and spacer group, as well as the contributions from significant orientation-dependent anisotropic interactions.[33]

Acknowledgment. We thank IBM (U.K.) for awarding a Visiting Scientist Fellowship to C.V.

Registry No. ($ClCOC_6H_4$-*p*-$O(CH_2)_6OC_6H_4$-*p*-$COCl$)(2,4-$(HO)_2C_6H_3(CH_2)_6O$-*p*-$C_6H_4N{=}NC_6H_4$-*p*-OCH_3) (copolymer), 121157-62-8; ($ClCOC_6H_4$-*p*-$O(CH_2)_6OC_6H_4$-*p*-$COCl$)(2,4-$(HO)_2C_6H_3(CH_2)_6O$-*p*-$C_6H_4N{=}NC_6H_4$-*p*-OCH_3) (SRU), 104167-11-5.

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A Model for the Curing Reaction of Epoxy Resins

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ABSTRACT: A parametric formula describing the curing reaction of cross-linkable polymers and based on the interdependence of the reaction rate and relaxation time is presented. Changes in the relaxation time due to cross-linking are described by analogy with the physical annealing process in glasses. A computer program developed for this study has been found useful in designing the curing process and in predicting the viscoelastic properties of the resulting cured resins. The processing variables that directly affect product reliability can be accurately estimated by this technique.

Introduction

Polymers that can withstand temperatures in excess of 150 °C are found in a wide range of electronic and aerospace applications. Among them, epoxy resins are one of the oldest and most vigorously developed high-temperature polymers in use today. Millions of pounds are produced annually for use in printed circuits, precision connectors, and VLSI encapsulation packages.

Epoxy resins attain their high-temperature properties by virtue of a densely cross-linked molecular network. As in all high-temperature thermosetting resins, the last stage of the curing reaction slows as molecular motion becomes restricted in the highly cross-linked network of polymer molecules. A model for describing curing reactions must include a thermodynamic parameter for the molecular mobility, which changes as the reaction proceeds. Our model is based on the similarity between the cross-linking process and physical aging of thermoplastic (un-cross-linked) glassy polymers. In both cases, chain mobility decreases with time, leading to increased relaxation times. This model can be used to design the optimal temperature-time program for the curing process and to predict the final viscoelastic and thermomechanical properties of the resin being used.

Relaxation Time and Thermodynamic Variables

Assuming that the curing reaction is analogous to the physical aging process, there are two questions that need to be answered. The first question is what kind of distribution of relaxation times is the most appropriate for the curing process. The second question is how the intensive quantities, i.e. the temperature and pressure, and the extensive quantities, i.e. the volume, entropy, and enthalpy, affect the relaxation time of the curing polymer.

(1) Distribution of Relaxation Times. It is agreed by most workers who have studied the glass transition[1-5] that a single relaxation time cannot adequately describe the thermodynamic recovery or physical aging process. One unequivocal proof for this statement can be found in Kovacs' classic experiment of the "memory effect".[1] While several models for the distribution of relaxation times have been suggested by various authors,[2,5] we use a spectrum obtained from dielectric relaxation of poly(vinyl acetate),[5] which gives a good fit for the thermodynamic recovery

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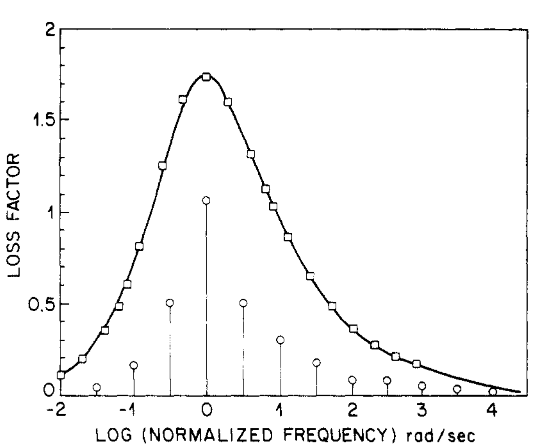

Figure 1. Distribution of relaxation times in poly(vinyl acetate) [reproduced from ref 5].

process. This distribution is reproduced from ref 5 in Figure 1.

