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Mechanisms of Solidification of Epoxy–Amine Resins During Cure

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ABSTRACT: Previous workers have studied the solidification mechanism of curing epoxy resin systems. It is generally believed that addition polymerization systems in which the average functionality of the reactants is greater than 2, solidify through the formation of an infinite network. Statistical analysis of the reaction system allows the prediction of the degree of reaction at which the infinite network can be observed. Analysis of the scaling properties of systems approaching the critical degree of reaction have predicted that certain scaling laws should be observed near the critical degree of reaction. The scaling predictions tested were the observation, near the solidification point, of a power law dependence of G' and G'' on frequency obtained near the time when G' and G'' are equal, for which the power exponent was 0.7 ± 0.02, and a scaling law involving a reaction coordinate, $\eta \sim \epsilon^{-k}$, with $k = 1.3 \pm 0.2$. However, gelation at the predicted point in the reaction and the predicted scaling were observed only in isolated cases. This work addresses the difference between systems that exhibit scaling as predicted and those which do not exhibit scaling. Work reported here shows, in a system for which the scaling predictions are observed, solidification occurs at the degree of reaction predicted by the simple statistical theory. This solidification mechanism appears to be observed only for those systems and cure conditions where the cure reaction is carried out at a temperature above the highest attainable glass transition temperature for the fully cured system. For the majority of epoxy systems, solidification does not occur near the predicted degree of reaction but may occur before or after the predicted point. For these systems the scaling properties predicted are not observed.

1. Introduction

Epoxy–amine resins are widely used as structural materials in high-performance composites and as adhesives. Network formation during cure of epoxy–amine resins is an important subject since it affects the ultimate structure and properties of cured epoxy resins. It is frequently assumed that gelation occurs during network formation of branching polymerization when the first infinite-molecular-weight network is formed. Mean-field theories of gelation of polymers[1–4] have been developed based on the classic Flory–Stockmayer theories.[5,6] In these theories, the probability of forming an infinite-molecular-weight network is defined from the probability of finding a branch point during the polymerization. For a reaction of a difunctional epoxy and an amine of functionality f, the extent of reaction at the gel point, p_G, can be calculated using the following equation:

$$p_G = \frac{1}{[1 + r\varrho(f-2)]^{1/2}} \tag{1}$$

where r is the ratio of the epoxide to the amine hydrogen and ϱ is the fraction of the amine hydrogen in the multifunctional reactants ($f > 2$). For a stiochiometric diepoxy–diamine reaction, $f = 4$, $r = \varrho = 1$, and $p_G = 0.577$.

It has been found in stoichiometric diepoxy–diamine reactions that the effects of intramolecular interactions and volume-excluded effects are not serious before gelation.[3,7] The effect of unequal reactivities of the primary and secondary amines results in a shift of the gel point toward a higher extent of reaction by 4% at the most;[4,7] i.e., the predicted extent of reaction at the gel point is in the range 0.58–0.62.

Percolation theory is a theory which has been applied to gelation of polymers by de Gennes,[8] Winter,[9] Martin,[10–12] and other researchers.[13–15] This theory predicts that near the gel point properties such as the weight-averaged molecular weight and the zero-shear-rate viscosity have a power-law dependence on a reaction coordinate, ϵ, defined by

$$\epsilon = \frac{|p - p_G|}{p_G} \tag{2}$$

The exponents in these power-law relationships are independent of the material.[13] The scaling law for the steady-state shear viscosity, η, near the gel point can be expressed by the equation

$$\eta \sim \epsilon^{-k} \tag{3}$$

The gel point can be defined by the point in the reaction when the power-law dependence of the storage modulus, G', and the loss modulus, G'', on the frequency, ω, is observed: $G'(\omega)$, $G''(\omega) \sim \omega^{\Delta}$.[9,15]

Recently, Martin and co-workers have developed a dynamic scaling theory using the results of percolation.[10–12] Their theory is based on the assumption of a length-scale-dependent viscosity and self-similarity near the gel point in a branching reaction system. By considering the effects of the hydrodynamic radius of the molecular species and the excluded-volume interactions in a polymer reaction bath, they predicted that the limits on the values of k and Δ in the power-law equations to be $0 < k < 1.35$ and $0.67 < \Delta < 1$. The two limits correspond to the presence of a strong hydrodynamic interaction (Zimm limit) and the absence of the hydrodynamic interactions (the free-draining condition given by the Rouse limit). Martin and co-workers determined the coefficients for the reaction of an epoxy resin with diethanolamine at 90 °C. They

