Gelation Behavior of Near-Zero Shrinkage Polybenzoxazines

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Received 21 December 1999; accepted 12 January 2000

ABSTRACT: A new class of phenolic thermosetting resins is developed that is based on the ring-opening polymerization of a benzoxazine precursor. These new materials seek to combine the thermal properties and flame retardance of phenolics with the mechanical performance and molecular design flexibility of advanced epoxy systems. These materials overcome many of the traditional shortcomings of conventional novolac and resole-type phenolic resins, while retaining their benefits. The viscoelastic behavior of the polybenzoxazines during isothermal cure is monitored by dynamic mechanical analysis. Isochronic measurements show that although the aniline-based benzoxazine has a lower activation energy for the gelation process than the methylamine-based resin, it has a slower rate of reaction. The purified monomer and as-synthesized precursor for each benzoxazine are found to polymerize by the same mechanism, despite the absence of an initiating species in the purified resins. The chemical gelation phenomenon of the methylamine-based resin is probed by a multifrequency dynamic cure analysis that allows determination of the instant of chemical gelation, as well as the network relaxation exponent, n. The constant value of the exponent regardless of cure temperature demonstrates that chemical gelation is, in fact, an isoconversion event for the methylamine-based benzoxazine. The multifrequency and isochronic analyses are shown to produce very similar gel times and activation energies for the gelation process. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 406–417, 2001

Key words: cure; polymer; phenolic resin; benzoxazine; rheology; thermoset

INTRODUCTION

Phenolic resins have been an important class of synthetic polymeric materials since Baekeland first commercialized them in 1910. Recently, a class of thermosetting polybenzoxazine materials has been developed that overcomes many of the deficiencies commonly associated with novolac and resole-type phenolic resins, while retaining their beneficial thermal, flame retardant, and dielectric characteristics.[1] These new polybenzoxazines have shown a mechanical and thermal performance that exceeds many epoxy resins, as well as conventional phenolics.[2] In addition to excellent water absorption and dielectric characteristics, these novel phenolic resins appear to polymerize with almost no volumetric shrinkage.[2]

As with any new resin, many parameters must be established before the material may be properly processed. The understanding of thermosetting resins, such as the polybenzoxazines, is complicated by the fact that they are reactive systems with continuously changing properties. Initially, the precursors of a thermosetting resin are of low

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Contract grant sponsors: National Science Foundation Graduate Fellowship Program (to D.J.A.); NSF Center for Molecular and Microstructure of Composites (CMMC)

Journal of Applied Polymer Science, Vol. 79, 406–417 (2001)

molecular weight and thus are highly fluid in nature. During the cure of these materials, however, chemical reactions occur that increase the molecular weight of the system and lead to branching and crosslinking, with an associated increase in viscosity. As a macroscopic chemical network structure evolves, the rheological characteristics change dramatically.

The gel point is a critical condition that is reached during the chemical reaction of a crosslinking system as its properties are in a transition state between those of a liquid and a solid. The gel point can be defined as the instant at which the weight average molecular weight of the branched molecules diverges to infinity. This phenomenon occurs at a critical extent of reaction and is independent of the cure temperature. Viscosity becomes infinite as the gel point is reached. Gelation is associated with the appearance of an equilibrium modulus that, once attained, prevents any applied stress from relaxing to zero. Beyond the gel point, the curing material is no longer able to flow easily and has limited processability.

Numerous rheological methods have evolved for detecting the point of gelation in a thermosetting resin. One of the simplest of these techniques is the standard ASTM test (ASTM D2471-88) that determines gelation by the time at which the cessation of flow occurs in a curing material. Other methods involve measurement of the evolving steady shear viscosity of the curing resin and extrapolation to the point at which its viscosity diverges to infinity.[3–5] Researchers have also estimated the point of gelation in crosslinking polymers by measuring the time of appearance of an equilibrium modulus.[5,6]

Additionally, Gillham pioneered the technique of torsional braid analysis (TBA) for mechanically monitoring the entire cure process of a thermosetting resin as it is transformed from the liquid state, through the rubbery region, and beyond the point of vitrification.[8] Through TBA experiments, the behavior of a crosslinking system as functions of cure time, temperature, and extent of reaction may be generalized graphically in the form of a time–temperature transformation cure diagram.[8–11] Derivatives of this technique, including dynamic spring analysis,[12] dynamic mechanical thermal analysis,[13,14] and torsion impregnated cloth analysis,[15] utilize various means of sample support to allow the analysis of reactive systems throughout the thermosetting change from the liquid to solid state. Dynamic melt rheology involves the dynamic mechanical analysis of a thermosetting resin as it cures while dispersed in a molten inert matrix polymer.[16] However, the above methods are complicated by the fact that they all use some form of sample support and consequently do not allow direct evaluation of the absolute value of the modulus of the curing resin. In particular, the formation of a matrix interphase in fiber reinforced composites is well known and its effect on the rheological properties of a composite system is significant.

One of the most common dynamic mechanical techniques for the determination of the gel point was proposed by Tung and Dynes[17] and involves small amplitude oscillatory shear. This method, which has recently been adopted as an ASTM (ASTM D4473-90) standard procedure, allows continuous monitoring of the viscoelastic properties of a resin as it undergoes the transformation from a liquid to a rubber. Gelation is then defined as the instant at which the evolving dynamic storage (G') and loss (G'') moduli cross over during an isothermal cure. However, analysis by this method is of limited value because of a dependence of the crossover time on the frequency at which it is measured. Because the instant of gelation is strictly material dependent, it should have no dependency upon the frequency of the rheological test. As a result, the equivalence of the dynamic moduli ($G' = G''$) at any given frequency may only be sufficient to define the *vicinity* in which gelation occurs.