(2) Thermodynamic Formulas for the Relaxation Time. An empirical equation known as the Vogel-Fulcher relationship[6] describes the temperature dependence of the relaxation time of materials in the equilibrium state

$$\ln \tau = \frac{H}{R(T - T_2)} + C \qquad (1)$$

where τ is the average relaxation time, H is the activation energy at the high-temperature limit, T is the temperature, and T_2 is the temperature below which the equilibrium state cannot be reached. R is the universal gas constant, and C is a constant. It can be shown that this two-parameter equation is a form of another well-known empirical relationship, the Williams-Landel-Ferry (WLF) equation.[7]

Equation 1 can be compared with the free-volume equation of Doolittle[8]

$$\ln (\tau/\tau_0) = \frac{1}{\alpha_f(T - T_2)} - \frac{1}{\alpha_f(T_0 - T_2)} \qquad (2)$$

where α_f is the thermal expansion coefficient of the free-volume fraction, $f = \alpha_f(T - T_2)$, in the equilibrium state. The subscript 0 refers to the properties at an arbitrary reference temperature T_0. T_2 is the extrapolated temperature at which the equilibrium relaxation time diverges and at which $f = 0$ at equilibrium. The free-volume equation implies that changes in the relaxation time are totally attributed to changes in the free-volume fraction, since T_0 and T_2 are fixed. Thus, since f is fixed at its value at T_g in the glassy state, the relaxation time is also predicted to be independent of temperature in the glassy state. However, experimentally, the relaxation time depends on the temperature in the form of an Arrhenius formula with a constant apparent activation energy. Kovacs thus concluded that the Doolittle equation cannot be used for nonequilibrium glasses and that an additional term is needed to account for the temperature dependence of τ.[1]

Adam and Gibbs[9] developed a formula for relaxation phenomena in the equilibrium state by considering cooperative motions of molecular segments in domains of varying sizes, with the configurational entropy, S, as the factor determining the critical size for such domains

$$\ln \tau = C + \frac{\Delta\mu s^*}{RTS} \qquad (3)$$

where $\Delta\mu$ is the activation energy for the transition involving the configurational change of the smallest possible unit with the configurational entropy s^*. The quantity S is the total configurational entropy. Equation 3 can take a form identical with eq 1, which has been shown empirically to be true, if S is assumed to be proportional to the quantity $1 - T_2/T$.

This temperature dependence of the configurational entropy makes sense thermodynamically[4,10-12] for the following reasons. The entropy, $S = \Delta C_p \ln (T/T_2)$, can be obtained by integrating the quantity $\Delta C_p/T$ with respect to temperature if ΔC_p is assumed to be constant, as Adam and Gibbs have done.[9] This has the same form as the relationship assumed above because the expression $1 - T_2/T$ is approximately equal to $\ln (T/T_2)$ when $T - T_2 \ll T_2$. For most polymers, ΔC_p is in fact not a constant but a weakly decreasing function of temperature. We[13] as well as many others have obtained C_p vs T data for various polymers which typically show C_p increasing with temperature both below and above the glass transition. However, $\mathrm{d}C_p/\mathrm{d}T$ above the glass transition is smaller than below; hence ΔC_p for a given polymer is smaller at higher temperatures. The assumption that eq 1 and 3 are consistent with each other thus leads to the formula $\Delta C_p = \Delta C_p|_{T_2} T_2/T$. Near T_2, ΔC_p is approximately constant and equal to $\Delta C_p|_{T_2}$. O'Reilly[14] pointed out that ΔC_p includes both intramolecular (configurational) and intermolecular (e.g., van der Waals energy) terms. DiMarzio[15] called the latter a free-volume effect. It is expected that the intermolecular contributions should diminish faster with rising temperature than the intramolecular terms and thus are the most likely source of the temperature dependence of ΔC_p.