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were $k = 1.4 \pm 0.2$ and $\Delta = 0.70 \pm 0.05$, which agreed with the theory in the Rouse limit.[10]

The above theories assume that the macromolecule has unrestricted conformational freedom during the reaction. The effect of the glass–rubber transition during reaction was considered by Gillham and coworkers during development of the time–temperature–transformation (TTT) theory.[16,17] According to the TTT theory, the solidification of the epoxy–amine curing system can be due either to vitrification or to gelation. Vitrification during the reaction is characterized by the approach of the glass transition temperature of the reacting system to the curing temperature. In the TTT theory, gelation may occur before or after vitrification depending on cure conditions. A parameter, $T_{g\infty}$ is defined as the maximum attainable glass transition temperature and is characteristic of a particular system. Gillham suggested that for systems where T_{cure} is greater than $T_{g\infty}$, solidification could occur through vitrification before the onset of gelation.

A third mechanism for solidification of a curing network system is progressive phase separation as suggested by Bobalek et al.[18] and Solomon.[19] This mechanism suggests that, as the reaction proceeds, insoluble material separates as a second phase from the residual material in the reaction bath. The process of solidification will be complex due to the presence of multiple phases and will be difficult to predict. De Gennes has suggested that phase separation may be competitive with gelation when branching density is increased.[8] Barnes et al. also analyzed the effect of phase separation in three-dimensional networks.[20]

A serious problem exists concerning the concept of phase separation. As has been described in detail by Dušek,[3] if the reacting system separates into multiple phases, chemical kinetics should show major changes as phase separation occurs. Very many kinetic studies of a wide variety of curing epoxy systems have not shown evidence of any such deviations up to and for at least a short way past the observed onset of solidification.

It is important to use a precise experimental criterion for the gel point. Four criteria that have been used by other researchers will be considered here. For the first criterion, the time when viscosity is equal to a predefined, high value is taken to indicate gelation.[16] In the second, the time when G' and G'' are equal is taken as the gel point. This point is called the "crossover" as G' is initially very small while G'' is finite. At the end of reaction G' is large and G'' becomes small.[21] A third criterion is the time when a finite detectable insoluble fraction could be determined in a branching polymerization.[16] The fourth is the time when scaling occurs, i.e., when $G'(\omega)$, $G''(\omega) \sim \omega^{\Delta}$.[10]

2. Experimental Section

The epoxy resin used in this study was DER331 (Dow Chemical) based on the diglycidyl ether of Bisphenol A (DEGBA). DER331 has an epoxide equivalent weight of 189. Ethylenediamine (Aldrich Chemical Co. Inc.) and polyoxypropylenediamine, Jeffamine D400 (Texaco Chemical Co.), were used as curing agents for the majority of the work referred to in detail in this study. The curing temperatures for the epoxy resin/ethylenediamine system were 40, 50, and 60 °C, and the curing temperatures for the epoxy resin/polyoxypropylenediamine system were 40, 50, 60, and 80 °C.

Several different amine curing systems with epoxy resins using the stoichiometric ratio were also evaluated for the observation of scaling properties during cure. A lower molecular weight polyoxypropylenediamine (Jeffamine D230) was tested at 50, 60, 70, and 80 °C. Other curing agents used included 1,3-propanediamine, *N*-methylethylenediamine, *N*,*N'*-dimethylethylenediamine, 1,3-diaminobenzene, bis-(4-aminocyclohexyl)methane (PACM-20), and 2,5-dimethyl-2,5-hexanediamine. The catalytic curing agent, diethanolamine, was also used at a mixing ratio of 12 parts per 100 parts (weight/weight) of resin.

Experimental details for all techniques are described in ref 22.

A Perkin-Elmer DSC-7 differential scanning calorimeter was used to obtain the glass transition temperature and the extent of reaction during the isothermal reactions of epoxy–amine systems simultaneously. Samples were scanned from −50 to +250 °C. T_g was obtained from the discontinuity observed at low temperature. The residual heat of reaction (H_t) was also calculated from the area under the residual exotherm at higher temperatures. The extent of reaction, p, was calculated according to the following equation:

$$p = \frac{H_0 - H_t}{H_0} \tag{4}$$

where H_0 is the area at zero time. The curves relating T_g and the extent of reaction to reaction time were then obtained simultaneously. Values for $T_{g\infty}$ were determined by postcuring a reacted sample at a series of increasing temperatures, e.g., 100, 150 and 200 °C for 2 h. The maximum value of the glass transition temperatures of these postcured samples was taken as $T_{g\infty}$.

