Synthesis and Characterization of an Isocyanurate–Oxazolidone Polymer: Effect of Stoichiometry

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ABSTRACT: Isocyanurate–oxazolidone polymers were synthesized by using various reactant stoichiometry of a diglycidyl ether of bisphenol-A (DGEBA) and a polymeric diphenyl methane diisocyanate (pMDI). The reaction was catalyzed by tris-2,4,6-dimethylaminoethylphenol (Ancamine K54). The effects of stoichiometry that the reaction had on the molecular structure and mechanical and thermomechanical properties were evaluated. Two main structures obtained from the reaction of DGEBA with pMDI, namely isocyanurate and oxazolidone, were clearly shown by Fourier transformed infrared spectroscopy (FTIR) analyses. It was found that the amount of DGEBA present determines the amount of oxazolidone formed. Where excess DGEBA was used, structural transformation reaction from isocyanurate to oxazolidone was observed. The amount of pMDI, on the other hand, influenced the amount of isocyanurate structure formed. As the relative amounts of isocyanurate and oxazolidone contents changed with stoichiometry of the reactants, the effects on the crosslink density in the samples were clearly shown by both mechanical and thermomechanical measurements. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 879–888, 2001

Key words: isocyanurates; oxazolidone; polyurethanes; crosslink density; DGEBA

INTRODUCTION

The use of isocyanate compounds is often associated with the synthesis and manufacture of polyurethane products. However, the reactions of isocyanates extend beyond compounds containing active labile hydrogen such as those found in polyols and amines. Isocyanate compounds are also known to undergo dimerization and trimerization reactions under certain conditions to form uretidiones and isocyanurates, respectively. These reactions are considered unfavorable, especially the isocyanurates, because they form highly crosslinked structures rendering the products extremely brittle. This brittle property of isocyanurate compounds has limited their application despite their inherently excellent thermal stability and flame resistance. Currently, polymers containing isocyanurate structures are limited to foams and structural laminates.

This article describes a relatively new method of enhancing the mechanical toughness of an isocyanurate polymer by reducing its crosslink density by introducing a linear oxazolidone structure. The process involves the reaction of a diglycidyl ether of bisphenol-A (DGEBA) with a polyisocyanate compound, resulting in a complex structure containing both isocyanurate and oxazolidone groups. The isocyanurate structure forms the crosslinked sites for the network, whereas the

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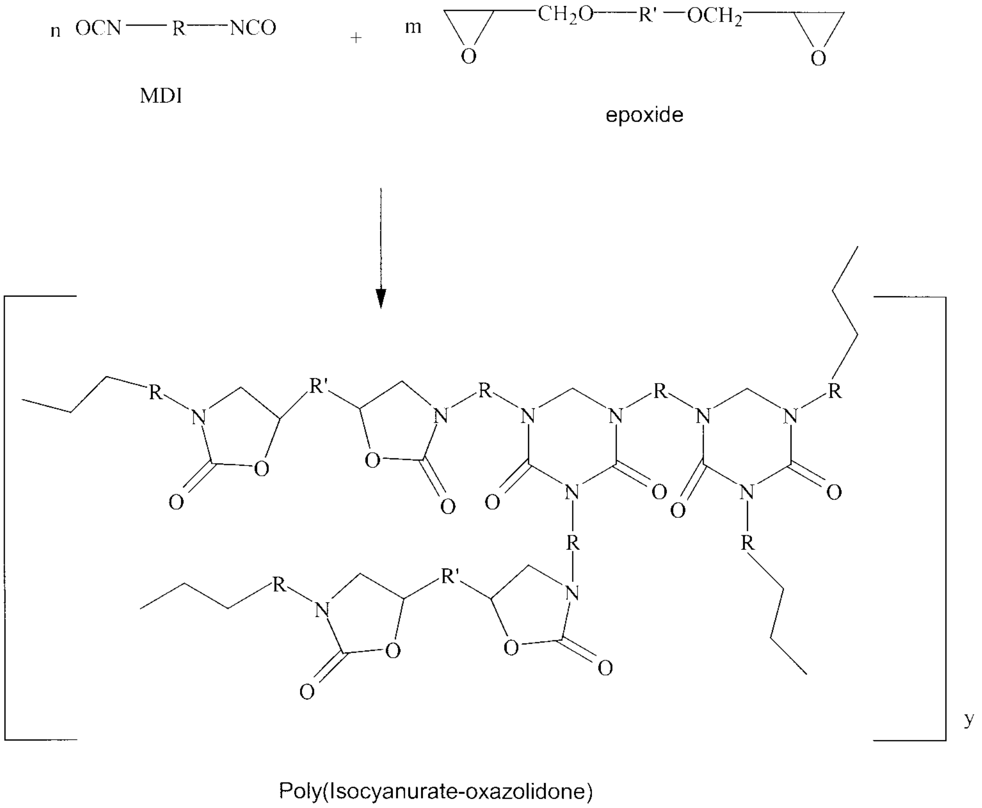

Figure 1 Reaction scheme for a poly(isocyanurate–oxazolidone).

oxazolidone forms the rigid linear structures responsible for reducing the overall crosslink density. Therefore, the properties of the isocyanurate–oxazolidone polymer will depend on the relative amounts of isocyanurate and oxazolidone present in the final structure. The effect stoichiometry has on the relative amounts of these isocyanurate–oxazolidone structures formed and the properties of the final polymer will be presented in this study.