More recently, Winter and coworkers investigated the viscoelastic behavior of crosslinking polymers at the gel point.[18–21] Their work led to the proposal of a simple constitutive equation, the gel equation, that successfully describes the rheological phenomena of finite zero-shear viscosity and zero equilibrium modulus at the gel point:

$$\tau(t) = S \int_{-}^{t} (t - t')^{-n} \dot{\gamma}(t') dt' \qquad (1)$$

In this definition of the stress tensor, τ, the strength of the network at the gel point is defined by a material parameter, S. The relaxation exponent, n, is network specific, while γ is the rate of deformation tensor. This gel equation predicts that the crosslinking material at the gel point, the critical gel, will behave with a power law relaxation modulus:

$$G(t) = St^{-n} \qquad (2)$$

The dynamic moduli of a reactive system under oscillatory shear also follows this power law at the gel point and exhibits a parallel behavior as demonstrated in the following relationship:

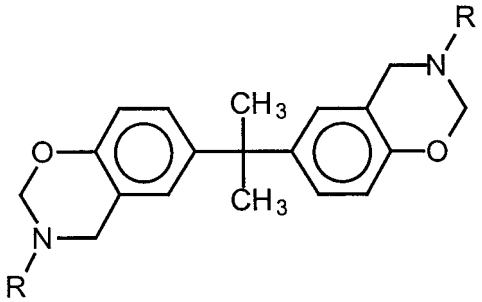
$$G' = \frac{G''}{\tan(n\pi/2)} = \frac{\pi}{2\Gamma(n)\sin(n\pi/2)} S\omega^n \quad (3)$$

The relaxation exponent may have values in the range from 0 to 1. For a special value of the exponent, $n = \frac{1}{2}$, as found with certain end-linking networks with balanced stoichiometry, the storage and loss moduli have been shown to exhibit congruence over a wide range of frequencies. Thus, the crossover point of G' and G'' in a dynamic cure experiment does in fact correspond to the instant of gelation for these select systems. For cases in which $n > \frac{1}{2}$, as was demonstrated for systems deficient in crosslinking agent, the gel point occurs just prior to the intersection of the moduli.

The gelation behavior of two different benzoxazines is initially investigated through an isochronic dynamic mechanical analysis of isothermal cure. With these experiments, the vicinity of the gel point is determined and allows qualitative comparisons of the reaction rates and mechanisms of the different materials. The critical gelation behavior of the benzoxazines is later investigated through a multifrequency cure analysis. These experiments allow the determination of the instant of chemical gelation, as well as the network relaxation exponent (n) of the critical gel. Finally, the isochronic and multifrequency results are compared to determine the suitability of utilizing single frequency cure measurements for the determination of the gel point in these benzoxazine systems.

EXPERIMENTAL

Two polybenzoxazine precursors were synthesized for this study:



BA-a: R = phenyl

BA-m: R = CH_3

The first difunctional benzoxazine monomer is based on bisphenol-A reacted with formaldehyde and aniline and is designated as BA-a. The other precursor is based on bisphenol-A with methylamine and is termed BA-m.

One gram-mole batches of each precursor were prepared in 2 L of dioxane with bisphenol-A, formaldehyde, and amine in the molar ratio of 1 : 4 : 2. Polycarbonate grade bisphenol-A was supplied by Shell Chemical. The formaldehyde (37% in water), aniline (99.5%), and methylamine (40% in water) were purchased from Aldrich Chemical Company and were used without further purification. A detailed description of the synthesis procedure and molecular characterization was previously described.[1] The as-synthesized benzoxazines were shown to contain monomer and small amounts of oligomeric species. As a result, a portion of the as-synthesized materials was subjected to a base-washing treatment to extract pure monomer from any small oligomers or unreacted amine.[1]

Rheological analysis was performed utilizing a Rheometrics dynamic mechanical spectrometer (model RMS-800) equipped with a 2000 g cm force-rebalance transducer. A forced air convection oven surrounded the test fixture, allowing elevated temperature control to better than 0.5°C. Samples where subjected to dynamic shear in a 25-mm parallel plate geometry using disposable aluminum plates.

Two different types of isothermal cure studies were initiated. The evolution of rheological properties was measured under isochronic cure conditions for each of the different benzoxazine materials at a frequency of 1 Hz (6.28 rad/s). An initial strain of 5% was applied to each sample and decreased throughout the course of the cure experiment so that the materials remained within their viscoelastic regimes and did not exceed the torque range of the spectrometer. A gap of 0.8 mm was maintained between the plate surfaces.

For the washed materials, a multiple frequency rheological analysis was also performed in which the curing material was subjected to a cyclic strain applied by means of a composite waveform. This wave was generated by the superposition of a 1.57 rad/s fundamental frequency with four of its integer multiples (4, 6, 10, 30). One cycle of this wave shape and its corresponding maximum strain is presented in Figure 1, while the individual frequency components and their associated strains are summarized in Table I.

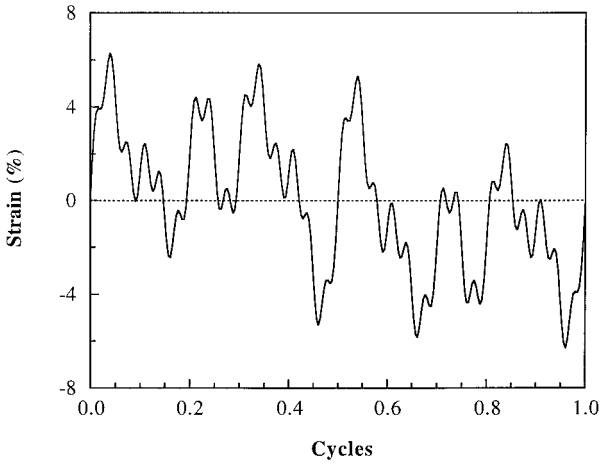


Figure 1 A composite waveform used in the multifrequency cure analysis of washed BA-m and BA-a.