Dynamic viscosity measurements were performed with a Bohlin VOR rheometer. In small-amplitude oscillatory shear measurement, the mechanical response, such as G' and G'', of the epoxy–amine reacting mixture during an isothermal curing process was recorded. Two parallel plates with a diameter of 25 mm and a gap about 1 mm were used for the oscillatory experiment. G' and G'' were determined at a range of frequencies from 0.01 to 20 Hz. The duration of the frequency sweeps (<3 min) was short compared to the total curing time (>60 min) so that time taken for the frequency sweep could be neglected when compared to the cure time.

An estimate of the steady-state shear viscosity, η, of the reacting mixture during the isothermal cure of epoxy–amine was also determined by the Bohlin VOR rheometer using 25 mm parallel plate geometry. A low rotational speed of about 0.100 cycle/s was used.

The insoluble fraction of the reacting mixture was obtained from an extraction experiment. Small amounts of unreacted mixture (about 1 g) were weighed into several small test tubes. The tubes were then placed in the oven at the curing temperature. They were taken out of the oven at intervals and quenched in liquid nitrogen. The insoluble fraction was calculated from the weight loss on extraction with dichloromethane in a Soxhlet extractor for more than 2 h.

3. Results and Discussion

3.1. $T_{g\infty}$ of the Epoxy–Amine Curing Systems. Values for $T_{g\infty}$ for the systems studied are shown in Table 1, together with the curing temperatures.

The systems were studied at cure temperatures up to the maximum that constant-temperature conditions could be maintained. At higher temperatures, heat generated by the exothermic reactions could not be dissipated under the experimental conditions.

3.2. Kinetic Data for Selected Reactions. As the rate constants for the reactions studied vary over a wide range, data are presented in terms of the degree of cure, p, for each reaction. As data was determined as a function of time, a method was needed to convert between time and extent of reaction. To avoid the use of theoretical, kinetic models,[24–27] the kinetic data were fitted to an arbitrary, fourth-degree polynomial. The polynomial was used to calculate the degree of cure for experiments in which only time was determined experi-

Table 1. Glass Transition Temperatures and Cure Temperatures for the Systems Studied[a]

curing agent	$T_{g\infty}$ (°C)	cure temp (°C)
ethylenediamine	105	40*, 50, 60
polyoxypropylenediamine (Jeffamine D400)	40	40*, 50, 60, 80*
polyoxypropylenediamine (Jeffamine D230)	80	50, 60, 70, 80
1,3-propanediamine	110	40
N-methylethylenediamine	90	40
N,N'-dimethylethylenediamine	40	40
1,3-diaminobenzene	165	100
bis(4-aminocyclohexyl)methane (PACM-20)	>100	60
2,5-dimethyl-2,5-hexanediamine	110	60
diethanolamine	90	90

[a] Systems reported in detail are marked with an asterisk.

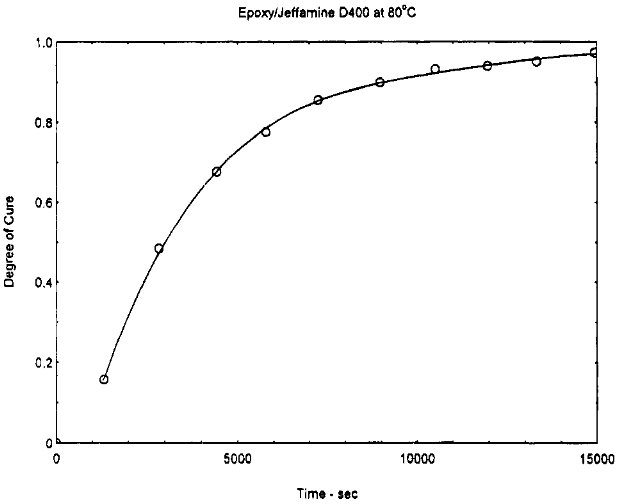

Figure 1. Variation of the degree of cure with time for epoxy/polyoxypropylenediamine (Jeffamine D400) at 80 °C. Experimental data are shown as circles. The solid curve represents the best-fit, fourth-order polynomial.

mentally. This numerical interpolation method can only be used over the time/degree of reaction ranges studied directly and cannot be used outside that range. For data outside the range used in the polynomial fits, p was estimated visually from the $p-t$ plot.

