Cure kinetics of elementary reactions of a DGEBA/DDS epoxy resin: 1. Glass transition temperature *versus* conversion

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(Received 18 January 1993; revised 26 April 1993)

The influence of elementary reactions (linear polymerization and crosslinking) on the development of the glass transition temperature (T_g) of diglycidyl ether of bisphenol A/diaminodiphenylsulfone (DGEBA/DDS) epoxy resin system has been analysed quantitatively according to a proposed model. The model was derived on the basis of the reaction mechanisms observed in the curing system and the assumption that the T_g has individual linear relationships with the degree of conversion of the two reactions. The conversions of elementary reactions during the cure were obtained experimentally by measuring the changes in the concentrations of epoxy, primary and secondary amine groups with time by near-infra-red spectroscopy. The T_g values were measured by differential scanning calorimetry (d.s.c.). In addition, and for the purpose of comparison, the overall conversion of the system was also obtained from d.s.c. in a dynamic scanning mode. The conversion–time data from the two different techniques were consistent. The proposed model successfully predicted the separate increases in T_g due to the linear polymerization and due to the crosslinking reactions. The Di Benedetto equation and the viscoelastic model of Gan *et al.* are also discussed.

(Keywords: epoxy resin; kinetics; elementary reactions)

INTRODUCTION

The glass transition is one of the more important phenomena exhibited by a polymer, determining its physical state and influencing the various properties such as rheological characteristics, mechanical stiffness and toughness[1]. The glass transition temperature, T_g, of a linear polymer as a function of its molecular weight is generally well understood[2,3]. To a first approximation, the T_g increases almost linearly with increasing molecular weight up to a critical range above which the T_g levels off.

On the other hand, the T_g of a thermoset polymer is not clearly understood in terms of specific molecular factors, in spite of a considerable research effort[4–13]. The most common approach is to relate the T_g of a crosslinked system to the overall conversion[9,11,12,14], although it is accepted that the variation in T_g is attributed to various molecular parameters such as the molecular weight, the stiffness of the crosslinked chains and the free volume entrapped in the network[14]. In this paper we show that the effects of the increasing molecular weight can be separated from those of the crosslinking and network formation. The increase of molecular weight is achieved by linear polymerization and branching reactions between epoxy and the crosslinking agent, while the increase of the stiffness of the network chain and changes in free volume are functions of both the branching and crosslinking reactions. Therefore, to separate the effects of the individual factors that influence T_g, we need to quantify the progress of the individual reactions (linear polymerization, and branching and crosslinking reactions) as well as monitor the change in T_g. The former task has not been approachable with the differential scanning calorimetry (d.s.c.) technique, which can only quantify the overall progress of the reaction by measuring the heat of reaction.

In a previous study of the reaction mechanisms we analysed the individual reactions by monitoring the conversion of individual functional groups (including epoxy, primary and secondary amine) using near-infra-red (n.i.r.) spectroscopy[15]. The main reactions observed during the curing process of the system were epoxy–amine reactions. Assuming that no side reactions occur in the stoichiometric diglycidyl ether of bisphenol A/diaminodiphenylsulfone (DGEBA/DDS) system, we can foresee that the primary amine–epoxy reaction would always result in a linear polymerization, and that the secondary amine–epoxy reaction would always result in branching or crosslinking. We also found that the primary amine–epoxy reaction had priority up to gelation over the secondary amine–epoxy reaction. At the gel point (approximately 65% epoxy group conversion from n.i.r. and dynamic mechanical thermal analysis (d.m.t.a.) measurements), most of the primary amine groups (95%) were consumed whereas only 28%

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0032-3861/93/234908–05

of the secondary amine groups were consumed. This observation implies that the increase of the molecular weight of the system by linear polymerization is the main factor for the increase of T_g up to gelation. Above gelation the effect of increasing molecular weight by branching and crosslinking on T_g can be assumed to be negligible. Instead, these reactions would increase the T_g by means of decreasing free volume and/or increasing the stiffness of the network chains. In this respect, the effect of molecular weight and the combined effects of free volume and chain stiffness can be expressed in terms of the extent of linear polymerization (primary amine–epoxy reaction) and crosslinking reaction (secondary amine–epoxy reaction, including branching reaction), respectively. This approach is used below to derive an equation for relating glass transition temperature to conversions resulting from linear polymerization and crosslinking reactions.