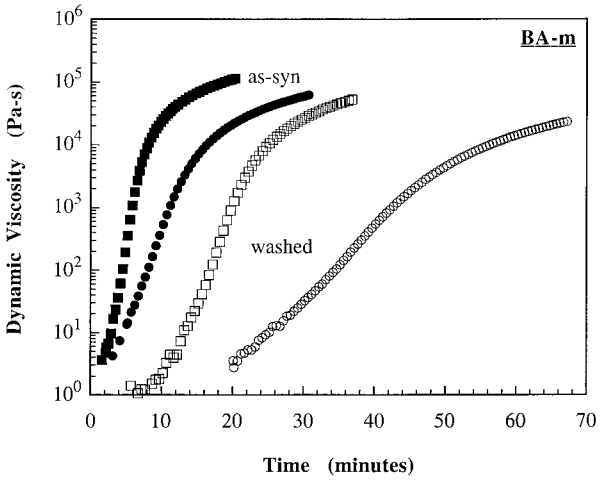
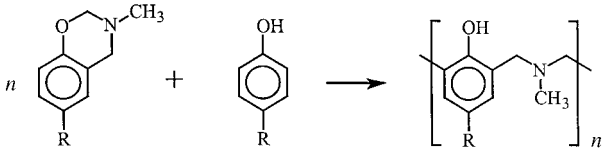


Figure 2 A comparison of the rates of dynamic viscosity increase during isothermal cure for as-synthesized BA-m benzoxazine [(●) 145°C, (■) 155°C] and washed BA-m benzoxazine [(○) 145°C, (□) 155°C].

RESULTS AND DISCUSSION

The BA-a and BA-m materials cure to high molecular weight species by a reaction that involves the opening of the benzoxazine rings. This ring-opening reaction can be initiated by free phenolic species as shown below for the BA-m precursor:



Because these benzoxazine materials are multifunctional, they may be polymerized into a 3-dimensional, crosslinked network structure.

Dynamic mechanical analysis allows continuous monitoring of the evolution of viscoelastic properties as a thermosetting resin cures from a low viscosity liquid, through gelation, and up to the onset of vitrification. This occurs as the benzoxazine is transformed from a low molecular weight monomer and oligomers into a high molecular weight, crosslinked polybenzoxazine structure. The increase in dynamic viscosity during a typical isothermal, isochronic polymerization of BA-m is shown in Figure 2 for both as-synthesized and washed materials. As one can see for the curing reactions at 145 and 155°C, the viscosity of the as-synthesized material evolves significantly faster than the washed material and thus must be reacting more quickly. The BA-a materials, shown in Figure 3 also exhibit a simi-

Table I Individual Frequency and Strain Components of Composite Waveform Used in Multifrequency Cure Analysis of BA-m

Multiplier	Frequency (rad/s)	Strain (%)
1	1.57	2
4	6.28	2
6	9.42	2
10	15.7	2
30	47.1	1

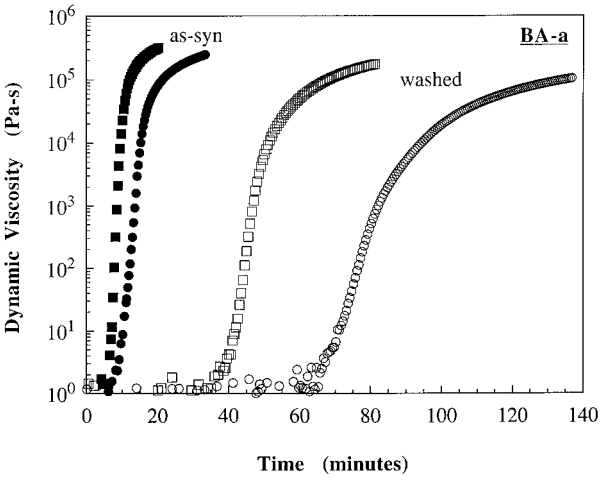


Figure 3 A comparison of the rates of dynamic viscosity increase during isothermal cure for as-synthesized BA-a benzoxazine [(●) 170°C, (■) 180°C] and washed BA-a benzoxazine [(○) 170°C, (□) 180°C].

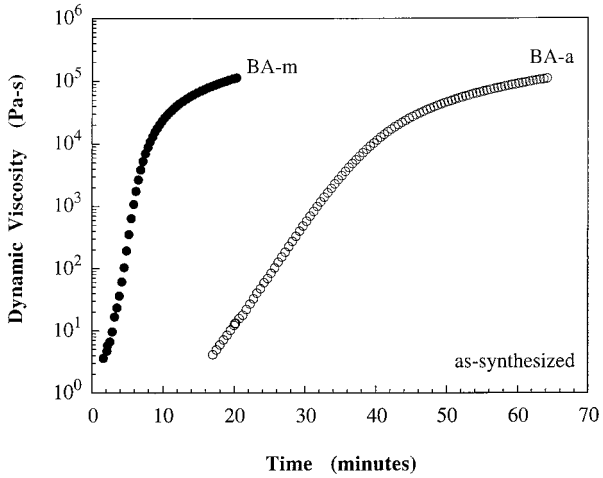


Figure 4 A comparison of the rates of dynamic viscosity increase during isothermal cure at 155°C for the as-synthesized (●) BA-m and (○) BA-a.

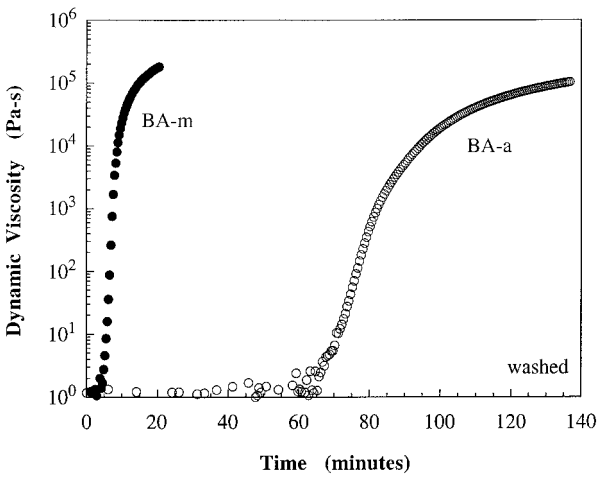


Figure 5 A comparison of the rates of dynamic viscosity increase during isothermal cure at 170°C for the washed (●) BA-m and (○) BA-a.

lar behavior with the as-synthesized material reacting faster than the washed.