Figure 1 shows the kinetic data for the system epoxy resin/polyoxypropylenediamine, for which $T_{g\infty}$ was found to be 40 °C, when cured at 80 °C. For this reaction T_{cure} is greater than $T_{g\infty}$. A smooth curve through all the points could not be obtained, so the data for time below 5 min were excluded. This means that the interpolation method is not valid below $t = 5$ min and the early reaction data were not used (only one point was excluded from the experiments).

Figure 2 shows the kinetic data for the system epoxy resin/ethylenediamine at 40 °C for which $T_{g\infty}$ was found to be 105 °C. This is well over the cure temperature. The fourth-degree polynomial fitted all the data determined up to $t = 100$ min when a discontinuity was observed (see below).

3.3. Variation of Properties during Cure. To allow comparison of the solidification point between systems with different kinetics, data for all other experiments are presented as a function of degree of cure. Figure 3 shows the modulus for these two systems as a function of degree of cure. Figure 4 shows the variation of the logarithm of the real and imaginary modulus with the logarithm of frequency near the point where $G' = G''$. Figures 5–7 show the insoluble fraction, viscosity, and the glass transition temperature,

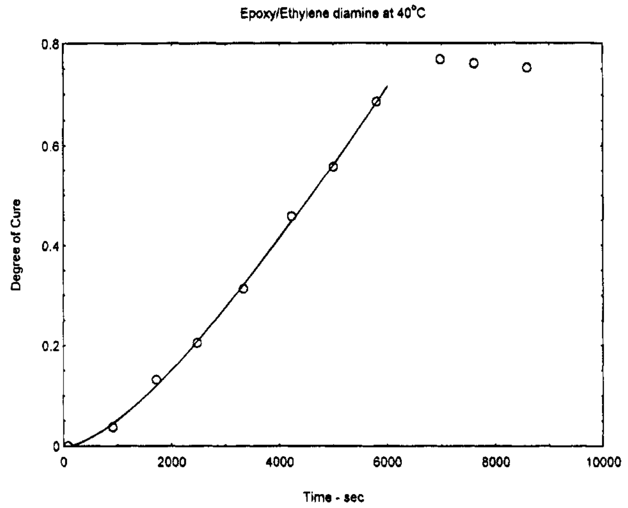

Figure 2. Variation of the degree of cure with time for epoxy/ethylenediamine at 40 °C. Experimental data are shown as circles. The solid curve represents the best-fit, fourth-order polynomial.

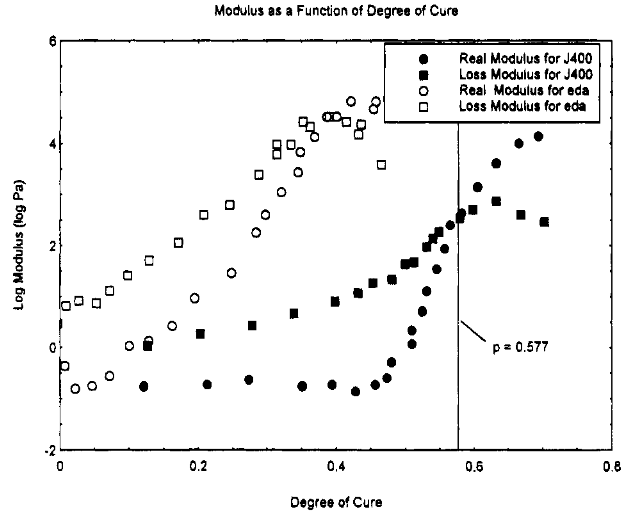

Figure 3. Variation of dynamic modulus with degree of cure for epoxy/ethylenediamine at 40 °C (squares), typical of a system showing phase separation, and for epoxy/polyoxypropylenediamine (Jeffamine D400: circles) at 80 °C, a system showing gelation. In this figure the point of reaction where gelation is predicted for both reactions using eq 1 is indicated.

respectively, as a function of cure for each system. Using eq 1, all systems studied in this work would be predicted to gel where the degree of reaction equals 0.577, and this point is indicated in each figure.