THEORETICAL MODEL

According to Horie *et al.*[8] the glass transition temperature of a crosslinked polymer can be expressed in a following form:

$$T_g = T_{g0} + (\Delta T_g)_M + (\Delta T_g)_v \tag{1}$$

where T_{g0} is the T_g of the unreacted monomer mixture, $(\Delta T_g)_M$ is the increase in T_g due to the increase of molecular weight, and $(\Delta T_g)_v$ is the increase in T_g due to the increase in crosslink density (accompanied by a decrease in free volume and an increase in the stiffness of the network chain). Earlier Fox and Loshaek[5] expressed equation (1) in a more specific form with terms of Kv instead of $(\Delta T_g)_v$, where K is a constant and v is the crosslink density. Based on the experimental observations in our previous[15] and present studies on the DGEBA/DDS epoxy system, we find that $(\Delta T_g)_M$ is dependent only on the conversion of the linear polymerization reaction (the conversion of the primary amine–epoxy reaction) and $(\Delta T_g)_v$ is dependent only on the conversion of the crosslinking reaction (the conversion of the secondary amine–epoxy reaction). Therefore, equation (1) can be written as follows, with modified terms:

$$T_g = T_{g0} + (\Delta T_g)_L + (\Delta T_g)_C \tag{2}$$

where $(\Delta T_g)_L$ and $(\Delta T_g)_C$ are the increases in T_g resulting from the conversion of the linear polymerization and the crosslinking reactions respectively. The number-average degree of polymerization, $\bar{X}_n$, increases with conversion of the linear polymerization reaction (α_L)[2,3]:

$$\bar{X}_n = (1+r)/[1 - r(2\alpha_L - 1)] \tag{3}$$

where r is the stoichiometric ratio of the reactant monomers. For $r = 1$, equation (3) becomes:

$$\bar{X}_n = 1/(1-\alpha_L) \tag{4}$$

Since $\bar{X}_n = \bar{M}_n/M_0$ where M_0 and $\bar{M}_n$ are the molecular weight of monomer and the number-average molecular weight of the growing polymer respectively, equation (4) can be written in terms of molecular weight:

$$\bar{M}_n = M_0/(1-\alpha_L) \tag{5}$$

According to the Fox and Flory[3] model, the glass transition temperature of a linear polymer, $(T_g)_L$, can be expressed as:

$$(T_g)_L = T_{g0} + (\Delta T_g)_L = (T_{g\infty})_L - K/\bar{M}_n \tag{6}$$

where $(T_{g\infty})_L$ is the limiting T_g of linear polymer of infinite molecular weight, and K is constant. The substitution of equation (5) into (6) results in:

$$(T_g)_L = (T_{g\infty})_L - K(1-\alpha_L)/M_0 \tag{7}$$

When $\alpha_L = 0$, $(T_g)_L = (T_{g\infty})_L - K/M_0$, $(T_g)_L = T_{g0}$ and therefore $K/M_0 = (T_{g\infty})_L - T_{g0}$. By rearranging equation (7), $(T_g)_L$ can be expressed as a linear function of the conversion of linear polymerization, α_L, as follows:

$$(T_g)_L = T_{g0} + (\Delta T_g)_L = T_{g0} + \alpha_L[(T_{g\infty})_L - T_{g0}] \tag{8}$$

We now propose that the $(\Delta T_g)_C$ in equation (2) also has a linear relationship with the degree of conversion of the crosslinking reaction. We write in analogy to equation (8):

$$(T_g)_C = T_{g0} + (\Delta T_g)_C = T_{g0} + \alpha_C[T_{g\infty} - (T_{g\infty})_L] \tag{9}$$

where α_C is the conversion of the crosslinking reaction, and $T_{g\infty}$ is the maximum glass transition temperature of the system when $\alpha_L = \alpha_C = 1$. Substitution of equations (8) and (9) into (2) results in the following relationship:

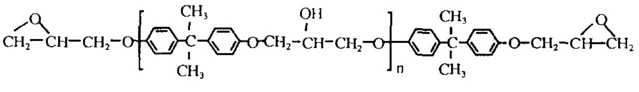
$$T_g = T_{g0} + \alpha_L[(T_{g\infty})_L - T_{g0}] + \alpha_C[T_{g\infty} - (T_{g\infty})_L] \tag{10}$$

T_{g0}, $T_{g\infty}$ and $(T_{g\infty})_L$ are usually known values or can be determined experimentally, and α_L and α_C can be measured for each sample.

