

A VISCOELASTIC DESCRIPTION OF THE GLASS TRANSITION-CONVERSION RELATIONSHIP FOR REACTIVE POLYMERS

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The glass transition temperature, T_g is a sensitive and practical parameter for following cure of reactive thermosetting systems. A new equation was developed for predicting the T_g -conversion relationship based on the Dillman-Seferis viscoelastic compliance model. It assumes that the changes in T_g are primarily due to changes in relaxation time as chain extension and crosslinking reduce the mobility of a polymer network. Such information is essential in combining kinetic and viscoelastic measurements, which monitor transformations of thermosets during cure. The equation derived from the viscoelastic model was shown to be applicable for a variety of experimental data. The success of the methodology was further demonstrated by comparing well-established relations, such as the Fox equation and the Di-Benedetto equation, to predictions made possible by adjusting two viscoelastic model parameters. Finally, the fitting power of the proposed equation was shown by fitting published epoxy data from the literature as well as experimental data on a relatively new resin system such as dicyanates used as a model in this study.

The glass transition temperature, T_g , is a sensitive and practical parameter for following the cure of reactive thermosetting systems. First, T_g sets an upper bound for use temperature of a polymer. Second, a wide range of values of T_g is encountered during cure and many important events can be characterized in terms of T_g [1, 2]. The molecular state of the unreacted material is also characterized by T_g as T_{g0} , as well that of the fully reacted material by $T_{g\infty}$ as T_g . A quantitative relationship between T_g and extent of

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conversion can provide a critical link in the description of the cure process [3].

It is well established that chain extension and crosslinking increase the T_g of a polymer. However, for most systems, the T_g is also strongly dependent on the chemical composition and phase morphologies complicating the expected behavior. Currently, there are several equations describing T_g in terms of crosslink density or extent of conversion. The Fox and Loshack equation predicts linearity of T_g as a function of crosslink density [4]. The DiMarzio equation predicts linearity of $1/T_g$ with crosslink density [5]. Also, the widely utilized DiBenedetto equation which accounts for the effects of both copolymer and crosslink density provides a generalized expression for T_g [6]. These equations, derived primarily on a thermodynamic basis, are applicable for homogeneous systems and often fail to fit experimental data at high conversion. One example is the sharp increase in T_g at higher degrees of conversion for very high crosslink density systems [7].

In this work, a methodology, based on viscoelastic modelling of the cure process, has been developed that is capable of quantitatively describing both isothermal and non-isothermal dynamic mechanical behavior of a reactive epoxy system in the vicinity of its primary viscoelastic transition [8, 9]. The present work shows that it is possible to develop a quantitative T_g - Conversion relationship based on viscoelastic modelling of reactive systems. Thus, it is possible to relate changes in glass transition to changes in relaxation time of the system as chain extension and crosslinking reduce the mobility of the polymer network. The success of the new viscoelastic approach was demonstrated by comparison with experimental results generated specifically for this study as well as with previously published experimental data. Furthermore, by direct comparison of these expressions to well accepted equations used for T_g -conversion, the generality of the viscoelastic approach was established.

Background

It is well known that conversion or crosslinking increases the glass transition temperature of a polymer. Thus, an increase in T_g may be viewed as two nearly independent effects: (1) the degree of crosslinking and (2) the copolymer effect. A number of studies has been published relating the degree of crosslinking to the shift in T_g of a polymer [4-6]. However, there is lack of agreement between investigators. For example, the Fox-Loshaek expression provided the linear relationship [4], viz.

$$T_g = T_{g\infty} - K/M \quad (1)$$

where K is the constant and M is the molecular weight which is proportional to $1/(1-\alpha)$ (α is the conversion). The widely utilized DiBenedetto equation is

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{[E_x/E_m - F_x/F_m]X_c}{1 - (1 - F_x/F_m)X_c} \quad (2)$$

where E_x/E_m is the ratio of the lattice energies for crosslinked and uncrosslinked polymers. F_x/F_m is the ratio of the segmental mobilities for the same two polymers. X_c is the mole fraction of monomer units which was crosslinked in the polymer. With the DiBenedetto equation, the problem determining the thermodynamic parameters remained.