Polyisocyanurates

Isocyanate compounds are well known for their high reactivity, and depending on the reaction condition, side reactions are common.[1,2] One of these important side reactions is the trimerization of the isocyanate group to form the isocyanurate structure.[3] The trimerization of reactions of isocyanurates is promoted with basic catalysts such as tertiary amines, and triphenylphosphines. Polyisocyanurates are highly crosslinked and therefore extremely brittle. However, these isocyanurate structures are well known for their thermal stabilities and are fire resistant because they do not contain any labile hydrogen in the isocyanurate ring system. Polyisocyanurates are widely used to enhance the thermal stabilities of polyurethanes and foams and in structural laminates.[4–7]

Polyoxazolidone

Polyoxazolidones are a new generation of isocyanate-derived polymers characterized by their thermal stability and they are finding new applications in foams, adhesives, and electrical applications. Several researchers[8–10] have reported the chemical syntheses of substituted 2-oxazolidones from reacting 1,2-epoxides and isocyanates. The reaction scheme is described in Figure 1.

The reaction kinetics and mechanisms of these oxazolidone syntheses are well studied and reported in the literature.[11–14] These oxazolidone structures are basically linear but are topologically bulky due to the presence of the cyclic groups along the main chain. This combination of a linear but sterically hindered structure and

Table I Stoichiometry of Formulations Evaluated

Sample	DGEBA	pMDI	Stoichiometry (P)
M10	1	1.10	0.91
M05	1	1.05	0.95
ISOX	1	1	1
E05	1.05	1	1.05
E10	1.10	1	1.10

high-thermal stability renders these oxazolidone structures attractive candidates for improving the mechanical toughness and fracture resistance of many highly crosslinked isocyanurates.

OBJECTIVE

The objective of this article is to report on the effect of reactant stoichiometry of DGEBA and pMDI on the properties of the fully cured polymer.

EXPERIMENTAL

Materials Used

The epoxy used was a medium-viscosity DGEBA, Araldite® GY 250 (Ciba Specialty Chemicals, Singapore) with an epoxide equivalent weight (EEW) of 183–189.[15] The epoxy resin was dried by using a rotary evaporator until the water content was < 0.02 wt % (determined by Karl Fisher coulometric titration).

Polymeric 4,4′-diphenylmethane diisocyanate (pMDI) (Bayer Chemicals, Singapore), with an isocyanate content of 25.5%, was used as the hardener. The hardener was used as received.

Ancamine K54 (Air Products Inc), a tris-2,4,6-dimethylaminomethylphenol, was used as the catalyst. The catalyst was dried by using freshly regenerated type 4A molecular sieves until the moisture level was < 0.04 wt % (Karl Fisher coulometric titration).

Sample Preparation

The stoichiometry of the formulation, P, was calculated on the basis of the equivalent weight ratios of DGEBA to pMDI. Table I summarized the formulation evaluated. The catalyst used was fixed at 0.5 wt % on the basis of the weight of DGEBA.

Predetermined amounts of DGEBA and catalyst were mechanically mixed in a dry glass beaker for approximately 2 min. An appropriate amount of pMDI was then added to the DGEBA–catalyst mixture and mixing continued for another 2 min. The mixture at this stage was termed an A-staged sample because little or no reaction was assumed to have occurred in the mixture.

Curing Procedure

The curing profile used for this work was as follows: A-staged sample was initially heated at 90°C for 10 min, followed by 200°C for 60 min. Postcuring was subsequently carried out at 220°C for 60 min. After the above curing profile, all the samples showed zero residual cure exotherm on the DSC analyses.

Sample Characterization

Fourier Transform Infrared Spectroscopy (FTIR)

A Nicolet Magna-560 FTIR system was used to monitor the changes in the characteristic functional groups of the various cured samples. All the solid samples were mixed with anhydrous spectroscopic grade potassium bromide (KBr) powder and finely ground before being pressed into thin discs. The samples are scanned 50 times in transmission mode from 4000 to 600 cm^{-1} wave number at 4 cm^{-1} wave-number resolution. The characteristic functional groups[16–19] of interest are the isocyanurate carbonyl (1711 cm^{-1}), oxazolidone carbonyl (1754 cm^{-1}), and an internal phenylene (830 cm^{-1}) reference peak.