The system cured with Jeffamine D400 at 80 °C, for which T_{cure} was greater than $T_{g\infty}$, shows scaling (see Figures 4 and 8) whereas the ethylenediamine system, for which T_{cure} was less than $T_{g\infty}$, does not (see Figure 4). The third system studied, epoxy resin/polyoxypropylenediamine cured at 40 °C, for which T_{cure} was less than $T_{g\infty}$, appeared qualitatively similar to the system cured with ethylenediamine and did not show scaling. Of the remaining systems, only the system cured with diethanolamine, for which T_{cure} equaled $T_{g\infty}$, showed scaling. Even the system cured with *N,N'*-dimethylethylenediamine, for which T_{cure} was equal to $T_{g\infty}$, did not show scaling.

It is concluded that the observation of scaling depends only on T_{cure} being greater than $T_{g\infty}$ and does not appear to be aided by a decrease in final cross-link density (both substituted ethylenediamine systems appeared similar

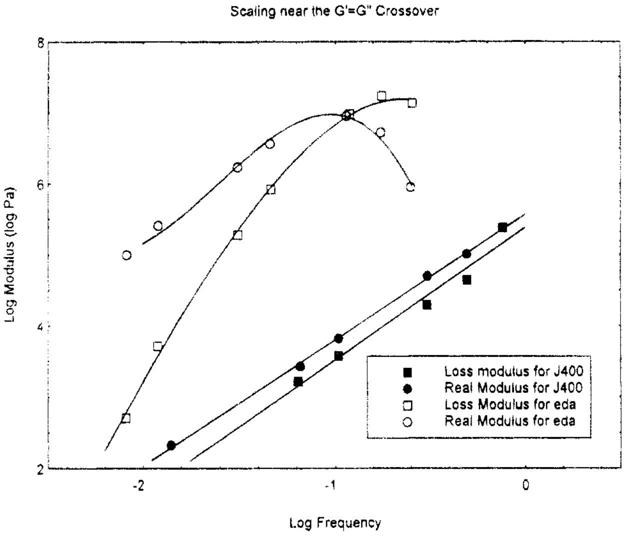

Figure 4. Variation of dynamic modulus with frequency for epoxy/ethylenediamine at 40 °C and for epoxy/polyoxypropylenediamine (Jeffamine D400) near the crossover point where the storage modulus, G', equals the loss modulus, G''.

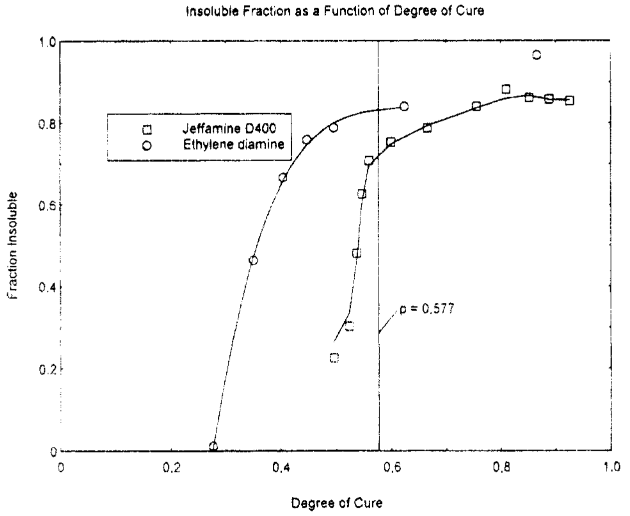

Figure 5. Insoluble fraction as a function of the degree of cure for epoxy/ethylenediamine at 40 °C and for epoxy/polyoxypropylenediamine (Jeffamine D400) at 80 °C. The predicted gelatin point for both systems is indicated.