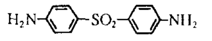
EXPERIMENTAL

Materials and sample preparation

The epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBA; Epikote 8283, Shell Chemicals, $M_n = 380$, liquid), and the amine curing agent was 4,4′-diaminodiphenylsulfone (DDS; Anchor Chemicals, $M_n = 248$, powder). The chemical structures of the materials used are as follows:



(DGEBA, n = 0.14)



(DDS)

The mixture of DGEBA and DDS in stoichiometric ratio (1:1), based on the functionality of the two monomers, was prepared in a rotary evaporator under vacuum starting from a temperature of 80°C and finishing at 120°C. In order to minimize chemical reaction between the monomers during the mixing process, the heating time was limited to less than 30 min. The flask was rotated at a constant speed during the process. When the temperature reached 120°C, the mixture became a clear transparent solution. At that point set volumes of the mixture were cast into aluminium foil cups to form discs of about 15 mm diameter and 2 mm thickness. The samples were placed in an air oven at two different temperatures, 130 and 205°C, for various intervals so that different degrees of cure were achieved. Samples prepared in this way were used for the d.s.c. and the n.i.r. studies.

Data collection

Samples of 15–20 mg, obtained from the cured epoxy discs, were used to measure the glass transition temperatures (T_g) and the overall conversion (α) on a DSC-7 differential scanning calorimeter. The operation was carried out in a dynamic scanning mode from −30 to 410°C, at a heating rate of 20°C min^{-1}. The area of the exotherm peak, which appears beyond the T_g endotherm peak in partially cured samples, was taken as the residual heat of reaction. The residual heat of reaction for uncured DGEBA/DDS mixtures was used as a total heat of reaction. The overall conversion (α) was calculated from the measured heat of the reaction according to the following equation[16]:

$$\alpha=(H_T-H_R)/H_T \qquad (11)$$

where H_T is the total heat of the reaction for uncured samples and H_R is the residual heat of the reaction for partially cured samples. More details about d.s.c. methods for monitoring epoxy cure reactions can be found in a recent publication by Barton[16].

The i.r. absorption spectra of the cured samples were recorded on an Alpha Centauri *FT*i.r. spectrophotometer (Mattson Instruments Inc., USA) in the region from 11 000 to 4000 cm^{-1} using 32 scans at a resolution of 8 cm^{-1}. The conversions of reacting groups were obtained by analysing the changes in their concentrations according to the quantitative analysis method described in our previous paper[15]. In particular, we were able to obtain conversions for epoxy, primary amine and secondary amine independently.

RESULTS AND DISCUSSION

The overall conversions, α, obtained from n.i.r. and d.s.c. measurements, are shown in *Figure 1* as a function of cure time. Although the values from n.i.r. are slightly higher than those from d.s.c. in the early stage of the cure, the overall contours of the graphs from the two different techniques are identical. The conversion increases rapidly up to gelation (approximately 166 min at 130°C and 13 min at 205°C cure from d.m.t.a. measurements) and then slows down significantly owing to the increase of the system viscosity with increasing conversion. *Figure 2* shows the T_g values of the tested samples. The development of T_g with cure time is similar to that observed in the conversion *versus* cure time curves shown in *Figure 1. Figure 3* shows the experimental results for conversion of primary amine (conversion of linear polymerization reaction, α_L) and secondary amine (conversion of crosslinking reaction, α_C) plotted as a function of α (overall epoxy group conversion). The linear polymerization dominates the process in the early stages of cure, while the crosslinking reaction does so in the later stages of cure. The crosslinking reaction is in fact not observed until at least $\alpha > 0.2$. Close to gelation ($\alpha = 0.65$) the linear polymerization is almost arrested ($\alpha_L = 0.95$) whereas the crosslinking reaction is still in its initial stages ($\alpha_C = 0.28$). In order to see the invididual influence of the linear and the crosslinking reactions on T_g, we plotted T_g as a function of both α_L and α_C in *Figure 4*. Notice that up to approximately $\alpha_L = 0.8$, which corresponds to $\alpha = 0.4$, where the linear polymerization reaction dominates, T_g increases only by 40°C. Above that, T_g increases dramatically with increasing α_C. The rapid increase of T_g at $\alpha_L = 1$ is because the T_g continues to increase with increasing α_C even after the termination of the linear polymerization reaction.