The peak height of the characteristic peak of interest was normalized against the phenylene reference absorption peak. The normalized absorbance, which quantifies the relative amount of the characteristic group, was obtained by using the peak-height method that was based on the ratio of the height of the characteristic to internal reference absorbance peak. (Peak-height method was used in preference to the usual peak area because of the overlap of the isocyanurate carbonyl and oxazolidone carbonyl peaks.)

Dynamic Mechanical Analyses (DMA)

Gabo® dynamic mechanical analyzer was used to characterize rectangular samples (25 × 5 × 4 mm) in dynamic tensile mode. The gauge length of the sample was fixed at 20 mm. Both the dynamic load and the strain were set at 25*N* and 4%, respectively, and a test frequency of 1 Hz was used. The samples were heated from −150 to 250°C at a heating rate of 2°C/min. Data obtained from the DMA analyses included (a) glass-transition temperature (T_g), and (b) storage moduli at temperatures below (−70°C) and above (170°C) the T_g (i.e., E_g' and E_r', respectively). The subscripts *g* and *r* signify the glassy and rubbery states, respectively. E_r' was used to determine the crosslink densities of the cured samples.

Macrodensity

The densities of the samples were measured at 22°C by using a density bottle (pycnometer) with toluene as the immersion medium.

Crosslink Density

The crosslink density, χ, was taken[20] to be equal to $(3M_c/2)^{-1}$, where M_c is the molecular weight between crosslinks and was approximated from DMA modulus value obtained at 170°C (i.e., E_r'). The empirical expression[21] relating the DMA modulus (E_r') and M_c is given as follows:

$$\mathrm{Log}_{10} E_r' = 7 + \frac{293\rho}{M_c}$$

where ρ is the macrodensity.

Thermomechanical Analyses (TMA)

TMA analyses were carried out by using the TA-2940 TMA system to determine the effect stoichiometry had on the coefficient of thermal expansion (CTE) of the samples. Samples 5 × 5 × 4 (height) mm were analyzed by using a quartz expansion probe with a static load of 0.01*N*. The samples were heated from −50°C to 200°C at a heating rate of 10°C/min. The CTE values below and above the T_g (i.e., α_g and α_r) were obtained and correlated to the stoichiometry of the formulation used.

Flexural Analyses

An Instron universal tensile tester, fitted with a 5-kN load cell, was used to determine the flexural behavior of the samples. The samples dimensions, 50 × 8 × 4 mm, were subjected to a three-point bend deformation. The sample span and strain rate were set at 40 mm and 0.1 mm/s, respectively. The flexural moduli and toughness were determined from the initial slope and area under the load-deflection curve, respectively.

RESULTS AND DISCUSSION

FTIR

Figure 2 shows a typical FTIR spectra of a fully cured sample of ISOX. A plot of the sample stoichiometry against the [I/O] ratio, isocyanurate [Iso], and oxazolidone [Oxa] is shown in Figure 3. The [I/O] ratio was used to indicate the relative amounts of the crosslinked isocyanurate in relation to the oxazolidone structures formed. A sample containing a higher [I/O] ratio would indicate a relatively higher crosslinked structure.

The results showed that with increasing stoichiometry, the amount of the isocyanurate structure, [Iso], decreased, whereas that of the oxazolidone, [Oxa], increased. The net effect was a general reduction in the [I/O] ratio with increasing stoichiometry. The decrease in [Iso] with increased DGEBA was, however, unexpected. The [Iso] was expected to reach a plateau value in the course of the curing reaction. Similarly, an increase in [Oxa] at higher stoichiometry (i.e., $P > 1$) was interesting because it occurred at stoichiometry where [I/O] showed dramatic decrease. Hence, the simultaneous decrease in [Iso] but increase in [Oxa] with increasing stoichiometry suggested a possible structural transformation reaction occurring during curing. The structural transformation of isocyanurate-to-oxazolidone structure was reported in literature but the mechanism remained unresolved.[22] Although the structural transformation mechanism remained unknown, the role of the excess DGEBA in the formulation was evident. One possible mechanism postulated was the unusual breakdown of the thermally stable isocyanurate structure in the presence of excess DGEBA to liberate the isocyanate groups for oxazolidone formation.