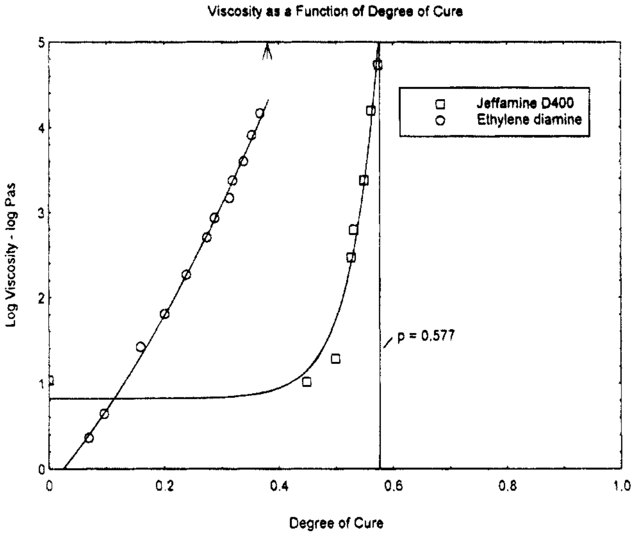

Figure 6. Steady-state viscosity as a function of the degree of cure for epoxy/ethylenediamine at 40 °C and for epoxy/polyoxypropylenediamine (Jeffamine D400) at 80 °C. The predicted gelation point for both systems is indicated.

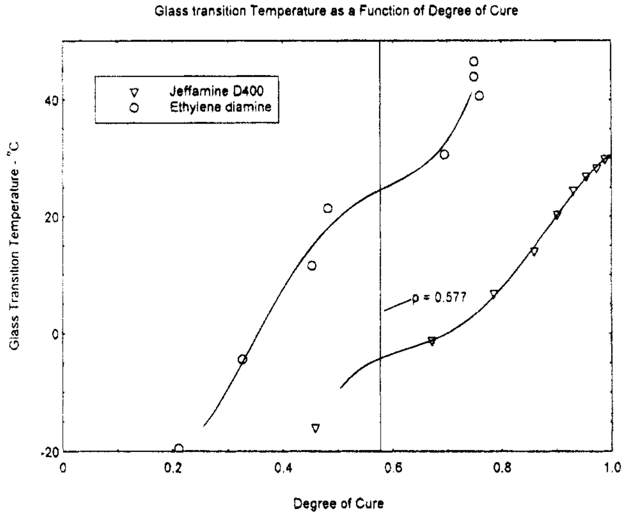

Figure 7. Glass transition temperature as a function of the degree of cure for epoxy/ethylenediamine at 40 °C and for epoxy/polyoxypropylenediamine (Jeffamine D400) at 80 °C. The predicted gelation point for both systems is indicated.

to the unsubstituted system), a decrease in absolute amine reactivity (amine reactivity follows the order aliphatic > alicyclic > aromatic), or an increase in reactivity difference between the primary and secondary amines (2,5-dimethyl-2,5-hexanediamine is reported to have a relatively large reactivity difference between functionalities).[23] The properties of the two types of systems during cure will be discussed separately.

3.4. Solidification Data for Systems for Which T_{cure} Is above $T_{g\infty}$. For the system epoxy resin/polyoxypropylenediamine at 80 °C, in which T_{cure} is greater than $T_{g\infty}$, there is no noticeable, abrupt tendency for the reaction to stop or slow at the solidification point or at the late stages of the reaction. The reaction among the reactive groups does not appear to be inhibited by any phase changes during reaction. The reaction will, eventually, be terminated due to the approach of the system to the topological reaction limit.[3]

Application of the experimental criteria for gelation is shown in Table 2.

From this table, it can be seen that all criteria give approximately the same gel time of 55 ± 2 min. The extent of the reaction at the gel point as defined is approximately 0.56, which compares well with the value of 0.577 predicted by the mean-field theories. It is observed that near the time when G' and G'' cross over, scaling occurs and $G'(\omega)$, $G''(\omega) \sim \omega^{\Delta}$, with an exponent $\Delta = 0.70 \pm 0.03$ (Figure 4). Figure 8 shows the scaling relationship of the steady-state viscosity, η, and the reaction coordinate, ϵ, near the gel point during the isothermal cure of epoxy resin/polyoxypropylenediamine at 80 °C. The exponent in the power law, $\eta \sim \epsilon^{-k}$, is $k = 1.3 \pm 0.2$. The values of Δ and k near and at the gel point are as predicted by Martin's theory in the Rouse limit where there is no hydrodynamic interaction existing in the reaction bath.[10]

3.5. Solidification Data for Systems for Which T_{cure} Is Equal to or Is Less Than $T_{g\infty}$. Figure 2 shows the extent of reaction as a function of time and Figure 7 shows the glass transition temperature as a function of degree of cure for the system epoxy resin/ethylenediamine at 40 °C, for which T_{cure} is less than $T_{g\infty}$. The reaction proceeds smoothly up to about 75% reaction (110 min). Near this point the glass transition temperature of the reacting mixture reaches the curing temperature, and the reacting system vitrifies. Vitri-