These viscosity diagrams demonstrate that both the as-synthesized and washed materials may be thermally cured without the use of an external initiator. It was previously shown that the benzoxazine ring may be opened by phenolic species.[24] The dimers and other higher oligomers of the as-synthesized precursors contain sufficient free phenolic groups to catalyze the ring-opening reaction. Because the washed materials contain primarily monomeric benzoxazine, there are few free phenolic species available to initiate the ring-opening reaction. However, Reiss et al. showed that polymerization of the monomer may be thermally initiated by self-dissociation of the oxazine ring at elevated temperatures.[24] This induction period, as the benzoxazine ring thermally dissociates, causes a delay in the polymerization and subsequent viscosity increase for the washed materials. The as-synthesized materials already contain sufficient amounts of the initiating species and thus may begin to polymerize almost immediately upon exposure to elevated temperatures. Consequently, the as-synthesized materials react more quickly than the washed benzoxazines and exhibit the sharp increase in viscosity much sooner.

A qualitative comparison of the rates of reaction for the BA-m and BA-a materials as determined by the viscosity increase for isothermal cure at 155°C is shown in Figure 4. The BA-m material reacts much faster than BA-a at any given temperature. It may be initially postulated that this faster rate of reaction is due to a greater concentration of oligomeric species present in BA-m than the BA-a material. Although BA-m was shown to contain more oligomeric species,[1] this theory fails to explain why it reacts faster than BA-a, even when both are in washed form and have few dimeric or higher oligomeric species present (Fig. 5). From these differences in the reaction rates for the washed form it appears that the thermally initiated polymerization of the benzoxazine ring is easier and thus more rapid when it contains a methyl substituent rather than a phenyl ring attached to its nitrogen component.

Figure 6 shows the evolution of the dynamic

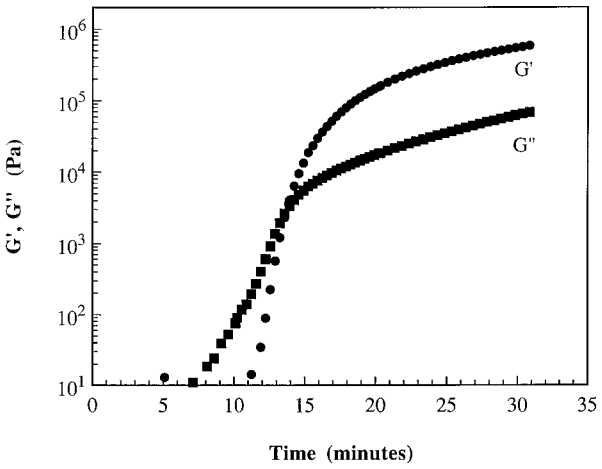


Figure 6 The evolution of the storage modulus, (●) G', and loss modulus, (■) G'', as a function of time for the isothermal cure of washed BA-m at 160°C.

Table II Gelation Times of As-Synthesized BA-m Benzoxazine as Determined from Isochronic, Isothermal Cure Studies

Temperature (°C)	Crossover (min)	Rate Equivalence (min)
130	58.8	45.7
140	19.4	16.7
145	12.0	10.2
150	8.3	7.3
155	5.9	5.2

Table IV Gelation Times of As-Synthesized BA-a Benzoxazine as Determined from Isochronic, Isothermal Cure Studies

Temperature (°C)	Crossover (min)	Rate Equivalence (min)
155	40.7	36.7
160	26.6	24.7
165	20.2	18.7
170	15.1	14.3
175	12.8	12.2
180	10.0	9.2

moduli versus time for the cure of washed BA-m at 160°C. This cure profile shows a number of characteristics common to all of the isothermal, isochronic cures of the benzoxazine material. In the initial stages of reaction, the curing material has a very low viscosity and is below the sensitivity range of the transducer. As the reaction proceeds and the viscosity changes become detectable, both the loss modulus, G'', and storage modulus, G', increase with time. At this point the loss modulus is much greater than the storage modulus, indicating the very fluid nature of the system. As the benzoxazine molecules lengthen and start to build internal structures, the storage modulus begins to increase at a faster rate than the loss modulus, resulting in an intersection of the two moduli curves. The time at which these curves intersect or cross one another is often utilized as the point of gelation for a reactive system. Although it was shown that this is strictly valid only for a few specific systems, the crossover point does occur, at least, within the vicinity of gelation. In the later stages of the polymerization reaction, the material becomes an elastic solid and thus has a modulus that is dominated by its storage component. To simplify the initial studies of the BA-m and BA-a benzoxazines, we assumed that the crossover point corresponds to the instant of gelation. Later, the *critical gel* and its frequency dependence is also investigated and compared to the crossover results.

The gelation times of the as-synthesized and washed BA-m materials as determined by the moduli crossover point in the isothermal, isochronic cure studies are summarized in Tables II and III, respectively. Similar data is presented in Tables IV and V for the as-synthesized and washed BA-a benzoxazines. For experiments in which the moduli crossover occurred between measurements, a linear interpolation was performed on each curve for the points just prior and just subsequent to the crossing over of the moduli. The point of gelation was then estimated as the time at which these interpolated curves intersect.

The reacting material just prior to crossover gelation may also be described in another manner. In all of the isothermal cures of benzoxazine, it is evident that the loss component of the dynamic modulus initially increases at a faster rate than the storage component, but later a reversal

Table III Gelation Times of Washed BA-m Benzoxazine as Determined from Isochronic, Isothermal Cure Studies

Temperature (°C)	Crossover (min)	Rate Equivalence (min)
140	68.3	61.1
145	44.2	40.7
150	29.2	27.2
155	19.5	18.2
160	13.7	12.9
165	9.6	9.2
170	7.0	6.5

Table V Gelation Times of Washed BA-a Benzoxazine as Determined from Isochronic, Isothermal Cure Studies

Temperature (°C)	Crossover (min)	Rate Equivalence (min)
160	167.8	162.2
170	90.0	87.7
180	67.4	66.1
190	39.9	39.1
200	26.4	25.6
210	17.2	16.1

takes place such that G' increases more quickly than G''. Obviously, there must be an instant at which the rates of increase of the storage and loss components of the dynamic modulus are equal. Ishida and Smith[25] postulated that at the time of the equal rate increase, the curing reaction is at a stage where considerable flow properties are still observed, yet the elasticity of the system is increasing at the same rate as a result of the physical chain interactions and chemical crosslink formation. For the isothermal cure of the benzoxazines, the equivalence of a rate increase was determined as the point at which the time derivatives of the dynamic moduli components (dG'/dt and dG''/dt) become equal. These results are also shown in Tables II and III for the BA-m materials and in Tables IV and V for the BA-a benzoxazine.