The Adam-Gibbs equation (eq 3) can also be used to characterize a nonequilibrium glassy state by invoking a "fictive temperature", T_f, which is defined as the temperature at which the liquid state (with a specific configurational entropy) has been "frozen" to form a given glassy state. The entropy of the glassy state is thus equal to $s^*(1 - T_2/T_f)$. T_2 is often found to be about 50 °C below the apparent T_g and can be identified with the zero entropy temperature suggested by Kauzmann.[16]

When an epoxy resin is cured by cross-linking, the configurational entropy will decrease. Thus, during cross-linking the parameter T_2 and the relaxation time will increase, instead of the fictive temperature, T_f, decreasing as during aging of thermoplastic polymers. This is a major difference in the analogy between the curing and aging processes. For our model, we have assumed that T_2 varies proportionately with the degree of cure, α

$$T_2 = T_{2_0} + \alpha(T_{2_\infty} - T_{2_0}) \qquad (4)$$

where T_{2_0} and T_{2_∞} are the values of T_2 at $t = 0$ and $t = \infty$, respectively, and α is the extent of reaction. The values of T_2 obtained with eq 4 are used in the Adam-Gibbs expression to determine τ as a function of time and temperature.

Influence of the Relaxation Time on the Reaction Kinetics

The basic chemistry of the epoxy curing reaction is well-known. Here we are concerned with one special aspect of the physical chemistry of the curing reaction, i.e., the late stage during which further cross-linking is restricted by an increase in the relaxation time of the polymer matrix.

The isothermal cross-linking reaction is described in terms of a simple differential equation:

$$\mathrm{d}\alpha/\mathrm{d}t = k(1 - \alpha) \qquad (5)$$

Here, t is time, k is the reaction "constant", and the quantity α is the extent of reaction, i.e., the mole fraction of the reacted epoxy moiety. The temperature dependence of the reaction constant during the initial stage of reaction,

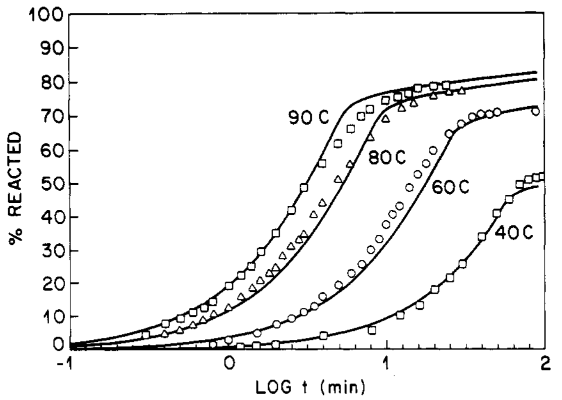

Figure 2. Extent of reaction vs logarithmic time during isothermal curing reaction of a Bisphenol A type epoxy system.

k_1, can be evaluated from the time-dependent heat of reaction determined by differential scanning calorimetry for different isothermal curing conditions, as described in detail elsewhere.[17]

In the later stage of curing, however, the apparent T_g increases and finally exceeds the reaction temperature, indicating that molecular motions are increasingly restricted. This aspect of increasing T_g will be discussed in detail later in this article.

The reaction constant k in eq 5 is now made equal to the reciprocal of the sum of two terms: $1/k_1$, which is the catalytic reaction time constant, and $1/k_2 = \tau$, which continues to increase as the reaction progresses. Because τ is initially very small, the k_1 term dominates at first. Later, however, τ becomes the rate-controlling factor. As an example, the extent of reaction is plotted in Figure 2 against logarithmic time for an amine adduct cured diglycidyl ether of Bisphenol A (DGEBA). With our model (solid lines), it is possible to predict the apparent final extent of reaction of epoxy resin that has undergone a given curing thermal history. A computer program has been created that can be used not only for isothermal reactions but also for reactions with any temperature–time history. From eq 4, we calculate T_2, which allows us to determine the configurational entropy S and, therefore, the fictive temperature, T_f. Using eq 3, we obtain τ and can now predict the extent of cure, α, from eq 5. These parameters allow us to predict the mechanical properties of a resin that has undergone a known curing history.

