Critical Gel Phenomena in the Rheology of Epoxide Network Formation

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ABSTRACT: Multiple frequency dynamic mechanical experiments are generated by the linear addition of harmonic sinusoidal waves in order to study the gelation behavior of a crosslinking epoxy-bisphenol-A copolymerization. The following three criteria are investigated as kinetic parameters for the network formation: equivalence of the moduli increase, the critical gel condition, and the mechanical gel condition. The effect of strain magnitude is investigated for both the gelation phenomena and the scaling exponent of the critical gel behavior. The exponent is found to vary from 0.85 to 0.65, depending on the reaction temperature and waveform of the strain input. When Arrhenius type behavior is found, the activation energy of the gelation process is found to be 21 ± 1 kcal/mol. The effects of vitrification, network rupture, and nonlinear viscoelastic response were found with respect to the frequency probe. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 593-600, 1999

Key words: critical gel; dynamic mechanical analysis; epoxy resin; bisphenol A; network structure

INTRODUCTION

Gelation behavior of thermosetting polymers has received great attention over the past three decades. While the practical aspects of determining suitable processing conditions has been a principle driving force for this attention, the fundamental question of the true rheological nature of gels also influenced the researchers' efforts. Many practical methods have been suggested as standard methods of gel point determination,¹⁻⁶ each appropriate for various applications. One of the more popular techniques involving forced oscillatory analysis was proposed by Tung and Dynes,⁷ where the gel point was defined as being the condition at which the storage (G') and loss (G'') moduli were equal during the curing reaction.

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The universality of this condition was prohibited, as the authors explained, by the dependence of this rheological condition on the frequency of the experimental measurement.

The most active and significant advances in gelation analysis of crosslinking resin systems was presented by Winter and coworkers.^{8–15} Employing a parameter to describe a curing polymer in terms of a gel strength, the rheological behavior at the point of gelation could be completely described. Most relevant to the technique is the relationship between the moduli, as follows:

$$G'(\omega) = G''(\omega)/\tan(n\pi/2)$$
$$= \Gamma(1-n)\cos(n\pi/2)S\omega^{n}$$

where S denotes the gel strength of the material at the condition of critical gelation. The exponent n has been found experimentally to have a value 0 < n < 1.0; the strength does appear to be

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coupled to the exponent n through a characteristic material function, as follows:

$$S = G_0 \lambda_0^n$$

where G_0 and λ_0 are constants of the precursor material, and *n* retains dependence upon composition of the reactants.

Theoretical attempts at modeling the gelation of crosslinking systems most frequently rely upon percolation arguments to describe the dimensionality of the gel. Predictions of the relaxation exponent n are bound explicitly by the fractal dimension employed. Through the recent literature, $^{16-20}$ the exponent n has been shown to have a value of $\frac{1}{2}$ under conditions of swelling of the percolation clusters; $\frac{2}{3}$ when corrections for polydispersity are considered; $\frac{1}{3} - \frac{3}{5}$ considering simple Rouse-type, monodisperse molecules; and, finally, 0-1.0 when the fractal dimensions are allowed to lie within the range of $1 \le d_f \le 3$.

The correlation of gel characteristics with respect to chemical structure and molecular architecture remains unclear. In this article, a practical approach to the characterization of a copolymerizing epoxy system is presented. Since the viscoelastic properties of this system are known to exhibit significant thermal dependence due to the physical interactions of the molecular architecture, the value of the scaling exponent n is sought for comparison with other chemical systems. Additionally, it is with equal emphasis that new rheological methods for the kinetic analysis of crosslinking systems are investigated.

EXPERIMENTAL

The reactions were carried out with Epon 825 and polycarbonate grade bisphenol-A, both manufactured by Shell Chemical. The reaction was catalyzed by the addition of 2% by weight *p*-chlorophenyl-1,1,dimethylurea (DuPont). The isomeric bisphenol, 3,4'bisphenol-A was manufactured by Mitsui Petrochemicals, Ltd. All materials were used as received without further purification.