According to gelation theory, a material reaches its gel point at a critical extent of reaction.[26] Thus, the critical gel is an isoconversion property of any given thermosetting system and will occur at the same conversion, regardless of cure temperature, if the polymerization proceeds with a single cure mechanism. The following general expression can be used to define the rate of polymerization for our systems:

$$d\alpha/dt = kf(\alpha) \tag{4}$$

where k is the reaction rate constant and $f(\alpha)$ is a function of conversion that depends on the mechanism of polymerization. Because the chemical conversion, α_{gel}, at the instant of gelation, t_{gel}, is constant for any given system, the above equation may be integrated such that

$$\int_0^{\alpha_{gel}} \frac{d\alpha}{f(\alpha)} = \text{(C)onstant} = k \int_0^{t_{gel}} dt = kt_{gel} \tag{5}$$

Assuming that the kinetic rate constant follows an Arrhenius-type dependence on the cure temperature,

$$k = A \exp(-E_a/RT) = C/t_{gel} \tag{6}$$

and

$$\ln t_{gel} = \ln(C/A) + E_a/RT \tag{7}$$

The activation energy of the polymerization reaction may be calculated by plotting the time to gelation against the inverse of the isothermal cure temperature. For both the as-synthesized and washed BA-m materials, the times for moduli crossover and equal rate increase from the isothermal cure reactions are plotted against the inverse temperature in Figure 7. In order to calculate the activation energies, a linear regression analysis was performed on each data set. In each case, the correlation coefficient of the fitted line was better than 0.99. The activation energy of the gelation process as calculated from the crossover data was 32 kcal/mol for the as-synthesized BA-m benzoxazine and 28 kcal/mol for the washed materials. For the rate of the moduli increase data, activation energies of 30 and 27 kcal/mol were found for the as-synthesized and washed BA-m materials, respectively.

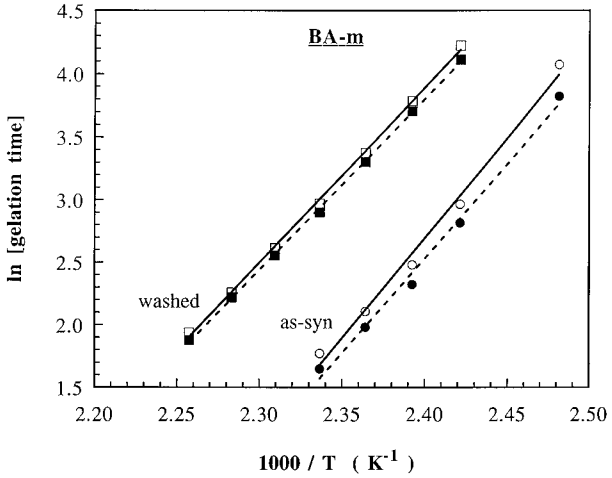


Figure 7 An Arrhenius plot of gelation time vs. the inverse cure temperature for washed BA-m [(□) crossover, (■) rate equivalence] and as-synthesized BA-m [(○) crossover, (●) rate equivalence].

This activation energy data is significant for a number of reasons. First, for both methods of calculation, the activation energies of the as-synthesized and washed materials are nearly identical. Any differences in their values may be attributable to the uncertainty with which they are calculated. This indicates that the as-synthesized and washed BA-m materials polymerize to a gelled state by the same mechanism. Thus, as postulated earlier, the differences in curing rates may be entirely attributable to different amounts of initiating species present when the reaction commences. The as-synthesized material, because of the presence of dimers and other low molecular weight oligomers, has sufficient free phenolic species to begin initiation almost immediately after exposure to elevated temperatures.

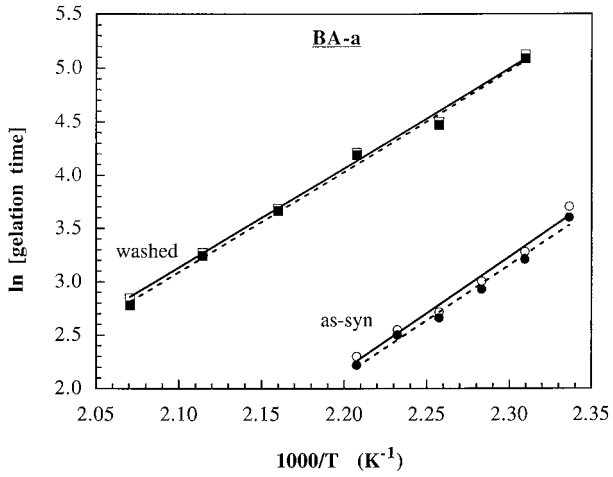


Figure 8 An Arrhenius plot of gelation time vs. the inverse cure temperature for washed BA-a [(□) crossover, (■) rate equivalence] and as-synthesized BA-a [(○) crossover, (●) rate equivalence].

The washed materials, however, contain few oligomers and therefore few initiating species. Consequently, propagation does not begin until after an induction period, during which the benzoxazine ring may thermally dissociate and eventually provide sufficient free phenolic species to begin propagation. Once propagating, the washed and as-synthesized BA-m materials would both appear to follow the same polymerization mechanism.

The activation energies as determined by the two different methods (crossover and equivalence of rate increase) appear to be very similar. For both the washed and as-synthesized materials, the activation energy as calculated by rate equivalence is slightly lower than that calculated by the crossover method. Again, the differences may be within the error of measurement. In any case, it would appear that the phenomenon responsible for causing the equivalence of rate increase is in fact related to the gelation process. Further discussion of this significance is presented with the multifrequency work.