A viscoelastic modelling methodology suitable for describing the physical properties of reacting polymer systems has been developed [8]. Based on a constitutive approach combining relaxation and kinetic phenomena, it has been successfully utilized in describing dynamic mechanical, dielectrical and viscous behavior of curing thermosetting polymers [10, 11, 12]. In general, the dynamic mechanical behavior of a polymer is a function of the quantity $\omega\tau$, where ω is the measure angular frequency and τ is the relaxation time of the system [12, 13]. The effect of temperature is implicitly accounted for in the relaxation time which may also be expected to be strongly influenced by the reaction kinetics especially for thermosetting systems [8, 9].

In Dynamic Mechanical measurements (DMA), T_g is defined as the maximum value of loss modulus, loss compliance or $\tan\delta$ [16]. It has been shown that these parameters are functions of the quantity $\omega\tau$. The description of the DMA data of both reacting and nonreacting systems has been previously established based upon the compliance model [8, 9]:

$$J^* = J' - iJ'' = J_u + \frac{(J_r - J_u)}{[1 + (i\omega\tau)^\beta]^\alpha} \quad (3)$$

where:

J_u = unrelaxed compliance

J_r = relaxed compliance

ω = experimental angular frequency

τ = mean retardation time

β = a parameter ranging from 0 to 1 which accounts for a symmetric retardation time distribution

α = a parameter ranging from 0 to 1 which accounts for an asymmetric retardation time distribution.

Several commonly used viscoelastic models may be obtained from Eq. (3) by a suitable choice of parameters. If both α and β are set equal to one, the model reduces to an ideal single relaxation/retardation time model that has been extensively used in describing quantitatively the behavior of solid non-reacting systems [12, 13]. In this simplified case, the real and imaginary terms of Eq. (3) can be easily separated giving the following expressions:

$$J' = J_u + \frac{(J_r - J_u)}{1 + (\omega \tau)^2} \quad (4)$$

$$J'' = \frac{(J_r - J_u) \omega \tau}{1 + (\omega \tau)^2} \quad (5)$$

$$\tan \delta = \frac{(J_r - J_u) \omega \tau}{J_r + J_u (\omega \tau)^2} \quad (6)$$

They may be re-expressed in terms of moduli as

$$G' = \frac{G_r G_u (G_u + G_r \omega^2 \tau^2)}{G_u^2 + G_r^2 \omega^2 \tau^2} \quad (7)$$

$$G'' = \frac{G_r G_u (G_u - G_r) \omega \tau}{G_u^2 + G_r^2 \omega^2 \tau^2} \quad (8)$$

$$\tan \delta = \frac{(G_u - G_r) \omega \tau}{G_u + G_r \omega^2 \tau^2} \quad (9)$$

If β assumes values from 0 to 1 (as may be the case for the real polymers exhibiting symmetric distribution), Eq. (3) becomes

$$J^* = J_u + \frac{J_r - J_u}{1 + (i \omega \tau)^\beta} \quad (10)$$

which in terms of the moduli may also be expressed

$$G^* = G_u - \frac{(G_u - G_r)}{1 + (i\omega\tau^*)^\beta} \quad (11)$$

where

$$G_u = 1/J_u, \quad G_r = 1/J_r \quad \text{and} \quad \tau^* = \tau (G_r/G_u)^{1/\beta}$$

The above expressions may be separated into real and imaginary components in terms of both compliance and modulus, viz.

$$J' = J_u + \frac{(J_r - J_u)(1 + (\omega\tau)^\beta \cos\beta\pi/2)}{1 + 2(\omega\tau)^\beta \cos\beta\pi/2 + (\omega\tau)^{2\beta}} \quad (12)$$

$$J'' = \frac{(J_r - J_u)(\omega\tau)^\beta \sin\beta\pi/2}{1 + 2(\omega\tau)^\beta \cos\beta\pi/2 + (\omega\tau)^{2\beta}} \quad (13)$$

$$G' = G_u - \frac{(G_u - G_r)(1 + (\omega\tau^*)^\beta \cos\beta\pi/2)}{1 + 2(\omega\tau^*)^\beta \cos\beta\pi/2 + (\omega\tau^*)^{2\beta}} \quad (14)$$

$$G'' = \frac{(G_u - G_r)(\omega\tau^*)^\beta \sin\beta\pi/2}{1 + 2(\omega\tau^*)^\beta \cos\beta\pi/2 + (\omega\tau^*)^{2\beta}} \quad (15)$$