Samples were prepared within the test fixture immediately prior to the measurements. The resin was prepared as a two part system of epoxy with catalyst, and epoxy with bisphenol-A and isomeric bisphenol-A. The isomer was incorporated at a level of 10% of the total bisphenol content in order to reduce the melting point of

Table I Waveform Contributions for Multifrequency Dynamic Cure Studies Principle Frequency Equal to 1.57 rad/s

Rate (rad/s)	Low Strain (%)	Medium Strain (%)	High Strain (%)
1.57	3	3	5
3.14	2	3	5
6.28	2	3	5
9.42	1	3	5
15.7	1	3	5
47.1	1	2	5
78.5	1	2	5
Maximum	6.84	13.8	24.7

bisphenol-A. The two-component composition allows equal volume delivery of each resin part to obtain the desired chemical stoichiometry. For this study, the stoichiometric ratio of epoxy to bisphenol-A was maintained at a value of 1.0 (mol epoxy/mol bisphenol). The liquid resin was dispensed directly on the preheated fixture and mixed mechanically.

All rheological experiments were performed on a Rheometrics RMS-800 dynamic mechanical spectrometer. The instrument is equipped with a force rebalance transducer with an upper limit of 2000 g/cm, a forced air oven for temperature control of ± 0.5 °C, and Rhios and Recalc software. Thermal equilibrium was found to be reestablished within 3 min of the sample loading. Samples were studied in parallel plate geometry using 25-mm diameter plates.

The multiple frequency experiments were designed on a fundamental frequency of 1.57 rad/s. Harmonic multipliers of 2, 4, 6, 10, 30, and 50 were employed for the waveform. Three different strain levels were employed for the investigation of critical gelation phenomena. The rates and corresponding strains are listed in Table I and will be correspondingly be designated as low, medium, and high strain throughout this article.

RESULTS AND DISCUSSION

The isothermal cure experiments reported in our previous work²¹ were repeated using the multiple frequency capability. The results are now interpretable in two distinct manners. Isochronic measurements, namely, the viscoelastic properties as a function of a single frequency, are decoupled



Figure 1 Isochronic plot of isothermal reaction at 130° C, $\omega = 1$ Hz, G' (l), G" (n).

from the material response as a function of the seven individual frequencies contained within the input waveform. Frequency sweep measurements are collected at 30-s intervals during the reaction. It is the second method of analysis that becomes most useful in the analysis of gelation during the copolymerization. Since each frequency sweep is performed within a matter of seconds, there is no significant change in the molecular structure during the data acquisition.

Figure 1 presents the isochronic plot at 1 Hz for curing with the low strain conditions, at 130°C. As expected, the initial rapid increase is seen for both G' and G''. For the long reaction time, the curves are seen to reach plateau values with the storage modulus greater than the loss modulus. The point of intersection of the storage and loss moduli curves is also apparent at 22 min. This point will be referred to as the existence of the mechanical gel.

While it is now nearly unanimously recognized that the intersection of G' and G'' does not define the gel point of the material, the multiple frequency experiment dramatically illustrates the effects of strain rate upon this condition. Figure 2 represents the behavior or tan δ versus reaction time for the seven frequencies probed. The difference in times at which the curve intersects the value of 1.0, where G' = G'', clearly demonstrates that the mechanical gel is almost an arbitrary measure of the kinetic state of the sample.

As mentioned earlier, the strength of the multiple frequency analysis lies within the ability to determine the material response within the frequency domain. Our choice of harmonic multipli-



Figure 2 Tan δ versus reaction time for 130°C reaction. ω as determined by multipliers in the harmonic waveform. Tan $\delta = 1$ represents mechanical gelation.

ers allows the experiment to probe nearly two decades of frequency in a matter of seconds. Figure 3 shows the results of the 130°C isothermal



Frequency ω [rad/s]

Figure 3 Loss and storage moduli as a function of frequency during the reaction: (A) 16, (B) 18, (C) 20, and (D) 22 min. G'(1), G''(n) critical gel occurs near 18.0 min.

reaction. At short reaction times, the storage and loss moduli curves are well separated. The storage modulus lies below the curve of the loss modulus and exhibits greater curvature within the frequency window. Since the material is similar to a viscous liquid, the frequency dependence of the loss modulus is much lower than the storage modulus.