The Arrhenius plots for the BA-a benzoxazines are shown in Figure 8. Again, linear regression provided a fitted line for each data set with a correlation coefficient of better than 0.99. This indicates that a single mechanism is governing the process of polymerization and gelation. For the as-synthesized BA-a, an activation energy of 21 kcal/mol was calculated from both the rate equivalence and crossover data. Similarly, the washed material provided an activation energy of 19 kcal/mol for each method. Once again it appeared that the washed and as-synthesized materials were polymerized by the same mechanism. As before, the differences in their gel times are attributable to the presence of oligomeric species available for initiation in the as-synthesized BA-a. The identical activation energies provided by the two different methods of calculation provide further credibility for using the time of moduli rate equivalence as an indication of the onset of gelation. Analysis of the BA-a benzoxazines by differential scanning calorimetry showed similar activation energies in the range of 24–26 kcal/mol.[27]

As discussed earlier, the intersection of G' and G'' in the cure of a thermosetting material corresponds to chemical gelation in only a few very specific systems, which are those in which the relaxation exponent is equal to $\frac{1}{2}$. For the majority of systems, this technique is only sufficient to provide an estimation of the time of gelation. Thus, detection of the true chemical gel point, or critical gel, is more complicated for systems with relaxation exponents that are unknown or are not equal to $\frac{1}{2}$. But, because the dynamic moduli in these systems follow the same power law at the gel point, their moduli are parallel. Consequently, the loss tangent, $\tan \delta = G''/G'$, of the critical gel is independent of the frequency of the dynamic rheological experiment. Holly and coworkers[28] designed a multifrequency experiment utilizing Fourier transform mechanical spectroscopy for detecting the gel point based on this approach. The advantage of this technique lies in its ability to simultaneously measure the rheological properties of an evolving system over a wide range of frequencies. With this method, the molecular structure being probed is then nearly constant during the course of each measurement, even for reactive systems.

The isothermal cure experiments on the washed BA-m and BA-a materials were repeated using a variation of this multifrequency approach. These experiments allowed frequency sweeps spanning nearly two decades to be collected every 30 s during the polymerization of the material. The gel point is determined by plotting G' and G'' versus the frequency on a log–log scale for each rate sweep. The curing material has first reached its critically gelled state at the instant in which the storage and loss moduli display a parallel dependence on frequency.

Figure 9 shows the frequency dependence of the evolving storage and loss moduli for the BA-m

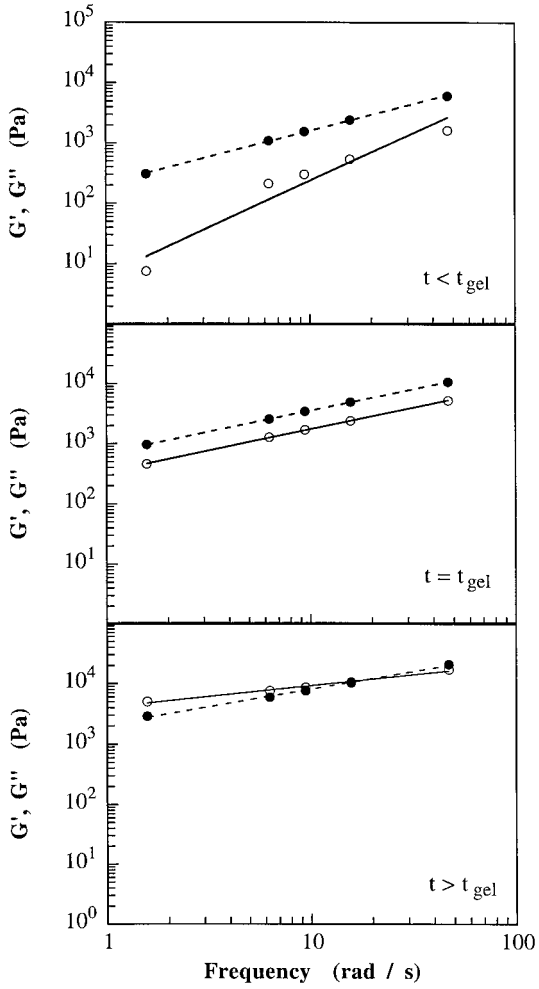


Figure 9 The frequency dependence of the (○) storage and (●) loss moduli prior to gelation (top), at the time of critical gelation (middle), and after gelation occurs (bottom) and crossover begins. The slopes of the moduli correspond to the relaxation exponents at each stage of cure.

system as it is isothermally cured at 150°C. As can be recalled from the earlier expression relating dynamic moduli, the relaxation exponents for each frequency sweep are equal to the slope of the dynamic moduli as determined by a linear regression analysis of this logarithmic data. During the initial stages of cure, the fluid nature of the reactive system dominates and thus the loss modulus has a greater magnitude than the storage component throughout each frequency sweep. The storage modulus, however, shows greater frequency dependence than the loss modulus and has a higher relaxation exponent. At the gel point, G' and G'' have an identical dependence on frequency, show a parallel relationship, and therefore have identical relaxation exponents. It should be noted that G'' is greater than G' at the critical gel state of this material and all others that have critical relaxation exponents greater than $\frac{1}{2}$. Consequently, the critical gel occurs prior to the crossover point in these systems and thus using the crossover point overestimates the time to gelation. Beyond the gel point, the loss modulus shows a greater frequency dependence as the system is beginning to behave more like an elastic solid and shows evidence of moduli crossover.

From the power law equation at the gel point, the ratio of the dynamic moduli, tan δ, may be used to determine the time of gelation and the corresponding value of the relaxation exponent.

$$\tan \delta = \frac{G''}{G'} = \tan\left[\frac{n\pi}{2}\right] \tag{8}$$

When tan δ is plotted as a function of time for each of the individual frequencies, as shown in Figure 10 for washed BA-m at 155°C, the gel point occurs where the tan δ curves intersect and thus are independent of frequency. From this intersection point, the exact gel time and the relaxation exponent are determined and are summarized for the multifrequency analysis of BA-m in Table VI.

Now that the multifrequency data has been obtained, the activation energy for the formation of the true critical gel can be calculated. The Arrhenius plot of the critical gelation times for the washed BA-m benzoxazine is presented in

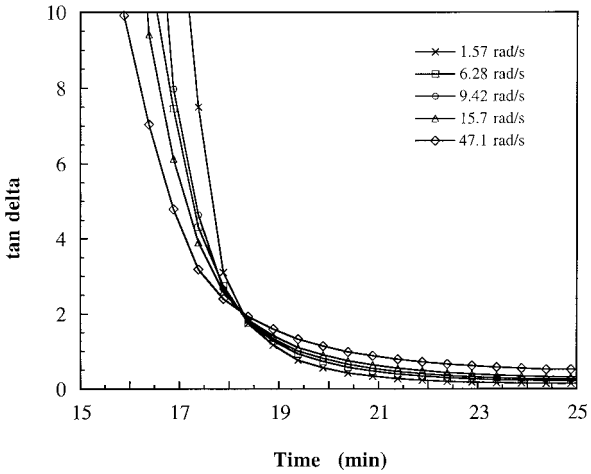


Figure 10 The tan δ plotted as a function of curing time for the individual frequencies of washed BA-m cured at 155°C.