$$\begin{aligned} \tan\delta &= \frac{(G_u - G_r)(\omega\tau^*)^\beta \sin\beta\pi/2}{G_r + (G_u - G_r)(\omega\tau^*)^\beta \cos\beta\pi/2 + G_u(\omega\tau^*)^{2\beta}} \\ &= \frac{(J_r - J_u)(\omega\tau)^\beta \sin\beta\pi/2}{J_r + (J_r - J_u)(\omega\tau)^\beta \cos\beta\pi/2 + J_u(\omega\tau)^{2\beta}} \end{aligned} \quad (16)$$

The above expressions contain three parameters which may be dependent on the extent of conversion in the system: J_r ($1/G_r$), J_u ($1/G_u$) and τ . The relaxed compliance, J_r , represents the compliance of the material at low frequency or high temperature when the sample is relatively flexible (i. e., in the rubbery state). The unrelaxed compliance, J_u , represents the compliance at higher frequency or low temperature when the sample is relatively stiff (e.g., in the glassy state). These compliances do not appear to change significantly after gelation; therefore, J_u and J_r are assumed constant with conversion. Consequently, their inverses G_u and G_r may also be assumed

constant. Chain extension and crosslinking during cure may be expected to cause a decrease of τ [14]. In general, the effect of cure on the retardation time should be large enough to render changes in the other parameters insignificant. With these assumptions, the viscoelastic properties may be viewed as a function of retardation time τ only. This implies, mathematically, that the first derivative must be zero at a maximum. The values of $\omega \tau$ giving the maximum of loss compliance, loss modulus and $\tan \delta$ are listed in the following Table 1.

Table 1 T_g related to DMA data and viscoelastic models

T_g defined as maximum of	$\alpha = \beta = 1$	$\alpha = 1$ $0 < \beta < 1$
J''	$\omega \tau = 1$	$\omega \tau = 1$
G''	$\omega \tau = G_u / G_r$	$\omega \tau = (G_u / G_r)^{1/\beta}$
$\tan \delta$	$\omega \tau = (G_u / G_r)^{1/2}$	$\omega \tau = (G_u / G_r)^{1/2\beta}$

The table shows that T_g value will be complicated by the G_u , G_r and β unless it is defined in terms of loss compliance. Thus, the following definition of the glass transition may be obtained based upon the loss compliance.

In order to introduce T_g into these relationships, a temperature dependence of the relaxation time, τ , needs to be provided. Using the Andrade approach, relaxation is taken to be a thermally activated process [13], viz.

$$\tau(T) = \tau_x \cdot \exp(E_r / RT) \quad (17)$$

where E_r is the activation energy of transition from the glassy to rubbery state and R is the gas constant. τ_x is retardation time of the sample at the conversion X , E_r , to a first approximation, is assumed to be independent with the conversion. Thus the T_g defined as the maximum in J'' gives

$$T_g = -E_r / R \ln(\omega \tau_x) \quad (18)$$

In order to predict T_g as a function of the extent of conversion, the appropriate kinetic model must be incorporated into the viscoelastic model. Thus, the retardation time τ must also be described kinetically. The approach which we have adapted is based upon previous work in the development of a viscosity model for curing thermosets prior to the gel point [8, 9]. In this approach, the natural logarithm of viscosity was given as

$$\ln(\mu) = \ln(\mu_0) + \Phi(1 - X) \quad (19)$$

where

μ_0 : viscosity of unreacted polymer

μ : viscosity of the polymer at the conversion X

Φ : parameter accounting for the effects of chain entanglement

Assuming proportionality between viscosity and retardation time ($\tau = \mu/J_r - J_u$) and heterogeneous system of cured and uncured regions, the following expression is obtained [15, 17]:

$$\frac{1/\tau_x - 1/\tau_\infty}{1/\tau_0 - 1/\tau_\infty} = (1 - x)^\Phi \quad (20)$$

where:

τ_∞ = retardation time for fully cured resin

τ_0 = retardation time for uncured resin

When Eq. (18) is combined with an appropriate definition of T_g in terms of loss compliance, an expression for the relationship between glass transition and conversion is obtained, viz.