Change of Viscoelastic Properties during Cure

Let us first review the viscoelastic properties of an uncross-linked polymer. As emphasized above, the mechanical relaxation spectrum of a polymer encompasses an enormous time range. The shear relaxation modulus of a typical amorphous polymer, polyisobutylene, at a reference temperature equal to the "1-h" glass transition temperature, −70 °C, is plotted against time in Figure 3.[18] This figure was determined through time–temperature superposition[19] of isothermal data obtained at various temperatures, and the time scale extends from 10^{-6} s to 1 million years. The reference temperature was chosen because it is typical of the fictive temperature, T_f, of a quenched glass. The glass transition temperature determined by differential scanning calorimetry (DSC) is typically several degrees higher than this value, as will be discussed. The notation M in the figure refers to the molecular weight of a monodisperse polymer, and M_e refers to the critical molecular weight for entanglement. Commercial polymers almost always have molecular weights greater than this critical value in order to exhibit a respectable toughness and resistance to brittle failure and thus have extremely broad distributions of viscoelastic relaxation times. For all molecular weights, the relaxation time at long time depends on the 3.4th power of molecular weight, as is well-known.

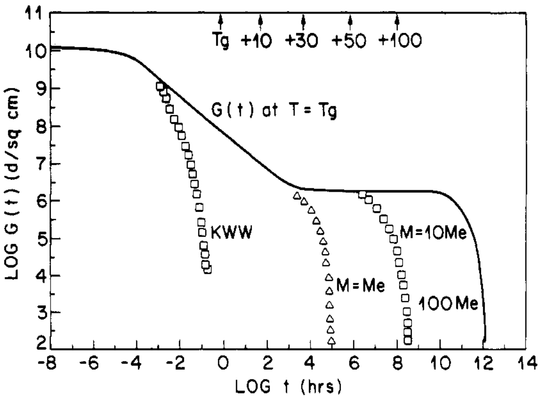

Figure 3. Shear relaxation modulus vs time for an idealized amorphous polymer at a reference temperature equal to its glass transition temperature; the curve marked as KWW was calculated from the KWW formula,[20] with a β of 0.5. Three molecular weights were chosen to illustrate differences in the relaxation modulus at long times.

The thermodynamic recovery time exhibits a narrower distribution than the viscoelastic relaxation for polymers. The thermodynamic recovery time distribution can be characterized by the Kohlrausch–Williams–Watts (KWW) equation,[20] which is known also to fit dielectric data.[4]

$$G(t) = C \exp(-t/\tau)^{\beta} \tag{6}$$

The curve corresponding to this distribution is shown by the label KWW in Figure 3. A nonpolymeric glass such as glucose at 20 °C exhibits a mechanical spectrum that fits the KWW form also, suggesting that its dielectric and viscoelastic spectra are similar.[4] For polymers, this is not true; only the short time end of the viscoelastic relaxation for the polymer fits well to the KWW formula as shown in Figure 3. We expect the mechanical spectrum at the start of the cross-linking reaction of the partially reacted epoxy monomers to be broader than that of a typical liquid (evident from the power law dependent viscosity on the shear rate[21]) but narrower than the fully developed polymer spectrum shown in Figure 3.

As the cross-linking reaction proceeds, the first critical change in molecular structure is observed during gel formation where the weight-average molecular weight reaches infinity. The viscoelastic function must now include an elastic modulus term, G_e, representing the rubbery plateau of the network, which will continue to increase proportionately with the extent of cross-linking, α.

Using the same parameters that were used to fit the reaction kinetic data shown in Figure 2, we have attempted to predict the viscoelastic properties of the same epoxy resin as it is isothermally cured. In Figure 4 we show how the dynamic modulus of the epoxy in Figure 2 increases as the cross-linking continues. The data were obtained with a torsional braid apparatus. A relaxation spectrum that corresponds to the first eight decades of the modulus for an amorphous polymer shown in Figure 3 was used, i.e.

$$G(t) = \sum_{1}^{16} G_i \exp(-t/\tau_i) + G_e(\alpha) \tag{7}$$

where G_i's are spaced every half decade in time, and the relative magnitude of $G_i = 1.78G_{i+1}$ was assigned between consecutive Dirac δ functions. $G(0) = 5.6$ and the rubbery modulus G_e was scaled to equal 0.5α in the calibration units of the torsional apparatus used. A similar comparison is

