequency of 35 Hz over a temperature range of −100 to 50°C. Specimens measuring $50 \times 10 \times 2$ mm were used for this purpose. The loss tangent was read directly by the instrument, whereas the storage modulus (E_1) and loss modulus (E_2) were calculated with the following equations:[28]

$$E^* = [L/(8ADWTh)](\text{dyne/cm}^2) \qquad (5)$$

$$E_1 = E^* \cos \delta \qquad (6)$$

$$E_2 = E^* \sin \delta \qquad (7)$$

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

RESULTS AND DISCUSSION

CLD as evaluated from swelling data

CLD, or the concentration of elastically effective chains, can be conveniently calculated from v_2 in a swollen polymer gel with the Flory–Rhener equation. The values thus obtained represent the combination of true chemical crosslinks and physical crosslinks such as chain entanglements and loops. It is extremely difficult to differentiate one from the other. However, some statistical approaches help to calculate the physical crosslinks, which was beyond the scope of this study. In this study, we compared the total CLD obtained with the swelling method

CLD Values Obtained with Various Approaches for Urethane–Allophanate Networks Based on HTPB and TDI at Various r Values

r	ν_e (mol/m^3)	ν_R (mol/m^3)	ν_{MR} (mol/m^3)	ν_Y (mol/m^3)	ν_{E1} (mol/m^3)
1.0	90	93	83	109	89
1.1	106	110	93	131	107
1.2	137	146	128	179	146
1.3	164	165	148	214	175
1.4	201	205	183	231	226
1.5	209	209	190	269	239

ν_Y = crosslink density as evaluated by Young's modulus.

with the values obtained from mechanical property data. CLD values obtained via swelling data are listed in Table I.

Crosslink density as evaluated from stress–strain curves (ν_E)

Stress–strain measurements at quasi-equilibrium[29] are among the most powerful and efficient methods for the determination of CLDs. They have the great advantages that the usual equipment for standard testing methods can be used and that the samples can be investigated directly in the state of interest without any additional preparations such as swelling or similar procedures. Stress–strain curves for the allophanate–urethane networks are shown in Figure 1. Because the materials were viscoelastic, the stress–strain plots were not linear but curved. The initial slope could be considered to be Young's modulus (E).[30] Thus, E values for various systems were determined from the initial slopes of the various stress–

strain curves. E is related to CLD by the following relationship:[5,6,30]

$$E = 3\nu_E RT \tag{8}$$

where R is universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). The CLDs calculated from the initial slopes of the stress–strain plots are tabulated in Table I.

Crosslink density as evaluated from the equilibrium relaxation modulus (ν_R)

To evaluate the equilibrium relaxation moduli (σ_{Eq}'s), the dumbbell specimens were subjected to an elongation of 100% under the application of a load. As the specimen was allowed to relax, the load required to maintain the elongation at 100% decreased with time and eventually reached an equilibrium value; the stress calculated from the equilibrium load was σ_{Eq}. The stress relaxation curves corresponding to different r values are shown in Figure 2. CLDs of the
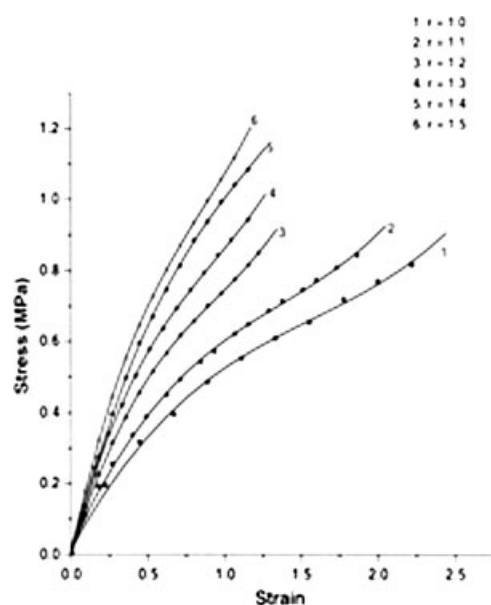
Figure 1 Stress–strain plots for allophanate–urethane networks based on HTPB and TDI at various r values.
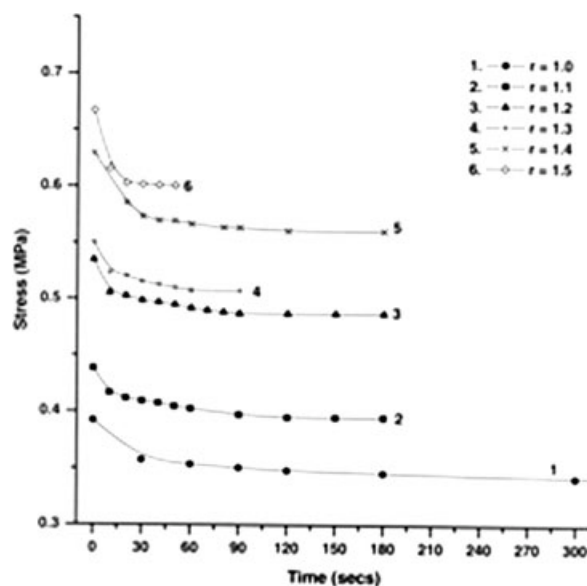
Figure 2 Stress relaxation curves for urethane–allophanate networks based on HTPB and TDI at strain = 1 and different r values.

elastomers could be calculated from σ_{Eq} with the following equation:[5–7,31]

$$\sigma_{Eq} = \nu_R RT(\lambda - 1/\lambda^2) \tag{9}$$

where λ is the extension ratio. λ is the ratio of the final length of the strained specimen to the original length of the undeformed specimen. CLD values for urethane–allophanate networks based on HTPB–TDI were evaluated from σ_{Eq}'s and are listed in Table I.