Macrodensity

The macrodensity of the sample will be largely dependent on the free volume and packing efficiency of the molecular chain. The effect of the sample structure on the macrodensity is shown in

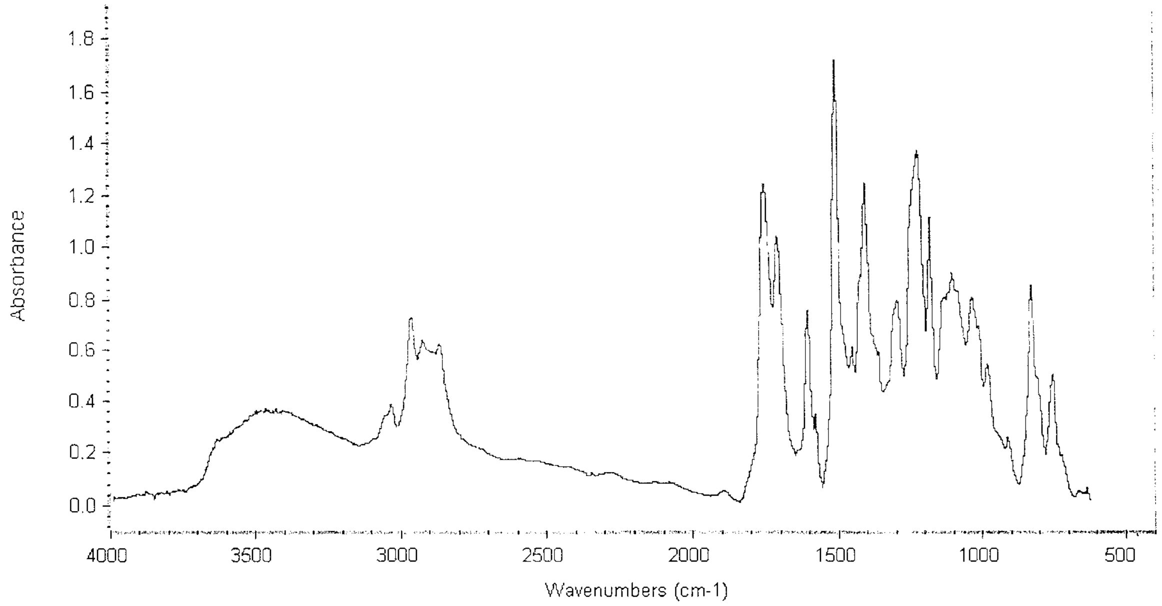

Figure 2 Typical FTIR spectra of a fully cured ISOX sample.

Figure 4. A plot of the [I/O] ratio against the macrodensity showed that the macrodensity of the sample initially increased with [I/O] ratio, reaching a maximum for stoichiometric sample after which a dramatic decrease in the macrodensity was observed. Because the [I/O] ratio is a measure of the relative amounts of the isocyanurate structure present in the sample, it is also indicative of the crosslink density of the sample. Samples with higher [I/O] are expected to be more highly crosslinked. Therefore, the reduction in the macrodensity with increased crosslinking of the sample indicates inefficient molecular chain packing. Similar studies on crosslinked epoxy networks had suggested that epoxies that are highly crosslinked often have lower macroden-

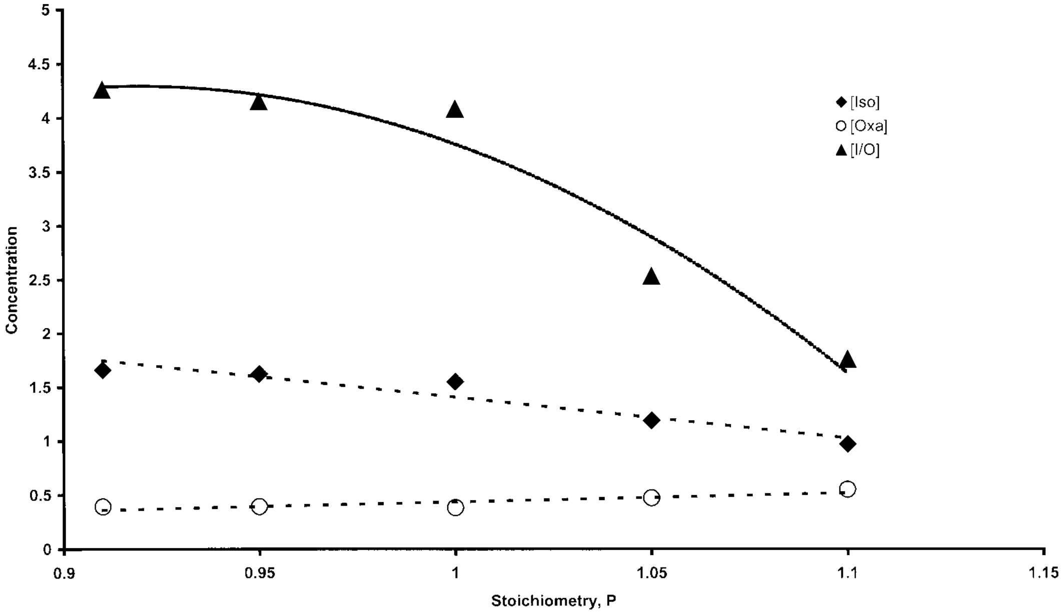

Figure 3 Effect of stoichiometry on [Iso], [Oxa], and [I/O].