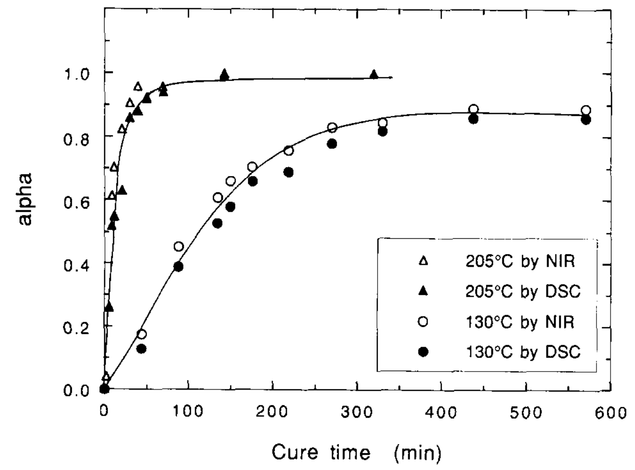


Figure 1 Plot of experimental conversions from n.i.r. and d.s.c. measurements *versus* cure time for DGEBA/DDS epoxy system, during the cure at 130 and 205°C

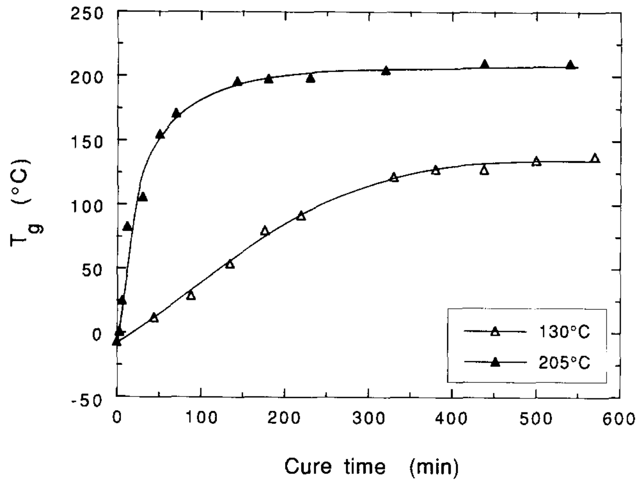


Figure 2 Plot of experimental glass transition temperature (T_g) against cure time for DGEBA/DDS epoxy system, during the cure at 130 and 205°C

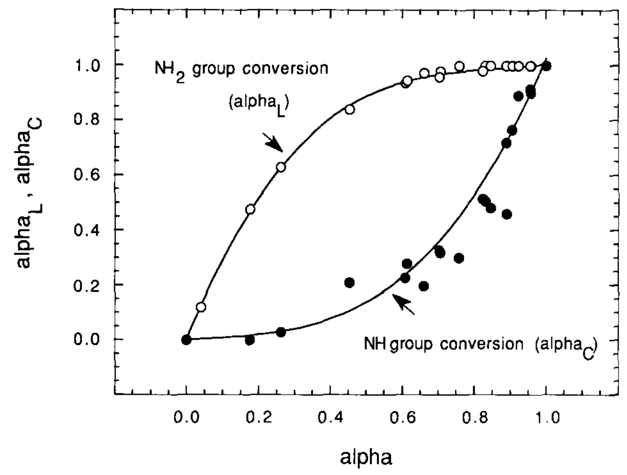


Figure 3 Experimental conversions of primary amine (linear polymerization) and secondary amine (crosslinking reaction) *versus* epoxy conversion

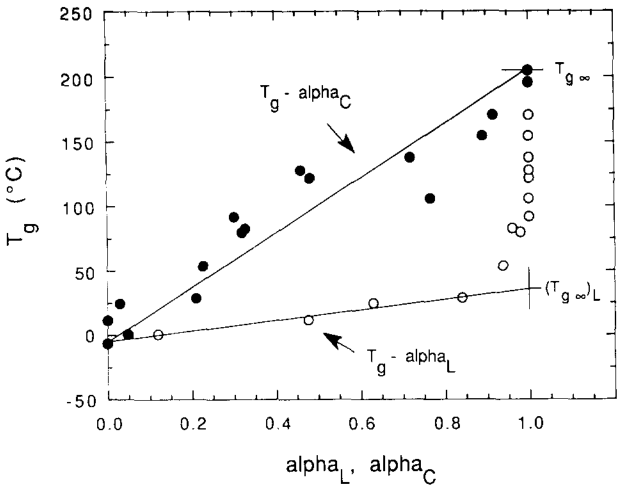


Figure 4 Plot of T_g against conversions of linear polymerization (primary amine conversion, α_L) and crosslinking reaction (secondary amine conversion, α_C)