Crosslink density as evaluated through Mooney–Rivlin plots (ν_{MR})

The Mooney–Rivlin equation is widely used for the evaluation of the degree of crosslinking for a wide variety of elastomers.[32–35] The equation can be conveniently applied in the dry and swollen states. The equation is based on the phenomenological theory of rubber elasticity,[33,36] which is given by the following equation:

$$\sigma/(\lambda - \lambda^{-2}) = C_1 + C_2\lambda^{-1} \tag{10}$$

where σ is the tensile stress based on the original cross-sectional area of the undeformed test specimen. By plotting $\sigma/(\lambda - \lambda^{-2})$ against λ^{-1}, one can obtain straight-line plots for which the intercept is C_1 and the slope is C_2. Mooney–Rivlin plots for various r values are shown in Figure 3. ν_{MR} can be conveniently calculated from C_1 with the following expression:[25,33,35]

$$\nu_{MR} = C_1/RT \tag{11}$$
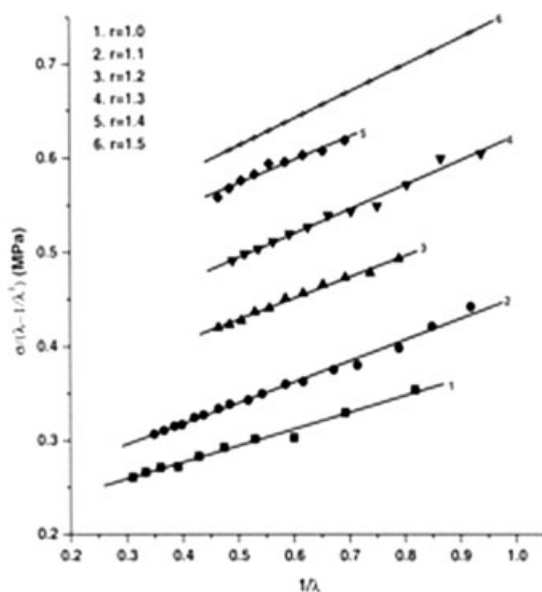
Figure 3 Mooney–Rivlin plots for urethane–allophanate networks based on HTPB and TDI at various r values.
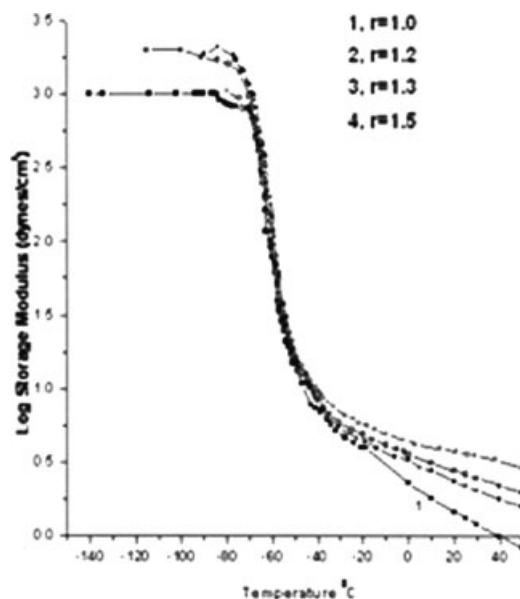
Figure 4 Plots of E_1 versus temperature for urethane–allophanate networks based on HTPB and TDI at various r values.

The constant C_2 is reported to be associated with intermolecular forces operating in the polymer networks.[37] CLD values calculated by Mooney–Rivlin approach are tabulated in Table I.

Crosslink density as evaluated from the storage modulus (ν_{E1})

CLD may also be calculated from experimentally measured rubbery plateau E_1 values through an equation derived from the theory of rubber elasticity.[25,35] The equation is

$$\nu_{E1} = E_1/(6RT) \tag{12}$$

The variation of E_1 with temperature is shown in Figure 4. CLD values were calculated from E_1 at 20°C and are tabulated in Table I.

Comparison of CLD values obtained from various methods

The CLD values calculated through the different approaches are tabulated in Table I. Among the various sets, the values obtained with swelling and σ_{Eq} data were closer to each other. The values obtained with Mooney–Rivlin plots were slightly lower than the swelling values. The values obtained from E and E_1 moduli were significantly higher than those calculated from the swelling values. Except for the swelling method, the other methods involved the straining of the elastomer specimen. In such methods, the ultimate parameters are dependent on the rate of strain. In other words, the timescale involved in the

stress–strain methods played a definite role in the determination of the final results. In both the swelling and relaxation methods, the final measurements were made only after the equilibrium was established. The time involved in these two cases was sufficiently long, and thus, the entanglements that were not trapped had enough time to disentangle, which eventually resulted in lower values for the CLD. On the other hand, the processes that involved E and E_1 measurements were quite fast, and the time available was not sufficient for chain disentanglements to take place; this led to overstated values. However, the reason for the lower values obtained with the Mooney–Rivlin method was not very clear, and further studies are required for a comprehensive understanding.

CONCLUSIONS

CLD was evaluated for urethane–allophanate networks based on HTPB and TDI by the adoption of various approaches, namely, swelling data, σ_{Eq}, E, Mooney–Rivlin constants, and E_1 methods. The values obtained with the equilibrium swelling and σ_{Eq} methods were fairly close to each other, whereas those obtained with E and E_1 were significantly higher than the swelling values. The values obtained with the Mooney–Rivlin approach were slightly lower than the swelling values.

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