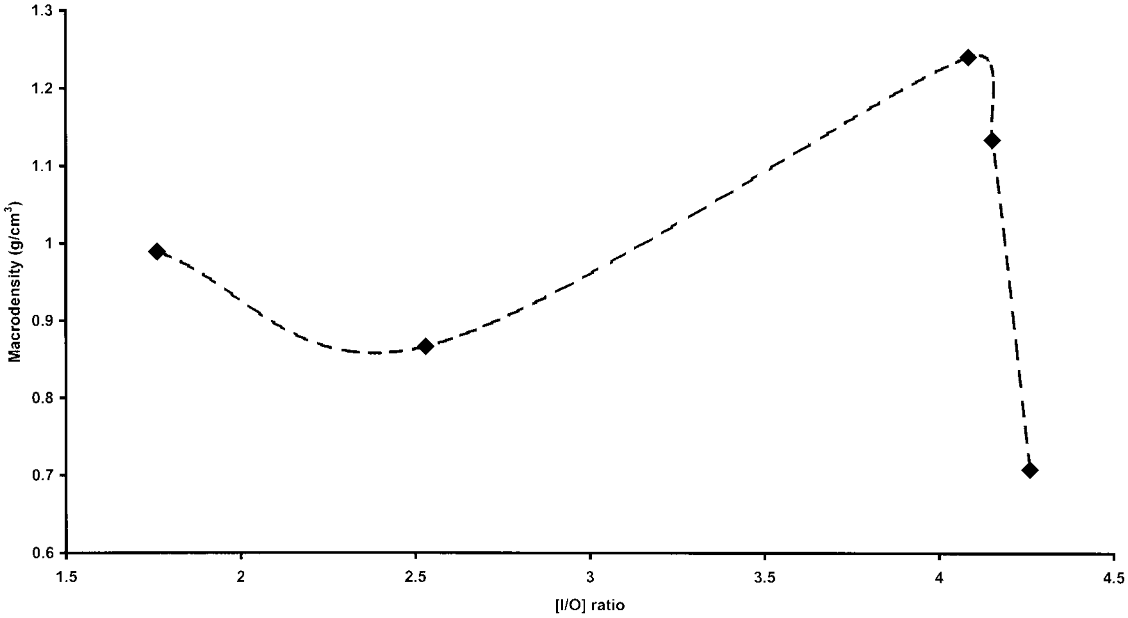

Figure 4 Effect of [I/O] on macrodensity.

sity.[23–25] Despite a lower [Iso], the decrease in macrodensity for samples with higher [Oxa] clearly reflect a low packing efficiency of the sterically hindered oxazolidone structure.

DMA

The thermal and mechanical properties of thermosets are known to be dependent on their molecular structures. Two such factors are (a) size and type of the structural groups along the main polymer chain and (b) their crosslinking density. Thermosets containing bulky or sterically hindered structures such as the heterocycles or the phenylene groups along the main chain generally impart stiffness to the polymer. This increased chain stiffness is often reflected in increased glass-transition temperatures and elastic moduli. Similarly, as the crosslinking density increases, the general mobility of the polymer chains and segments also decrease. DMA data often provide useful information pertaining to the molecular structure of the polymer in terms of their thermomechanical properties.

Plots of the stoichiometry against the T_g, dynamic moduli (E_g' and E_r'), are shown in Figures 5 and 6, respectively. The results showed that the T_g of the sample decreased with increased stoichiometry. As discussed earlier, as the amount of the oxazolidone in the sample increases with stoichiometry, the decrease in the T_g can be accounted for by the increase in oxazolidone. This is due to the higher chain mobility of the linear but sterically hindered oxazolidone structure compared to the highly crosslinked and rigid isocyanurate network. This was further confirmed by samples, synthesized from excess pMDI ($P < 1.0$), which contain higher isocyanurate contents, showing higher T_g values. The reduced chain mobility that caused the T_g to increase are also responsible for the enhanced dynamic moduli, E_g' and E_r'. Both moduli showed a corresponding increase with isocyanurate contents in the samples. It was interesting to note that below T_g, comparing the stoichiometric sample, ISOX, with E10, the reduction was approximately 15%, but above T_g, the decrease in the moduli was more significant (i.e., −200%). Hence, the incorporation of the oxazolidone structure did not significantly reduce the mechanical strength of the isocyanurate polymer because of its inherently linear but rigid structure.