$$\frac{\exp(E_r/RT_g) - \exp(E_r/RT_{g\infty})}{\exp(E_r/RT_{g0}) - \exp(E_r/RT_{g\infty})} = (1 - x)^\Phi \quad (21)$$

Upon separation of terms, and explicit expression is obtained, viz.

$$\frac{1}{T_g} = \frac{\ln[C_1(1 - x) + C_2]}{E_r} \quad (22)$$

or

$$T_g = \frac{E_r}{R \ln[C_1(1 - X)^\Phi + C_2]} \quad (23)$$

where:

$C_1 = \exp(E_r/RT_{g0}) - \exp(E_r/RT_{g\infty})$

$C_2 = \exp(E_r/RT_{g\infty})$

In general, utilization of Eq. (14) requires knowledge of four parameters: T_{g0} , $T_{g\infty}$, E_r , and Φ . In practice, T_{g0} can be determined from dynamic ex-

periments on the uncured sample, and $T_{g\infty}$ can only be estimated from a fully cured sample. The transition activation energy, E_r , may be measured from multiple frequency dynamic measurements [12, 13]:

$$E_r = - \frac{d(\ln \omega)}{d(1/T_{\max})} \quad (24)$$

The E_r may also be obtained from time-temperature superposition of the shift factor (e.g., frequency-temperature).

Finally, only one parameter, Φ remains undetermined. Unfortunately, Φ cannot be determined analytically and typically ranges from 0 to 20, depending mainly on the molecular weight or functionality.

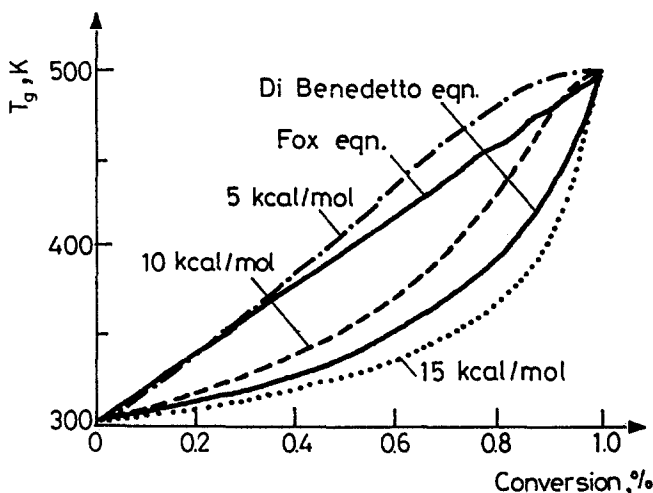


Fig. 1 T_g -conversion relations. Comparison of the Fox equation, DiBenedetto equation ($E_x/E_m = 0.4$ and $F_x/F_m = 0.24$) and the viscoelastic equation (Activation energy from 5 to 15 kcal/mol)

The transformation of polymers from glassy to rubbery solids, T_g , is easily detected as a distinct change in the viscoelastic properties when plotted as a function of temperature. Its activation energy is an indication of the activated transition process. Polymers with higher crosslink density and more rigid segments will have higher activation energies. For comparison, a T_g vs. conversion was predicted in Fig. 1 from the Fox-Loshaek equation, the Di-Benedetto equation (assuming values $E_x/E_m = 0.4$ and $F_x/F_m = 0.24$) and also the viscoelastic equation with different E_r (from 5 to 15 kcal/mol). For fitting experimental data for thermosets, the Fox-Loshaek equation would

fail at high conversion since T_g is predicted to increase rapidly with a small change of conversion. The DiBenedetto equation gives more realistic results. However, the flexibility of the viscoelastic equation was apparent. For low E_r values, it reduces to the Fox-Loshack equation. For high E_r values (e.g., 12 kcal/mol), it approximates the DiBenedetto equation. In summary, the viscoelastic equation has the potential of describing the behavior of a variety of polymers, such as linear, branched, and crosslinked by assuming different activation energies associated with each case.