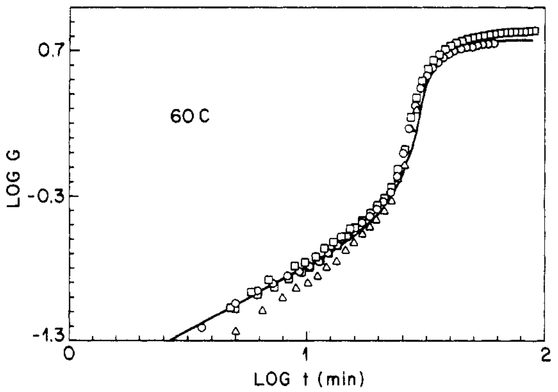

Figure 4. Dynamic modulus obtained by a torsional braid apparatus at approximately 1 Hz during isothermal cure at 60 °C. The line was calculated with the model by using the spectrum corresponding to $[G_i, \tau_i]$ in eq 8.

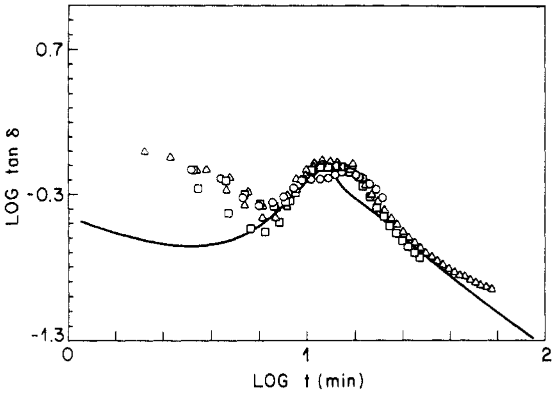

Figure 5. tan δ obtained on a torsional braid apparatus during isothermal cure at 80 °C. The line was calculated with the model.

made for tan δ, calculated in the same way and shown in Figure 5.

We have developed a computer program that can handle not only isothermal curing conditions but also temperature ramps with a rate $q = \mathrm{d}T/\mathrm{d}t$. The calculations show a good fit with the data in Figure 6, where the temperature has been raised at two different rates after isothermal curing at 60 °C for 1 h. These results give us confidence in our model's ability to predict curing kinetics.

In Figure 7, we have shown the calculated time-dependent increase in the relaxation time τ for the same epoxy polymer. During the last stage of curing the relaxation time increases approximately linearly with elapsed time. This behavior is expected from the physical aging behavior of a number of glassy linear polymers.

The glass transition temperature is not an inherent thermodynamic property like the thermodynamic melting point of a crystal. Since it is a measure of the ability of a glass to respond to stimuli, the apparent T_g depends on time-dependent variables such as the elapsed time (isothermal aging), the rate of heating/cooling (DSC), and the measurement frequency (dynamic mechanical or dielectric measurements). When we measure the apparent T_g of a partially cured epoxy by differential scanning calorimetry, we first quench the sample to room temperature and then reheat it at a finite rate, e.g. 20 °C/min; hence, the time scales of the curing and the heating are vastly different. In this case, the fictive temperature, T_f, which is the temperature at which the liquid state is frozen and is equal to the reaction temperature, can be substantially lower than the T_g measured by DSC. The lag is due to the inability of the molecules to respond to rapid heating; i.e., the relaxation time of the material is much longer than the heating time. The difference becomes particularly great when curing is allowed to progress for a long time, since the relaxation times of the network increase not only from increased degree of cross-linking but from physical aging as well.

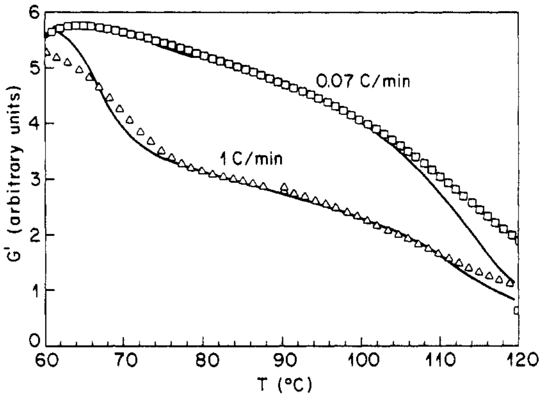

Figure 6. Histograms for the dynamic modulus of the Bisphenol A epoxy compound heated at two different heating rates: 1 °C/min (A) and 0.07 °C/min (B), both following a 1-h isothermal cure at 60 °C.