With continued reaction, the shape of the moduli curves are further altered by the increased structure within the sample. At 18 min, the curves appear parallel to each other indicative of the critical gel formation. This conceptually translates to the material exhibiting the extreme characteristics of both a liquid and solid: an infinite steady shear viscosity and a zero equilibrium relaxation modulus. At this state, the material exhibits identical dependence on frequency for both the storage and loss moduli. For longer reaction times, the G' curve shows less frequency dependence than G'' since the material is becoming more elastic and solid. Within this time frame, the intersection of the two moduli curves becomes apparent, corresponding to the mechanical gel formation noted in the isochronic plots.

Other researchers have reported the effects of large strain (defined as greater than 2%) on the measured rheological properties as the critical gel is reached. Their results indicated that larger strains induce a delay in the gelation as a result of the network disruption. One might then conclude that as a practical measurement of the kinetics of crosslinking systems, the critical gel experiment would have severe limitations in its execution. Most commercial instrumentation employed in this area of characterization is equipped with a large force transducer capable of characterizing the properties of the cured material in its glassy state, as well as the polymerizing resin. With the limitation of low strain, one might expect that many systems could not be well characterized as a result of the low torque response during the curing process.

Figure 4 presents the three input signals selected for our measurements with the total strain indicated for each. In our earlier work, the epoxy system was found to be well behaved at a strain level of 10%, for this reason, the three levels of total strain were chosen to be below the previous total, approximately equal to, and well above the previous total to maximize the torque response for all frequencies.

The appropriateness of these experiments to kinetic analysis was determined by the following



Figure 4 Waveforms for multiple frequency experiments: upper represents low strain; middle, medium strain; and bottom, high strain. Amplitudes and multipliers listed in Table I.

three separate criteria: the time to reach critical gelation, the time to reach mechanical gelation, and, finally, the time at which the rate of increase of both the loss and storage moduli are equal at the frequency of 1 Hz. For the low strain input signal, Figure 5 presents the results of these analyses as a function of isothermal reaction temperature.



Figure 5 Arrhenius plot of gelation times versus inverse reaction temperature for low-strain experiments: Slope equivalence = \Box ; critical gel = \bigcirc ; mechanical gel = \diamond .

If we focus on the critical gel data denoted as the circles, the samples cured at 130°C and above show an Arrhenius-type behavior of the time to reach gelation. The samples at 110 and 120°C appear to follow a retarded response to this behavior with respect to the formation of the critical gel.

The data for the moduli rate of increase with respect to reaction time, denoted by the squares, also shows a decreasing time dependence with increasing reaction temperature; however, the effect only approaches what may be termed Arrhenius-type behavior for the temperatures of 130°C and above. When we inspect the mechanical gel condition, diamond symbols, there is no strong time dependence for this parameter, except for the data of 160°C.

In general, it seems that for the temperatures 130°C and higher, the rate condition occurs first, followed by the critical gel, and, finally, the mechanical gelation. For 120 and 110°C, the critical gel is the earliest event, followed by the rate equivalence, and, finally, the mechanical gel. Activation energies determined for the data of 130–160°C are on the order of 5 ± 1 kcal/mol for the critical gelation and the rate equivalence criterion.

Figure 6 represents the analogous data treatment for the medium strain experiments. The values for times of 110 and 160°C deviate from a straight line fit through the data. Except for the lowest temperature, the rate equivalence precedes the critical gel. Over the temperature range, the mechanical gel does occur last as would



Figure 6 Arrhenius plot of gelation times versus inverse reaction temperature for medium strain experiments: Slope equivalence = \Box ; critical gel = \bigcirc ; mechanical gel = \diamondsuit .

be expected. Determination of activation energies for the 120–150°C temperature range yields values of 21 \pm 1 kcal/mol for all three gelation events.