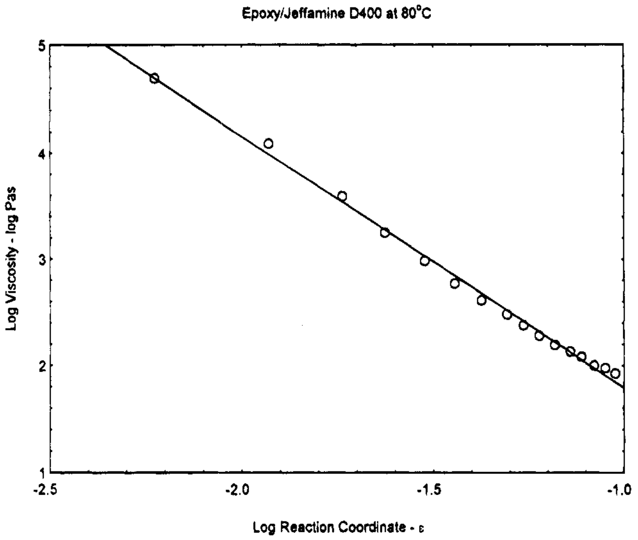

Figure 8. Variation of the logarithm of viscosity with the logarithm of the reaction coordinate for epoxy/polyoxypropylenediamine (Jeffamine D400) during cure at 80 °C.

Table 2. Critical Times for the Epoxy Resin/ Polyoxypropylenediamine System Cured at 80 °C

	gel criterion			
	$\eta \rightarrow \eta_{max}$	$G' = G''$	insol onset	scaling
reacn time (min)	55	57	50	56
extent of reacn, p	0.55	0.56	0.49	0.56
T_g (°C)	−10	−9	−13	−9

Table 3. Critical Times for Epoxy Resin/ Ethylenediamine Cured at 40 °C

	gel criterion			
reacn time (min)	$\eta \rightarrow \eta_{max}$	$G' = G''$	insol onset	scaling
reacn time (min)	60	62	58	no
extent of reacn, p	0.39	0.40	0.36	no
T_g (°C)	1	2	−2	no

Table 4. Critical Times for Epoxy Resin/ Polyoxypropylenediamine Cured at 40 °C

	gel criterion			
	$\eta \rightarrow \eta_{max}$	$G' = G''$	insol onset	scaling
reacn time (min)	734	785	701	no
extent of reacn, p	0.75	0.77	0.74	no
T_g (°C)	−2	−1	−2	no

fication slows down the reaction greatly and the reaction rate after the vitrification time is very small although the glass transition temperature continues to rise slowly. The reaction rate is probably controlled by diffusion.[28]

Tables 3 and 4 show that, at the critical times related to the liquid–solid transition of the epoxy–amine curing systems in which T_{cure} is less than $T_{g\infty}$, the glass transition temperature of the reacting mixture is still well below the curing temperature. It could be suggested that the time scale of the method for determination of T_g is not necessarily the same as is effective during the curing reaction. However, both the kinetic curve (Figure 2), and the glass transition/degree of cure curve (Figure 7), show the effect of the approach of the glass transition temperature to the reaction temperature at similar points in the reaction. At least at that point in the reaction, the rate effects on T_g are the same in the experimental determination of T_g and in the reaction. Vitrification is not the mechanism of solidification of the epoxy–amine systems studied here.

Tables 3 and 4 show the critical times for the curing systems epoxy resin/ethylenediamine at 40 °C and epoxy resin/polyoxypropyleneamine at 40 °C, respectively.

For the curing systems in which T_{cure} is less than $T_{g\infty}$, the values of the extent of reaction at the these critical times are either less than or greater than the values at the gel point predicted by Flory and other researchers.

3.6. Degree of Cure at Solidification. For the system studied curing at a temperature over $T_{g\infty}$, gelation occurs close to the degree of reaction predicted by the mean-field theories. The epoxy/low-molecular-weight polyoxypropylenediamine (Jeffamine D230) also showed similar behavior when cured at temperatures at or over $T_{g\infty}$. The system epoxy resin/diethanolamine also showed scaling near the solidification point, but no estimates of the degree of reaction were obtained for this system.