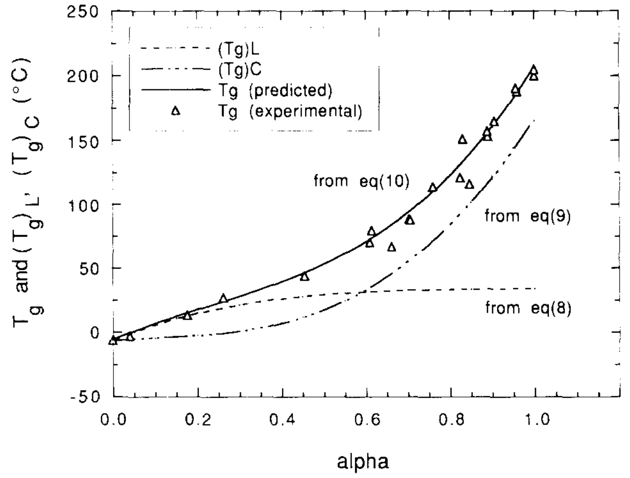


Figure 5 Plot of $(T_g)_L$, $(T_g)_C$ and T_g, predicted from the experimental values of α_L and α_C using equations (8), (9) and (10). Triangular points show experimentally obtained data

To analyse the results in terms of the proposed model (equation (10)), it is necessary to determine the glass transition temperature, $(T_{g\infty})_L$, for a linear DGEBA/DDS copolymer at $\alpha_L = 1$. It can be estimated by extrapolation of the data shown in *Figure 4*, and we find it equal to 34°C. Other constants in equation (10) are known: $T_{g0} = -6$°C and $T_{g\infty} = 205$°C from *Figure 2*. Using these data and the values for conversions from *Figure 3*, equation (10) could be evaluated. It is shown in *Figure 5*, together with experimental data for comparison. The agreement between theory and experiment is excellent considering that no adjustable parameters are used in equation (10). As mentioned above, the contributions to T_g due to linear polymerization and network formation (crosslinking reaction) could be separated, and these are also shown in *Figure 5*. The maximum T_g increase by linear polymerization, $(\Delta T_{g\infty})_L$, is only 40°C, whereas that by crosslinking reaction, $(\Delta T_{g\infty})_C$, is 171°C. This observation indicates that the degree of crosslinking reaction is a more critical factor for determining the T_g of crosslinked networks.

The success of this work is undoubtedly due to the fact that the DGEBA/DDS epoxy system behaves in a model fashion. First of all, the average functionality of this system places the gel point around 60% conversion, allowing for easily observable pre-gelation and post-gelation regions. Secondly, the inhibition of secondary amine reaction in the initial stages (resulting in linear polymerization), and no side reactions, further enhance the distinction between the two regions of behaviour. Thirdly, the near-infra-red technique is eminently suitable for measuring the essential parameters of this system, thus offering quantitative information on molecular mechanisms of reaction and kinetics of conversion. To the best of our knowledge there have been no previous reports in which the linear polymerization and network formation reactions were measured separately with a reasonable degree of accuracy.

Let us now consider two other theories relating glass transition temperature to molecular parameters in crosslinked systems. The Di Benedetto equation[11] is expressed in the following form[14]:

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{(E_x/E_m - F_x/F_m)\alpha}{1-(1-F_x/F_m)\alpha} \qquad (12)$$

where E_x and E_m are lattice energies of the uncrosslinked and crosslinked polymers, respectively, F_x and F_m are the segmental mobilities of the same polymers, and T_g and T_{g0} have the same meaning as above. The values of F_x/F_m and E_x/E_m for our epoxy system are calculated on the basis of the observation that α and T_g of gelation are cure-temperature-independent constants[12]. Their values are 0.370 and 0.662 respectively. For other systems the value of F_x/F_m has usually been calculated on the assumption that $E_x/E_m \simeq 1$[8,17]. The fit of the Di Benedetto equation to our experimental data is shown in *Figure 6*. Notice that the agreement is as good as that of our proposed equation (10). Equation (12) has been found to fit well many other experimental systems[9,12,18]. This is not surprising since Di Benedetto derived this equation on the basis of general thermodynamic considerations of a crosslinking system, including both the copolymerization and the network-forming effects. In fact, it is plausible that our specific equation (10) is a subset of the more general equation (12). If this is so, then the successful application of equation (10) to our system provides verification of the Di Benedetto approach. The only limitation of equation (12) is the difficulty