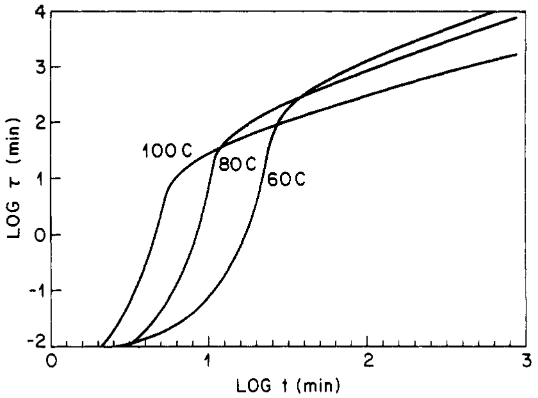

Figure 7. Calculated time-dependent change in the apparent relaxation time during isothermal curing of Bisphenol A epoxy.

During isothermal reaction, T_f is equal to the reaction temperature T, but T_2 continues to rise toward T_f, reflecting a decrease in excess entropy with cross-linking. The apparent T_g of a partially cured epoxy, measured by DSC as described above, can be substantially higher than T_f when it is determined by heating from room temperature. The apparent T_g is calculated from the equation

$$\ln(t/t_0) = \frac{H}{R}\left(\frac{s^*}{T_g S_t} - \frac{s^*}{T S_0}\right) = \frac{H}{R}\left(\frac{T}{T_g(T - T_{2,t})} - \frac{1}{T - T_{2,0}}\right) \quad (8)$$

where t_0 is the reaction time at which T_g has climbed to be equal to T, S_0 and $T_{2,0}$ are the entropy and T_2 at time t_0, and S_t and $T_{2,t}$ are referred to the reaction time t ($t > t_0$). Figure 8 is the plot for T_g thus calculated versus the extent of the reaction. The experimental T_g's from DSC (data points) are also shown.

An Example with an Encapsulation Grade Epoxy

Let us now trace the course of the cross-linking reaction in a commercial epoxy novolac resin used for the encapsulation of integrated circuit chips. In Figure 9, the extent of reaction at 140 °C is plotted against time, and T_g has been measured by DSC at each point as discussed above. The numbers on this figure indicate the T_g at each point of reaction. Note that T_g reaches about the same value

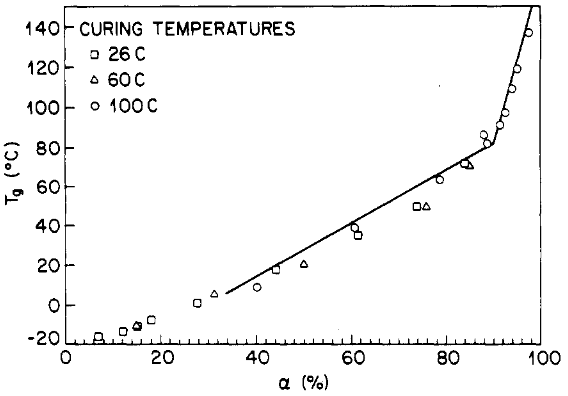

Figure 8. Extent of curing reaction, α, vs T_g. The line indicates the model calculations.

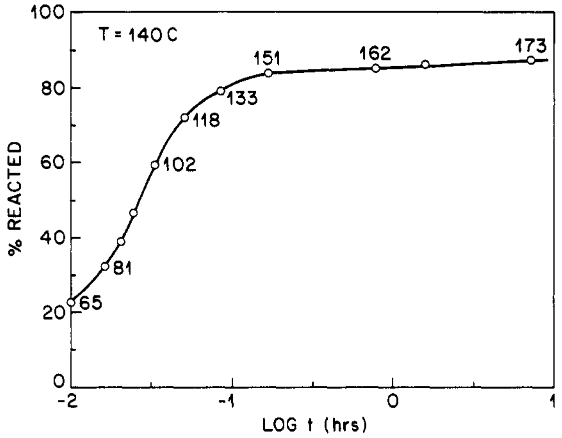

Figure 9. Extent of reaction vs time for a novolac epoxy system at 140 °C. The numbers indicate T_g's measured by DSC after quenching and then reheating each sample from 25 °C.