Crosslink Density

The crosslink densities of the samples were determined from the elastic moduli, E_r', obtained from DMA. The effect of stoichiometry on the crosslinking density could be observed in Figure 7. The crosslink density correlated well with the FTIR

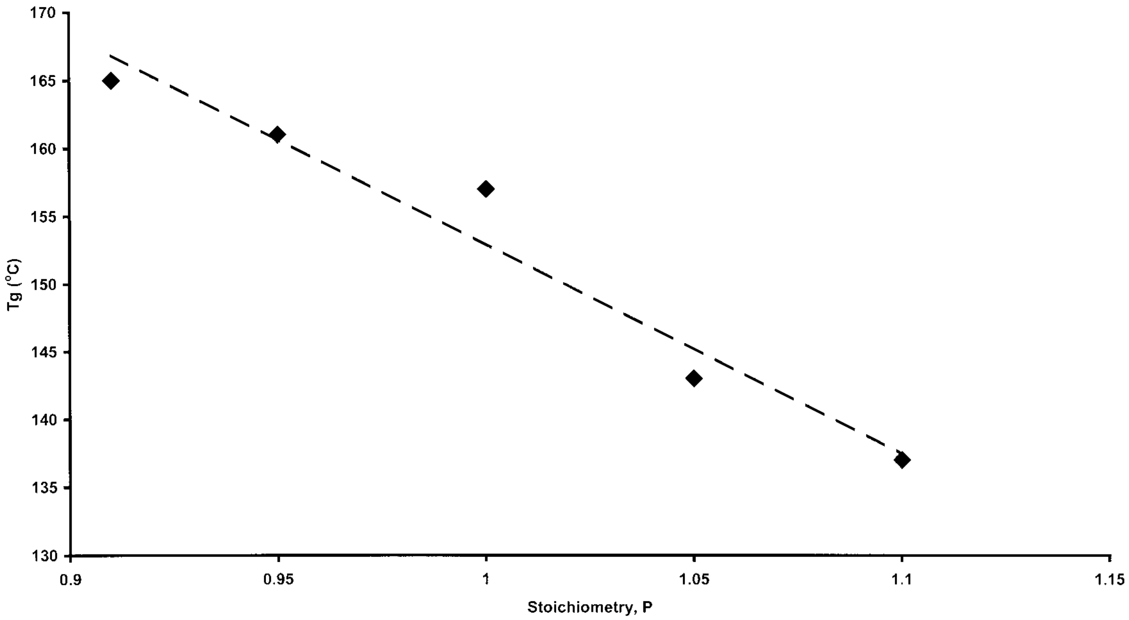

Figure 5 Effect of stoichiometry on the glass transition temperature, T_g.

results, showing that the amount of the isocyanurate structure increases with lower stoichiometry of the reactants. The increase in isocyanurate content in the sample was reflected in a higher crosslink density.

TMA

The plots of the stoichiometry, P, against the CTE data are shown in Figure 8. The expansion of polymers with temperature in the glassy states could be accounted for by the normal expansion processes caused by the increase in the vibrational amplitudes of their constituents. However, above T_g, in addition to the normal expansion processes, there is also the expansion of the free volume itself, which results in larger expansion of the rubber than the glass.[20] The expansion in the rubber, α_r, was more than two orders of magni-

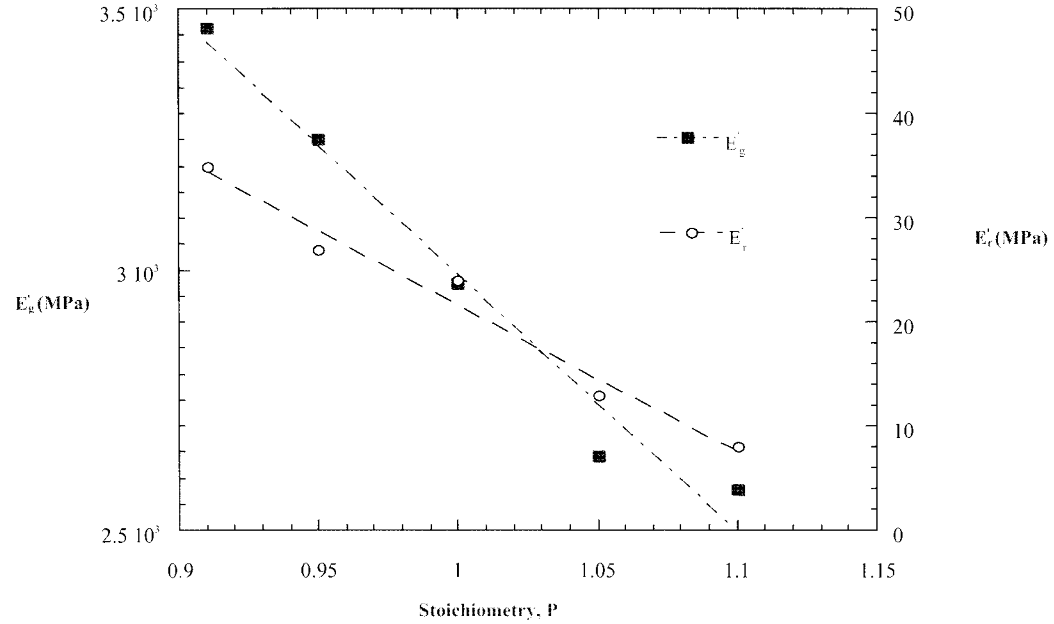

Figure 6 Effect of stoichiometry on E_g' and E_r'.