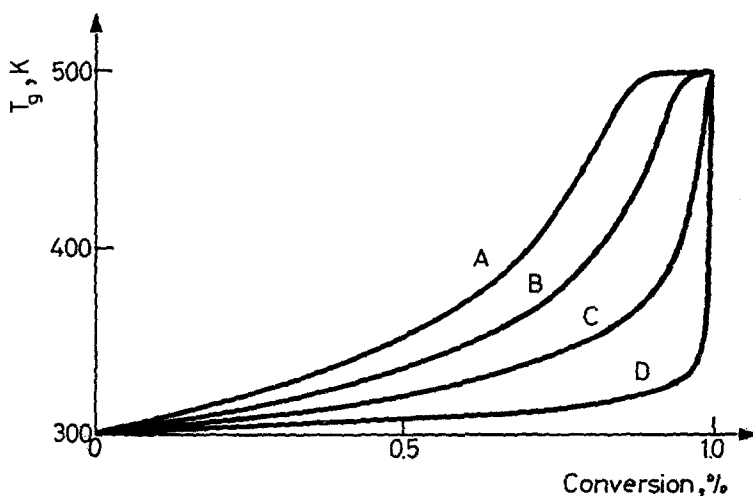


Fig. 2 T_g as a function of conversion described by the viscoelastic equation using different entanglement factors. Calculation was made assuming activation energy $E_r = 10$ kcal/mol for $\Phi = 7$ (see A); 5 (see B); 3 (see C); 1 (see D)

It was mentioned previously that there is no simple expression for Φ . In general, polymers with high molecular weight, high degree of branching and multifunctionality have higher Φ values. For instance, Φ has been reported to be 3.5 for some epoxy systems [8] while recently a value of 17 has been calculated for high performance rigid epoxy based systems [16].

The effect of Φ on the T_g -conversion relationship is shown in Fig.2. The higher values of Φ give a higher T_g at the same conversion. An important feature of the viscoelastic model is that it also predicts that thermosets may reach their maximum T_g before 100% conversion. No previous equation has been able to predict this very latest stage in the T_g -conversion relation. A 100% conversion is very difficult to achieve and, therefore, $T_{g\infty}$ is very difficult to measure. This may be attributed to the thermo-degradation which competes with cure at long cure times and high cure temperatures. At the

latest stage, spatially separated (isolated) unreacted groups cannot meet and react with each other easily due to the high connectivity of the network. A computer simulation has shown that the probabilities of monocycle formation or defects are higher at the very latest stage of cure [18]. It predicts that the increase rate of T_g would subside at the very latest stage of cure. The complete description of the relation should include this information. It is difficult to measure it and the appropriate equation which predicts the behavior at the very latest stage must be used. Presently, no equation is available. However, here the proposed viscoelastic model in its current form is capable of predicting this behavior. However, the earlier and later parts of the uncure resin can now be adequately described as may be seen in the experimental data.

Experimental

a) Model thermosetting resin

The resin used in this study was a high performance dicyanate resin. The chemical structure and cure mechanism for this system had been discussed [20]. Dicyanate resin was obtained commercially as ESR 327 from Hi-Tek Polymers, Inc. and was used as-received.

b) Dynamic Mechanical Analysis (DMA)

The Du Pont 982 DMA was used in the horizontal mode with a peak to peak amplitude of 0.2 mm and an arm separation of 6.5 mm [19]. Specimens were prepared by using thin metal mesh impregnated with the resin solution [19]. The solid content of the solution (methylene chloride) was approximately 50%. A nitrogen flow of 0.5 l/min was maintained to control the atmosphere. The samples were heated isothermally for a pre-established time. The cured samples were then scanned at 5 deg/min at room temperature to measure their glass transition.

c) DSC measurement

Dicyanate exhibits an exotherm during cure. It is assumed that the reaction rate dX/dt is directly proportional to the rate of heat generation dH/dt . The dH/dt is normally the ordinate of a DSC trace. The heat of reaction was determined using a DuPont 910 DSC instrument. The sample was cured in the DMA oven at a fixed temperature for a certain amount of time, quenched, and scanned in the DSC to obtain the residual heat of reaction

from which conversion was calculated. The degree of conversion may be calculated as [21]

$$1 - x = \frac{\Delta H_t}{\Delta H_{RXN}} \quad (25)$$

where X is the degree of conversion, ΔH_t is the residual heat per mole at isothermal time t and ΔH_{RXN} is the exothermic heat per mole of all reacting groups.

Results and discussion

Figure 3 shows the variation of T_g determined at the maximum of loss compliance J'' with log time at 150°, 175°, and 225°. T_g increased with cure time for all temperatures to a limiting value which depends on cure temperature.