Table VI Gelation Times and Corresponding Relaxation Exponents for Washed BA-m Benzoxazine as Determined from Multifrequency Cure Studies

Temperature (°C)	Critical Gelation (min)	Relaxation Exponent (n)
145	41.5	0.71
150	28.3	0.72
155	18.4	0.70
160	13.2	0.71
165	9.9	0.68
170	6.7	0.70

Figure 11. The crossover and rate equivalence data are also included for comparative purposes. The activation energy for critical gelation is calculated to be 27 kcal/mol, which is nearly identical to the activation energies of 28 and 27 kcal/mol calculated by the crossover and rate equivalence methods.

As can be seen in Figure 11 or from the tables, the times to gelation for the critical gel appear to fall between the values for the rate increase and crossover. For all but one of the isothermal cure temperatures, the rate equivalence condition is detected first, followed by critical gelation, and then finally the crossover of the dynamic moduli. Recent multifrequency studies of bisphenol-A/epoxy systems demonstrated a similar trend in the

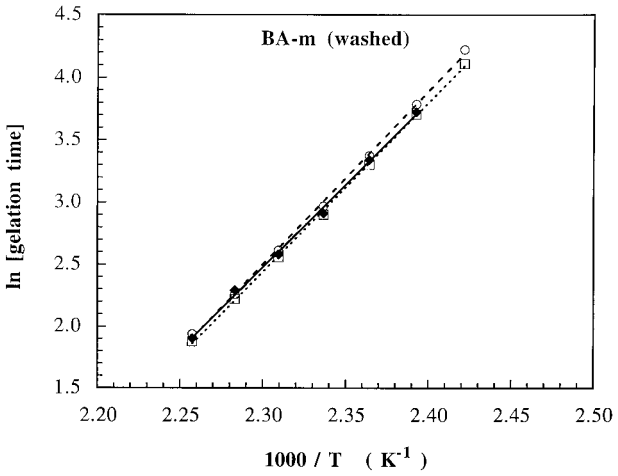


Figure 11 An Arrhenius plot for the calculation of activation energies for the washed BA-m benzoxazine using gelation times determined by the (○) moduli crossover, (◆) critical gelation, and (□) equivalence of rate increase.

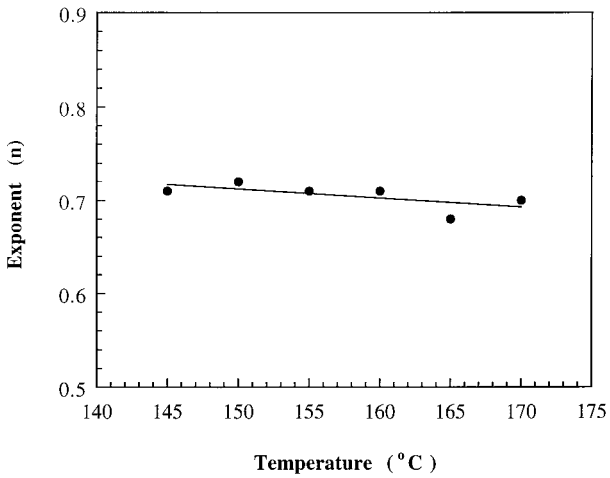


Figure 12 The relaxation exponent, n, from critical gelation as a function of cure temperature.

ordering of the gelation events.[29] Although far from conclusive, it would appear that the isochronic rate increase and crossover data may be sufficient for some systems to predict critical gelation without resorting to the more complex multifrequency analysis.

The relaxation exponent is a network specific parameter that is related to the distribution of cluster sizes in a material. As shown in Figure 12, the relaxation exponent of the critical BA-m gel is nearly constant with cure temperature. This indicates that the structure of the newly formed network at the gel point is also nearly constant, regardless of the cure temperature. This provides strong evidence in favor of the previous contention that gelation is an isoconversion property and has the same extent of reaction, no matter what the temperature of polymerization.

The range of relaxation exponent values found for the washed BA-m benzoxazine (n = 0.68–0.72) agrees well with those predicted by theoretical approaches that model the gelation of crosslinking systems. Simulations utilizing percolation theory under the assumption that elasticity is purely entropic in nature predict values of n = 0.7. Assuming no hydrodynamic interactions between polydisperse polymeric clusters, the Rouse model predicts $n = \frac{2}{3}$.[30] Thus, the value of the relaxation exponent for the BA-m is nearly identical to those predicted by both percolation and Rouse theories. It is doubtful that dynamic rheological experiments are sufficiently sensitive to resolve differences this small. Winter also showed similar values of n = 0.7 for polyurethane systems that were deficient in crosslinker.[21] The BA-m benzoxazine was

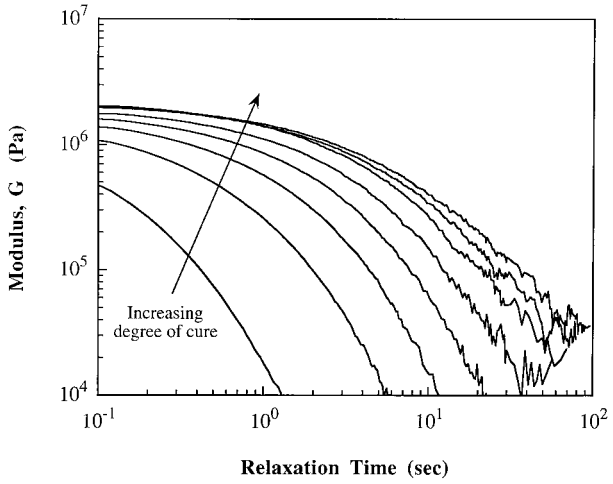


Figure 13 Stress relaxation spectra obtained during the isothermal cure of BA-a benzoxazine at 210°C. Collection of the first spectrum shown was initiated at t = 6 min, while the last was begun at t = 27 min.

shown to have a low crosslink density[2] and therefore may behave as though it were deficient in crosslinker.