as the reaction temperature (140 °C) when the reaction kinetics take a sharp turn into the relaxation-controlled mode. From this point on, a marked increase in T_g is observed, which reflects the increase in the relaxation time. To examine this point further, we conducted dynamic mechanical tests on three samples: sample 1, cured at 170 °C for 4 h (a standard manufacturing process); sample 2, cured at 170 °C for 1000 h (an excessive cure); and sample 3, obtained by heating sample 2 to 260 °C for a 0.5 h before quenching to room temperature (removing the effects of physical aging). The dynamic mechanical properties of these three samples are shown in Figures 10 and 11. As compared to sample 1, sample 2 exhibits higher values for T_g and plateau modulus, indicating a higher degree of cross-linking. When sample 2 has been heated to remove the effects of physical annealing, the plateau modulus remains the same, indicating no change in the cross-linking density, but the apparent T_g is lower. The latter fact suggests that the high T_g in sample 2 is due partially to physical aging. By heating and quickly cooling to eliminate these effects, T_g is actually reduced. With these data we demonstrate that the relaxation time depends not only on the degree of cure but also on physical aging.

Summary

We have shown that the curing kinetics and viscoelastic properties of epoxy systems can be predicted when several parameters are known. By analogy with the physical annealing process in glasses, the effect of changes in molecular mobility on the reaction kinetics can be determined. While the chemical kinetics during the early stages of cure are obtained by DSC, the effects of thermal history and changes in cross-link density can be obtained from the Adam–Gibbs relationship during the later stages of cure. A distribution of relaxation times obtained by dielectric spectroscopy is used to describe the curing network. With these results, the curing process can be modeled for both isothermal and nonisothermal curing histories, and the final properties of the cured resin can be predicted. The effects of physical aging and extent of cure can also be separated. These results have major implications on both the process and product design for many applications that utilize epoxy resins.

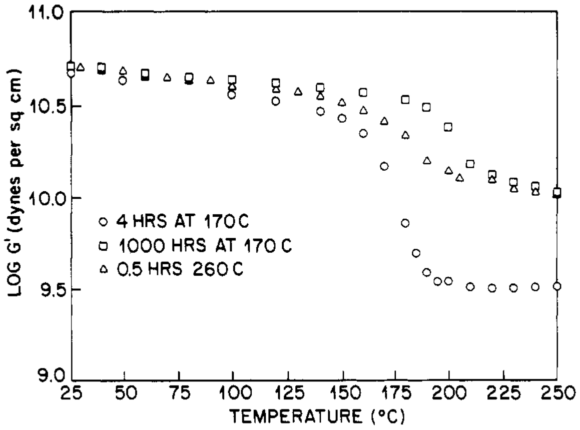

Figure 10. Dynamic mechanical storage modulus vs temperature for three samples of different curing and aging histories.

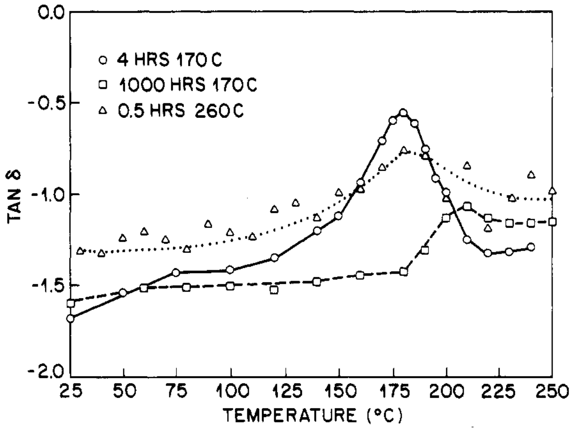

Figure 11. tan δ vs temperature for the same runs shown in Figure 10.

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Registry No. (Bisphenol A)(epichlorohydrin) (copolymer), 25068-38-6.