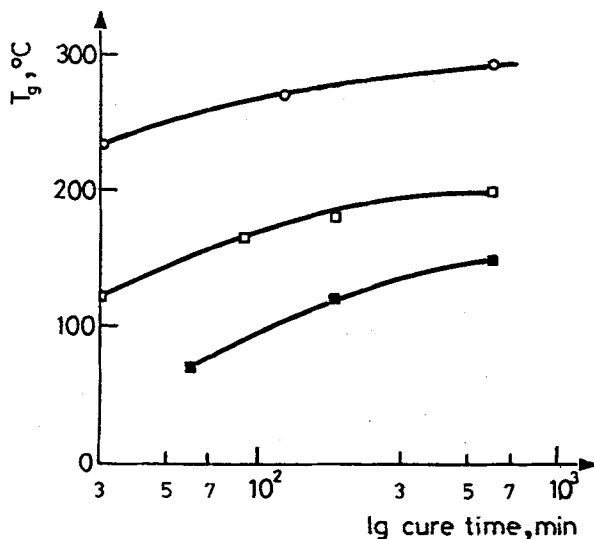


Fig. 3 T_g as a function of cure time at different cure temperatures indicated as $T_{cure} = 150^\circ\text{C}$ (■); $T_{cure} = 175^\circ\text{C}$ (□); $T_{cure} = 225^\circ\text{C}$ (o) for Dicyanate resin (ESR 327) without catalyst

The T_g against conversion values collapsed to a single curve, which means that the glass transition temperature is a function of extent of conversion only and not of cure temperature or time. This curve is plotted in Fig. 4.

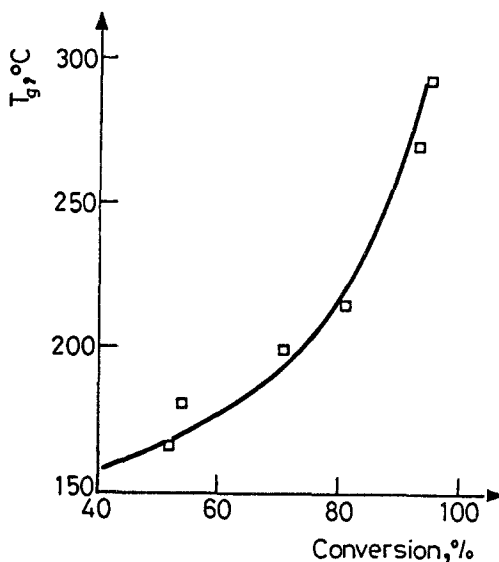


Fig. 4 T_g as a function of conversion as measured by DSC for dicyanate resin (ESR 327) without catalyst

At a higher degree of cure, small changes in conversion result in a sharp increase in T_g .

In order to obtain the information at the very latest stage of conversion, the sample was cured isothermally at 300° for 10 hours. Figure 5 shows the storage modulus of the DMA spectra taken at intervals of 0, 1, 4 and 10 hours. The glass transition as viewed from the onset of the drop in storage modulus, increases only slightly after 10 hours at 300°. The rubbery modulus (above T_g) increases with the cure time. It appears that the crosslink density increases with longer cure. Figure 6 shows the loss modulus of the same sample taken at intervals of 0, 1, 4 and 10 hours. The T_g , viewed as the maximum of E'' , slightly decreases with longer cure. The loss peak became broader. The results suggested that the sharp increase of T_g may subside at the very latest stage of conversion.

The experimental data from cure of the dicyanate resin was fitted to the Fox, DiBenedetto, and viscoelastic equations as shown in Fig. 7. The DiBenedetto and viscoelastic equations predict rapid increase of T_g between 65% to 95% conversion. In addition, the viscoelastic equation describing the behavior above 95% appears to become flat.