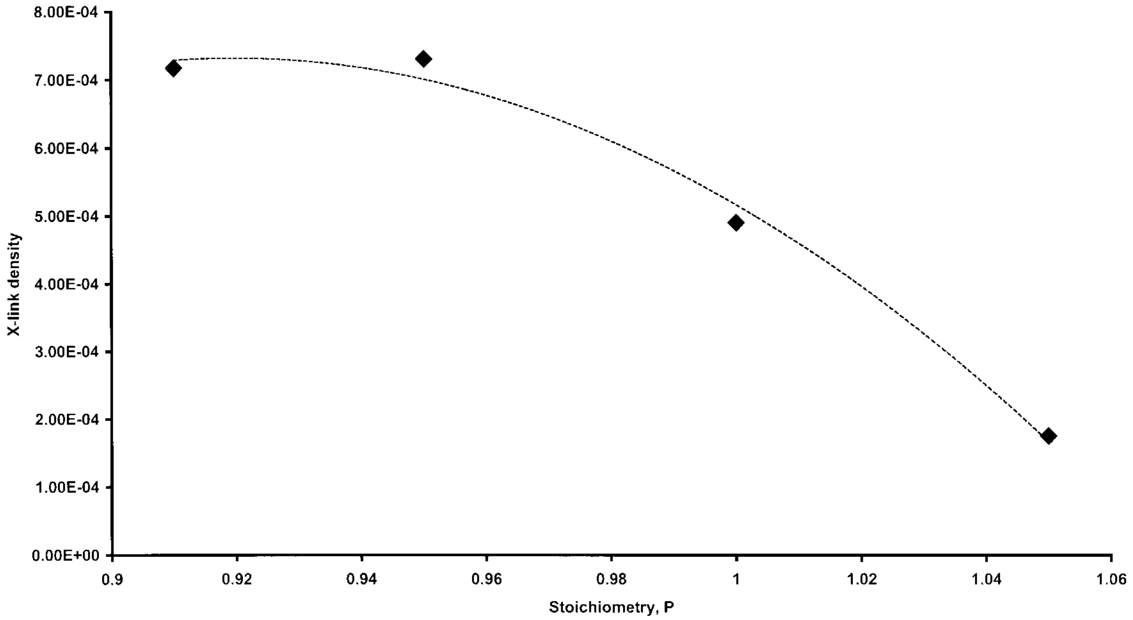

Figure 7 Effect of stoichiometry on the crosslink density.

tude greater than the glassy expansion, α_g. In this study, both coefficients of the thermal expansion (i.e., α_g and α_r) increased with the stoichiometry of the reactants. As the crosslinking density increased with decreased stoichiometry, there was a corresponding lowering of the CTE values in the sample.

Flexural Properties

The effects of the stoichiometry on the flexural properties are shown in Figure 9. Plots of the flexural moduli and toughness against the stoichiometry of the samples showed that while the flexural toughness increased with the stoichiom-