The BA-a benzoxazine was also analyzed by a multifrequency analysis. However, this material did not show critical gel behavior. The G' exhibited a nonlinear behavior when plotted on a log–log scale versus frequency and made subsequent critical gel determination impossible. For further investigation of this rather odd behavior, stress relaxation experiments were periodically performed on the BA-a material during cure at a temperature well above the glass transition. Figure 13 shows this series of spectra taken from stress relaxation experiments performed on the material at increasing degrees of cure. It is clear from the relaxation spectra that the BA-a material fails to develop the equilibrium modulus that is typically associated with a crosslinked material, even at times far beyond the moduli crossover. However, the benzoxazine structure was shown to be susceptible to large amounts of intermolecular and intramolecular hydrogen bonding even at elevated temperatures.[31] It is hypothesized that this hydrogen bonding interferes with network formation during the ring-opening polymerization and may limit network growth to a highly branched but unconnected structure. However, this hydrogen bonding is also believed to contribute significantly toward chain interactions and may lead to the gel-like behavior that was observed in the isochronic measurements.

CONCLUSIONS

The ring-opening polymerization of the benzoxazine resins was monitored by a rheological analysis of the curing process utilizing both conventional isochronic and a new multifrequency approach that can observe the critical gel. The attainment of gelation was detected by three distinct methods, including equivalence of the rate of change of the dynamic moduli, critical gelation, and crossover of the storage and loss moduli. The Arrhenius nature of the gelation times allowed activation energies to be calculated for the gelation process of each material.

The as-synthesized benzoxazines were demonstrated to polymerize much faster than their washed counterparts. It was shown by activation energy considerations that these materials must polymerize by the same mechanism, and thus differences in reaction rate are primarily due to the presence of initiating species in the as-synthesized materials. Although the methylamine-based benzoxazine has a higher activation energy for the gelation process than the BA-a benzoxazine at around 28 versus 21 kcal/mol for BA-a, BA-m appeared to be more reactive than the BA-a benzoxazine.

The washed BA-m material was found by multifrequency experiments to have a relaxation exponent in the range of 0.68–0.72 and was relatively insensitive to temperature. Because the relaxation exponent is a network specific parameter relating to cluster size, it appears that the material polymerizes to the same structure at the gel point, regardless of cure temperature, and thus supports the isoconversion at gelation arguments. The value of the relaxation exponent for the BA-m system agrees well with Rouse and percolation predictions and, because of its low crosslink density, is similar to that found experimentally in polyurethane materials that are deficient in crosslinker.

The BA-a material did not display a critical gel behavior in the multifrequency experiments. Rather, this material may be only highly branched, not chemically crosslinked, but may contain sufficient interactions to display the gel-like behavior during isochronic measurements.

REFERENCES

1. Ning, X.; Ishida, H. J Polym Sci Chem Ed 1994, 32, 1121.

2. Ishida, H.; Allen, D. J. J Polym Sci Phys Ed 1996, 34, 1019.
3. Lipshitz, S. D.; Macosko, C. W. Polym Eng Sci 1976, 16, 803.
4. Apicella, A.; Massi, P.; Nicolais, L. Rheol Acta 1984, 23, 291.
5. Adam, M.; Delsanti, M.; Durand, D. Macromolecules 1985, 18, 2285.
6. Farris, R. J.; Lee, C. Polym Eng Sci 1983, 23, 586.
7. Babayevsky, P. G.; Gillham, J. K. J Appl Polym Sci 1973, 17, 2067.
8. Gillham, J. K. Polym Eng Sci 1986, 26, 1429.
9. Enns, J. B.; Gillham, J. K. J Appl Polym Sci 1983, 28, 2567.
10. Wisanrakkit, G.; Gillham, J. K.; Enns, J. K. J Appl Polym Sci 1990, 41, 1895.
11. Simon, S. L.; Gillham, J. K. J Appl Polym Sci 1992, 46, 1245.
12. Senich, G. A.; MacKnight, W. J.; Schneider, N. S. Polym Eng Sci 1979, 19, 313.
13. Wingard, C. D.; Beatty, C. L. J Appl Polym Sci 1990, 40, 1981.
14. Hoffman, K.; Glasser, W. G. Thermochim Acta 1990, 166, 169.
15. Lee, C. Y.-C. Polym Eng Sci 1988, 28, 578.
16. Khanna, Y. P.; Kumar, R.; Das, S. Polym Eng Sci 1990, 30, 1171.
17. Tung, C. Y. M.; Dynes, P. J. J Appl Polym Sci 1982, 27, 569.
18. Winter, H. H.; Chambon, F. J Rheol 1986, 30, 367.
19. Chambon, F.; Winter, H. H. J Rheol 1987, 31, 683.
20. Winter, H. H. Polym Eng Sci 1987, 27, 1698.
21. Winter, H. H.; Morganelli, P.; Chambon, F. Macromolecules 1988, 21, 532.
22. Reiss, G.; Schwob, J. M.; Guth, G.; Roche, M.; Laude, B. In Advances in Polymer Synthesis; Culbertson, B. M.; McGrath, J. E., Eds.; Plenum: New York, 1985.
23. Ishida, H.; Smith, M. E. Rheol Acta 1991, 30, 184.
24. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953.
25. Ishida, H.; Rodriguez, Y. Polymer 1995, 36, 3151.
26. Holly, E. E.; Venkataraman, S. K.; Chambon, F.; Winter, H. H. J Non-Newtonian Fluid Mech 1988, 27, 17.
27. Smith, M. E. Ph.D. Dissertation, Case Western Reserve University, 1993.
28. Lairez, D.; Adam, M.; Emery, J. R.; Durand, D. Macromolecules 1992, 25, 286.
29. Wirasate, S.; Dhumrongvaraporn, S.; Allen, D. J.; Ishida, H. J Appl Polym Sci 1998, 70, 1299.