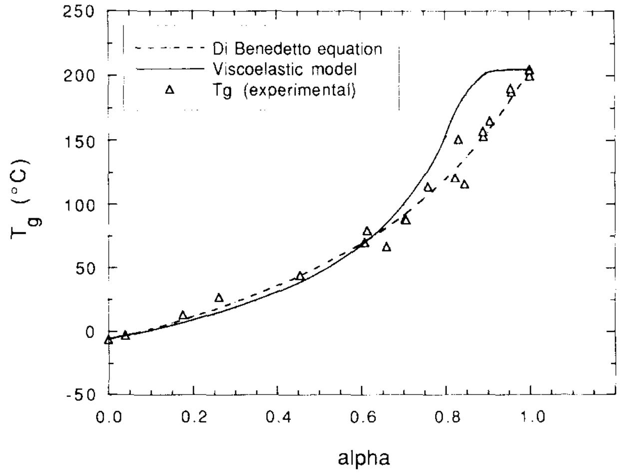


Figure 6 Comparison of T_g *versus* conversion data from the Di Benedetto equation and viscoelastic model with experimental data for DGEBA/DDS epoxy system

(perhaps impossibility) of calculating the lattice energies and segmental mobilities from fundamental molecular parameters, and therefore, for the time being, these parameters can only be adjusted as required to fit experimental data.

A different approach to the relationship between T_g and overall conversion of a network-forming system was published recently by Gan *et al.*[13]. Their final equation is as follows:

$$T_g = \frac{E_r}{R\ln[C_1(1-\alpha)^{\Phi}+C_2]} \tag{13}$$

where E_r is the activation energy for transition from the glassy to rubbery state, R is the universal gas constant, C_1 and C_2 are constants, α is the overall conversion and Φ is an exponent accounting for the effects of chain entanglement. The basis for equation (13) is a theoretical model that relates glass transition temperature to viscoelastic relaxation times (viscoelastic model), and an empirical relationship linking system conversion with viscosity (viscosity model). In the analysis of our experimental data by equation (13), $E_r = 13.4\,\mathrm{kcal\,mol^{-1}}$ is used, which is an average of the experimentally obtained activation energies[19], and the exponent Φ is determined by iteration of the fitting with experimental data. The best fit is obtained with $\Phi = 6$. This approach is believed to be reasonable when we consider the intrinsic characteristics of the two parameters, in that their effects are to act in opposite ways on T_g. The plot of equation (13) with these values is also presented in *Figure 6*. It can be seen that the equation describes well the experimental data up to gelation only ($\alpha < 0.65$). Above gelation, the viscoelastic model overestimates the T_g. This poor description above gelation may be attributed to the fact that equation (13) was derived on the basis of the viscosity model, which is only valid up to gelation[20].

Notwithstanding the poor fit, the principle underlying equation (13) is essentially correct, that is, the glass transition temperature is determined by the relaxation times of the molecules, and the relaxation times are determined by the microstructural features of the molecules and their environment. The latter effects include molecular weight, free volume and chain stiffening due to network formation. The good fit obtained from our proposed equation (10) implies that α_L is a good measure of the relaxation times as affected by molecular weight increases, and α_C is a good measure of the changes in the relaxation times caused by crosslinking and free volume. The hypothesis that α_C is linearly related to $(\Delta T_g)_C$ is worthy of further investigation. It can be carried out on another crosslinking system with similar reaction mechanisms to the DGEBA/DDS epoxy system. Alternatively, we can start with a linear polymer for which $T_g = (\Delta T_g)_L$, and introduce crosslinks by radiation (u.v., electron, gamma) or other means. The latter approach would specifically test the validity of the relationship expressed in equation (9).

CONCLUSIONS

The development of glass transition temperature in a stoichiometric DGEBA/DDS epoxy system has been quantitatively analysed as a function of the extent of the linear polymerization reaction (molecular weight) and the crosslinking reaction (crosslink density) according to a proposed model. It was derived on the basis of observed reaction mechanisms and the assumption that the T_g has linear relationships with the conversions of both reactions. The predicted T_g values were in good agreement with the experimental data, verifying the assumption made to derive the model. The proposed model is believed to be applicable to any thermoset system that obeys the conditions: (i) the primary amine always produces a linear polymerization and the secondary amine always produces a crosslinking reaction; (ii) no side reactions occur. In addition the Di Benedetto equation and the viscoelastic model were also evaluated. However, considering the fact that our model can predict T_g as a function of mechanistic reaction parameters and does not contain any adjustable parameters, it can be used more practically for T_g estimation of a crosslinked thermoset polymer.

ACKNOWLEDGEMENT

One of the authors, B.-G. Min, would like to thank CSIRO for financial support during the work.

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