Finally, we present the results of the high strain measurements in Figure 7. No direct Arrhenius behavior can be extracted from this figure. All of the gelation phenomena suffer from scatter and no consistent trend with increasing reaction temperature. The only clear indication is that the following sequence of the three gelation criteria agrees with the previous data: the rate equivalence, critical gel, and, finally, mechanical



Figure 7 Arrhenius plot of gelation times versus inverse reaction temperature for high-strain experiments: slope equivalence = \Box ; critical gel = \bigcirc ; mechanical gel = \diamondsuit .



Figure 8 Scaling exponent *n* for critical gelation as a function of reaction temperature and applied strain: low strain = \Box ; medium strain = \bigcirc ; high strain = \diamond .

gel for 130°C and higher. At lower reaction temperatures, the critical gel occurs first in the order.

Two observations must be noted at this juncture. For the low strain experiments, the low torque response was found to not only delay the time at which the sample was being accurately measured over the entire frequency range, but that the error in the decoupling of the torque response must be increased. With respect to the high strain experiments, the samples began exhibiting clear nonlinear viscoelastic behavior within the gelation regime. This situation also explains the virtual independence of gelation times on reaction temperature.

At this point, it is logical to attribute the tremendous variation in the experimental results directly to the strain magnitude of the waveform; however, it should also be noted that the component terms may individually influence the observed behavior. That is to say, both the magnitude and the rate of that component have contribution to the results. When either nonlinear measurements or gel damage occur, accurate determination is severely impaired. The nonlinearity will preclude the parallel behavior of the G'and G'' data as a function of frequency; thus, the critical gel behavior will be masked. Gel damage will result in delay in the storage modulus growth as well as possible curvature in the G' versus ω response.

As discussed earlier, the exponent, n can be related to both the gel strength and to the fractal dimension for the percolation models. Figure 8 represents the value of n as a function of reaction temperature for the measurements. The uniform value 0.73 obtained for the reaction temperature of 120°C is striking. Possibly, this results from the uniformity of the glass transition temperature increase as the molecular weight of the copolymer grows. The exponent is much greater, 0.82-0.86 for 110°C. A lower value is obtained for 130°C, ~ 0.62, while *n* varies considerably for the highest reaction temperatures. This data does provide some indication of the gel structures formed during these measurements.

To understand the experimental results, we need to review the isochronic data at equal frequency for the samples under discussion. Presented in Figure 9 is the storage modulus as a function of reaction time for 130, 140, 150, and 160°C reaction temperature. At short reaction times, the storage modulus behaves as expected with increasing reaction temperature, displaying a shorter induction time for the sharp increase. The postgel behavior is normal for 130, 140, and 160°C, where the storage modulus decreases as the reaction temperature is increased, indicative of the temperature dependence of the modulus. However, the modulus for 150°C is dramatically lower. Closer inspection of the curves shows that both the 140 and 150°C cures have subtle plateaus, followed by further increase in the modulus. Most significantly, the plateau occurs after the critical gel for 140°C, but prior to critical gelation in the 150°C experiment. This behavior indicates that the gel is, indeed, being affected by the strain input, most likely through a rupturing process. This data has been found to be reproduc-



Figure 9 Storage modulus versus reaction time for low strain measurements. Reaction temperature: (A) 130, (B) 140, (C) 150, and (D) 160°C.



Figure 10 Schematic representation of the network response during dynamic strain history.

ible with excellent agreement on not only the gelation conditions, but also the plateau appearance and shape.