To provide a measurement of the generality of proposed relation, T_g -conversion relationship for epoxy novolac with cresol-novolac hardener that had

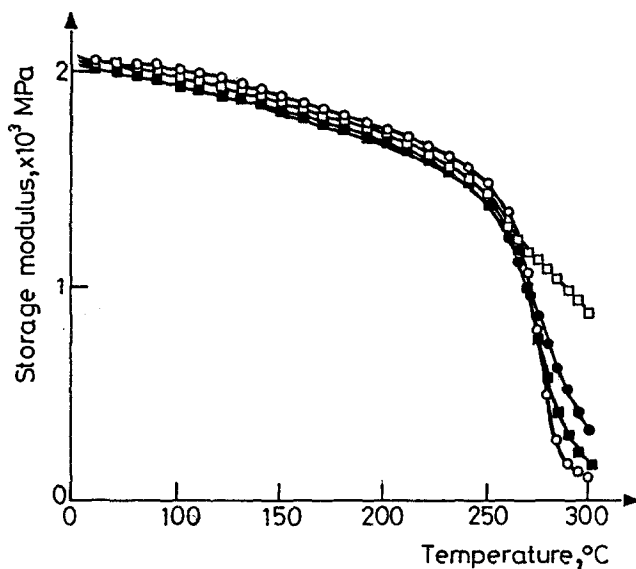


Fig. 5 The storage modulus of dynamic DMA spectra for dicyanate resin (ESR 327). The sample were cured according to the following times: 0.1 hour \circ 1 hour \blacksquare ; 4 hours \bullet ; 10 hours \square

been reported was used [7]. As shown in Fig. 8, three curves with epoxy functionality from 2.7 to 5.4 behaved similarly up to about 70% conversion. At high cure degrees of cure, small changes in conversion induced sharp increase in T_g . This increase is more pronounced for the higher functionality resins. This behavior cannot be explained by any of the equations currently available [7]. In the case of 5.8 epoxy functionality, the highest, T_g may be above 400° if the DiBenedetto equation is used to fit the data. Figure 8 showed that the data were fitted by the viscoelastic model with appropriately chosen E_r and Φ parameters. The higher epoxy functionality required higher E_r and Φ as expected. Thus, the viscoelastic expression described appropriately the general behavior of the relationship and predicted that it should reach maximum T_g before 100% for the highest epoxy functionality.

Conclusions

A new equation was developed to describe the T_g -conversion relationship based upon the loss compliance in dynamic mechanical experiments. It

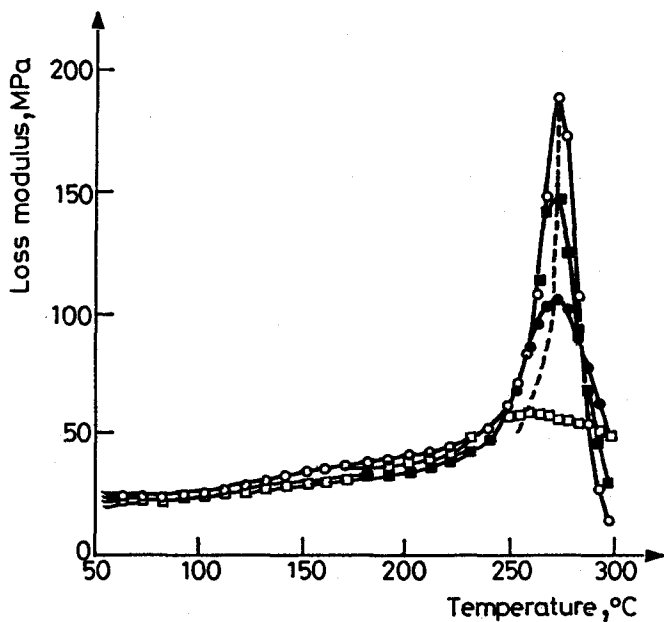


Fig. 6 The loss modulus of dynamic DMA spectra for dicyanate resin (ESR 327). The sample were cured according to the following times: 0.1 hour \circ 1 hour \blacksquare ; 4 hours \bullet ; 10 hours \square