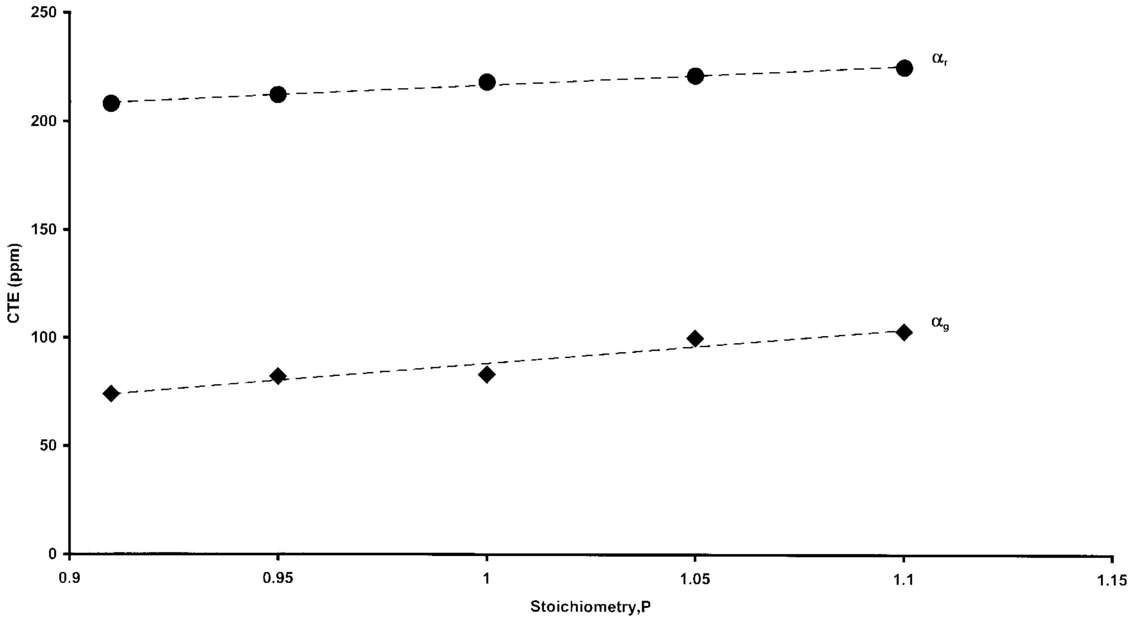

Figure 8 Effect of stoichiometry on CTE.

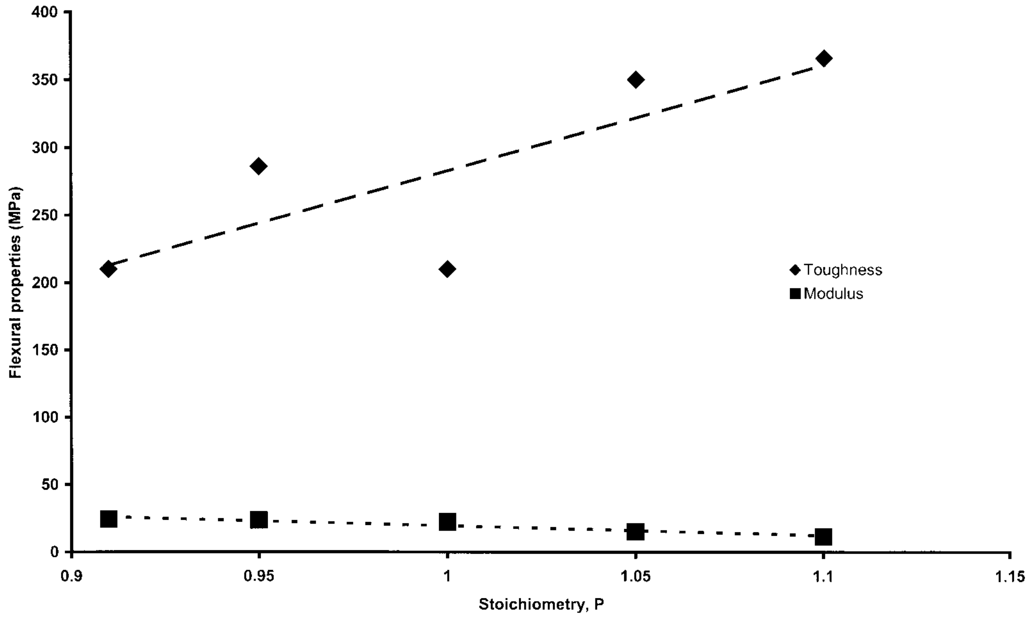

Figure 9 Effect of stoichiometry on flexural properties.

etry of the sample, the flexural modulus showed a corresponding decreased. The increased toughness reflected the increased [Oxa] (i.e., lower crosslinking density). The noted decrease in the modulus with increased stoichiometry was the result of an increase in the crosslink density of the sample. These observed behaviors were consistent with the effect of increased crosslinks shown by the increased isocyanurate structure present.

CONCLUSION

The effect of DGEBA-pMDI stoichiometry was found to have profound influence on the final structure of the isocyanurate–oxazolidone polymers. This study showed the important role DGEBA and pMDI stoichiometry had in determining the relative amounts of oxazolidone and isocyanurate formed in the fully cured samples. Where there were excess DGEBA reactant (i.e., $P > 1$), structural transformation reaction of the isocyanurate-to-oxazolidone structure was observed. The result of this transformation was an increase in the amount of the oxazolidone in the final structure. Increasing the amount of the oxazolidone structure resulted in lower crosslink density and moduli in the sample. However, other aspects of the material properties such as the macrodensity, coefficients of thermal expansion, and flexural toughness were enhanced. In conclusion, the reactant stoichiometry is a useful parameter for controlling the final structure of poly(isocyanurate–oxazolidone) polymers to achieve optimum materials properties. However, further work to elucidate the isocyanurate-to-oxazolidone transformation reaction are required to understand the curing mechanism of this polymer system.

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