For all systems studied when cured at temperatures below $T_{g\infty}$, solidification occurs at a degree of cure other than at the degree of cure predicted by mean-field theories for gelation. None of these systems exhibited scaling, as defined above, at any extent of reaction. For the system epoxy resin/ethylenediamine at 40 °C, the degree of reaction at solidification is 0.4 (see Table 3), which is well before the predicted degree of reaction for gelation of 0.577–0.62. The degree of branching should be inadequate to form an elastomeric solid, and the glass transition temperature is well below the cure temperature so the product cannot be a glass. In contrast, the system epoxy resin/polyoxypropylenediamine cured at 40 °C solidifies at a degree of reaction of 0.75 (see Table 4), well after the gelation point predicted for the system. According to the statistical predictions, the degree of branching required for the formation of an infinite network should have been obtained when the product was still liquid. Many studies of solidification of step polymerizations have reported similar high degrees of reaction at the solidification point (e.g., refs 16 and 17).

3.7. Steady-State Shear Viscosity. An approximation of steady-state shear viscosity data is shown in Figure 6. For the system cured with ethylenediamine, the viscosity can be seen to increase gradually and steadily to the highest values of viscosity the rheometer can measure in the range of 15000–20000 Pa s. Although the viscometer was not able to record data past this point in the reaction, the reaction mixture appeared to be solid and glassy very shortly after removing the specimen from the viscometer. The data in Figure 6 for epoxy/ethylenediamine are somewhat deceptive and appear to be trending upward relatively smoothly to the highest viscosity data point observed. The instrument is capable of measurement of data up to about a viscosity of 10^6 Pa s. The next data point was out of range of the instrument for both curves. The relatively slow buildup of viscosity is in contrast to the data for the epoxy resin/polyoxypropylenediamine system cured at 80 °C which shows a more abrupt change of viscosity near the solidification point.

3.8. Phase Separation and Gelation. The occurrence of phase separation would be a convenient way to explain the wide variation of degree of reaction at the solidification point. For systems showing phase separation, material could partition between the incompatible phases such that the more highly branched material was in the continuous phase when early solidification is observed and in the noncontinuous phase otherwise. True gelation would then only be observed when the system remained homogeneous.

This, however, would be inconsistent with the reported simplicity of the reaction kinetic schemes which suggest, very strongly, that the system must always be homogeneous. If the system is always homogeneous for all reactions, it is often postulated that cyclization reactions or similar mechanisms that lead to formation of elastically ineffective chains may become significant and lead to a change in the predicted point of solidification. It is difficult to see how the change of reaction temperature by a few degrees could have such a major effect. In addition, it is difficult to understand why the ultimate glass transition temperature is such a critical factor in the system which is at very low conversion and has a bulk T_g far below this temperature. Further work will be necessary to address these problems.

4. Conclusions

For all epoxy resin–amine systems studied, when cured above, or sometimes at, the glass transition temperature of the fully cured system, scaling of the modulus and frequency was observed near the point of solidification of the system. For those systems for which the extent of reaction was determined as a function of time, the degree of cure of the system at solidification was very close to the extent predicted by mean-field theory. The curing agents which yielded systems showing this behavior included polyoxypropylenediamines (low and moderate molecular weight; Jeffamine D230 and Jeffamine D400) and diethanolamine.

For these systems, in the regime near the gel point, a power-law dependence of G' and G'' on frequency, $G'(\omega)$, $G''(\omega) \sim \omega^{\Delta}$, with $\Delta = 0.70 \pm 0.03$, was obtained near the time when G' and G'' cross over. A scaling law, $\eta \sim \epsilon^{-k}$, with $k = 1.3 \pm 0.2$, was also observed. These results agreed with Martin's dynamic scaling theory.

For all other systems studied, including systems using polyoxypropylenediamines at low temperatures, unsubstituted ethylenediamine, N-methylated ethylenediamine, 1,3-propylenediamine, *m*-phenylenediamine, bis(4-aminocyclohexyl)methane (PACM-20), and 2,5-dimethyl-2,5-hexanediamine, scaling was not observed. For these systems solidification was observed to occur at degrees of reaction other than those predicted by the mean-field theories.

In addition to the previously reported connection between the difference between the cure temperature and the ultimate glass transition temperature and the occurrence of scaling, there also appears to be a relationship between the observation of solidification near the point predicted by the mean-field theory and the occurrence of scaling. For systems not showing scaling, solidification can be observed either before the predicted degree of reaction (e.g., with ethylenediamine) or after the predicted point (e.g., polyoxypolypropylenediamines at low cure temperatures).

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