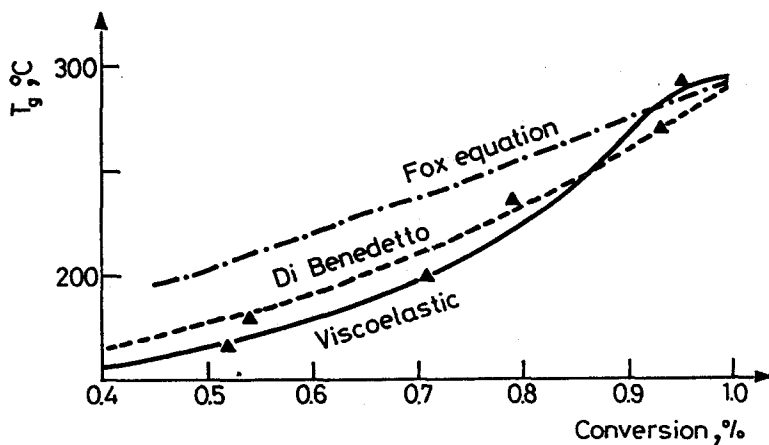


Fig. 7 T_g as a function of conversion data from Fig. 2 fitted by the Fox equation, the DiBenedetto equation and the viscoelastic equation

assumes that the changes in T_g are primarily due to changes in relaxation time as chain growth and crosslinking reduce the mobility of the polymer network.

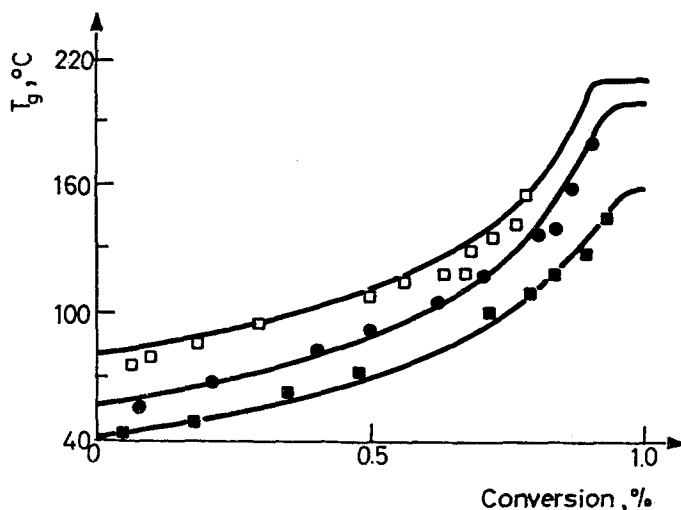


Fig. 8 T_g as a function of conversion data for different functionality epoxy fitted by viscoelastic equation using appropriate parameters. The experimental data was generated by C. W. Macosko and coworkers [7]. Epoxy functionality = 5.4, $E_r = 60$ kcal/mol, $\Phi = 20$ (□); epoxy functionality = 4.8, $E_r = 10$ kcal/mol, $\Phi = 4$ (●); epoxy functionality = 2.7, $E_r = 10$ kcal/mol, $\Phi = 2$ (■)

The equation was shown to fit potentially a variety of experimental data by adjusting two parameters, which can be experimentally determined or estimated. The success of the equation has been demonstrated by comparing it to previous equations and published data.

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Zusammenfassung — Der Glasumwandlungspunkt T_g ist eine empfindliche und praktische Größe zum Verfolgen der Aushärtung reaktiver Duroplaste. Basierend auf dem viskoelastischen Steifigkeitsmodell von Dillman-Seferis wurde eine neue Gleichung zur Vorhersage der Beziehung zwischen T_g und Konversion entwickelt. Dabei wird angenommen, daß die Änderung von T_g in erster Linie durch eine Änderung der Relaxationszeit bedingt ist, da Kettenverlängerung und Vernetzung die Beweglichkeit des Polymergefüges herabsetzen. Bei einer Kombination von kinetischen und viskoelastischen Messungen, mit denen die Umwandlungen während des Aushärtens von Duroplasten verfolgt werden können, ist diese Erkenntnis von großer Bedeutung. Die auf der Basis des viskoelastischen Modelles erhaltene Gleichung ist für eine große Breite von experimentellen Daten anwendbar. Den Erfolg dieser Methodik zeigt weiterhin ein Vergleich bewährter Beziehungen, wie z.B. der Foxschen Gleichung und der Gleichung von DiBenedetto, mit Aussagen, die durch Anpassung zweier viskoelastischer Parameter ermöglicht wurden. Die Stärke der vorgeschlagenen Gleichung wird letztlich durch Anpassen von Epoxy-Daten aus der Literatur sowie von experimentellen Daten eines relativ neuen und in dieser Untersuchung als Modell benutzten Harzsystemes gezeigt.