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Lattice Model for Interphases in Binary Semicrystalline/Amorphous Polymer Blends

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ABSTRACT: In this paper we examine the interphase in a system which consists of two polymers that are compatible in the melt but undergo phase separation due to the crystallization of one polymer in lamellar semicrystalline morphology. The problem is formulated on a cubic lattice in the Bragg–Williams mean-field approximation, under the assumption that the asymptotic amorphous phase of the system corresponds to the most favorable (for mixing) 50/50 composition. We find that the dissipation of the crystalline order through the interphase of partial order is little affected by the interaction energies between the two polymers. On the other hand, the interfacial region of varying polymer composition is strongly affected by the interaction parameter χ_{AB}, with the interfacial thickness varying with the reciprocal of $|\chi_{AB}|^{1/2}$. Hence, binary polymer mixtures with $\chi_{AB} \simeq 0$, which are miscible in the melts, are predicted to undergo nearly complete phase separation upon crystallization of one component, in agreement with experiments.

1. Introduction

The understanding of the behavior of polymer blends has taken on an increasing significance in the wake of the recent practical applications of these systems.[2] Of particular interest are systems that are completely miscible in the melt but phase separate on cooling due to the crystallization of one component. Examples of such blends include poly(vinylidene fluoride) (PVDF) as the crystallizable component, mixed with one of the following amorphous polymers: poly(methyl methacrylate) (PMMA),[3-10] poly(ethyl acrylate) (PEA),[11] poly(vinylpyrrolidone) (PVP),[12] poly(vinyl esters) like poly(vinyl acetate), poly(vinyl propionate), or poly(vinyl butyrate),[13] and a mixture of poly(ethylene oxide) as the crystallizable component mixed with PMMA.[14] Mixtures of crystallizable stereoregular polymers with atactic amorphous polymers from the same chemical monomers, isotactic/atactic polystyrene systems,[15] for example, have also been studied extensively in this regard.

In all cases, on cooling, the mixture separates into several distinguishable phases: the crystal phase, which has been assumed to be constituted purely of the crystallizable polymer, an interphase whose composition is not clearly known, and an amorphous phase that is either a homogeneous mixture of both polymers in the interlamellar region or is a pure phase of noncrystallizable material in the interfibrillar or interspherulitic space.

The presence of an interlamellar amorphous phase in which the two polymers are miscible due to the negative heat of mixing is expected to depress the melting point of the crystallizable component, a fact that has been observed in calorimetric experiments. For example, Nishi and Wang[4] used the depression of melting points of PVDF in PVDF/PMMA mixtures to derive interaction energies between the two polymers. (A Flory type analysis[16] was employed by the authors in this calculation.) From this calculation it has been suggested that the exchange energies between the polymers is relatively large, of the order $-{}^1/_2 k_B T$ per mole of chain segments.[4] Similar results were also obtained for the PVDF/PEA[11] and the PVDF/PVP[12] systems. It has also been pointed out that the structure and composition of the amorphous phase in these cases are sensitive to the technique of preparation, viz., melt crystallized versus solution crystallized.[4,6]

Recently, it has been suggested that the interphase between the crystal and amorphous phases constitutes an important facet of this problem that has not been considered properly in the past. Yoon and his co-workers,[7,8] Wendorff,[7,9] and Alfonso et al.[12] have illustrated the presence of the interphase and also delineated its importance in determining the behavior of the mixture when it is thermally treated.

In this paper we present a lattice theory that describes the structure and composition of the crystal–amorphous interphase in binary blends that are compatible in the melt. The size of the interphase and its dependence on the energy of interaction between the two polymers are investigated in detail.

2. Model Formulation

We consider chains placed on a lattice of coordination number Z. (For a cubic lattice $Z = 6$.) Each lattice layer has N_0 sites, and lattice layers are numbered as an ascending function of their distance from the crystal surface, which is numbered zero. Each lattice site is isodiametric, so that a lattice site is approximately 4.5 Å on a side in the case of polyethylene. For the sake of simplicity we limit the investigations to the chains of infinite molecular weights. It has been further assumed that the lattice is completely filled: i.e., no voids have been included in our calculations. The energy of interaction between two unlike monomers is characterized through the Flory–Huggins interchange energy parameter, χ_{AB}. It is assumed that only polymer A crystallizes and that the crystalline stems of polymer A are perfectly normal to the lamellar surface. It is also supposed that both A and B chains are completely flexible: i.e., the chains can take up any conformation afforded under the constraints of the lattice without any energy penalty. (We recognize that conformational energetic effects may play an important role in deter-

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