The behavior of the curing resin with respect to the structural aspects of the samples is depicted in Figure 10. The polymerized epoxy used in the current investigation is known to have a glass transition temperature near 100°C upon complete curing. The anomalous behavior of the critical gel below 130°C can be attributed to the vitrification effect during the molecular weight increase. The strain imparted to the sample is large enough to demonstrate that the material is still quite viscous; however the critical gel appears earlier than kinetically correct. Reaction temperatures of $\sim 30^\circ$ above the T_g show cooperative movement of all chain segments. It is in this regime that the critical gel can occur without thermodynamic chain restrictions. As the temperature is increased further, the material decreases in modulus and becomes susceptible to tearing. While this tearing can be repaired somewhat through continued chemical crosslinking, the bulk morphology can also be skewed toward that of a microgelled system. Finally, higher temperatures still (160°) allow enough flexibility of all length scales within the system so that the critical gel can proceed nearly unperturbed, while the mechanical gel is only slightly retarded as compared to the lower temperatures. It bears emphasis that these experiments were completely reproducible with respect to the gel tearing process for the temperatures reported.

The significance of microgelation was explored for the epoxy resin system. Samples were prepared by first introducing the bisphenol-A to the parallel plate assembly and allowing some cooling to induce crystallization. The epoxy was subsequently added and mixed while small particles of bisphenol A were still visible in the sample. The samples prepared in this manner were capable of crosslinking; however, the inhomogeneity of the structure precluded critical gel formation within the temperature range studied.

At this point, we can postulate on the significance of the exponent with respect to network structure and molecular architecture of the gel. When vitrification effects approach the gel effect at a reaction temperature, two phenomena are expected. First, the reaction begins to become limited by simple chain mobility; however, in our system, this effect should not be especially significant since the crosslinking reaction involves a terminal epoxide group reacting with a secondary hydroxyl group along the copolymer backbone. These hydroxyl groups are in abundant population since they are produced at each epoxy-bisphenol A linkage. The other effect is the increased rigidity of the sample as the glass transition is approached. Continued strain input will jeopardize the existing network structure and lead to some disentanglement and chain breakage. Correspondingly, we have found that the scaling exponent n demonstrates its highest value under these circumstances.

At $T_g + 30$ °C, the exponent is decreased to it's lowest value for the measurements reported. While not thermally restricted, the sample may exhibit enough stiffness at this state to allow a nearly unperturbed continuation of the crosslinking process. We cannot assume, however, that the value of 0.62 is the correct minimum exponent attainable since it is entirely possible for the critical gelation to converge toward the mechanical gelation to yield a value closer to 0.50.

At the highest reaction temperatures, the molecular weight increase is much more rapid and, thus, capable of constructing a coherent structure in the presence of the dynamic probe perturbation. Unfortunately, the increased temperature weakens the chain entanglement strength and apparently promoted the slippage of molecular aggregates or nodes of the network structure. This structural damage yields increased exponential dependence of the moduli on frequency when the critical gelation event occurs.

CONCLUSIONS

Gelation analysis can be performed using three criteria: the rate equivalence of the change in moduli as a function of reaction time, the critical gel, and the mechanical gel. For reaction temperatures of 30°C above the ultimate T_g of the material, these gel conditions occur in the order listed.

When vitrification effects are present, the critical gel will occur prior to the equivalence of the rate.

Arrhenius behavior of the gel times was found over the broadest temperature range for a total strain of 14%. Lower strain input initially suffers from a low torque response and was capable of causing gel damage in the vicinity of the critical gel, while large strains demonstrated nonlinear viscoelastic behavior past the gel point and was determined as retarding gelation with increasing reaction temperature.

The activation energy determined from the multiple frequency experiment employing 14% strain was 21 ± 1 kcal/mol for samples reacted at 120-150°C. The low strain experiments yielded a much lower value of 5 ± 1 kcal/mol for 130-160°C, as determined by the critical gel and rate equivalence times.

The scaling exponent was found to vary with reaction temperature. Values of *n* range from 0.85 at the lowest temperatures to an average value of 0.66 for reaction temperatures of T_g + 30°C.

The additive method of sinusoidal strain input has been successful in the determination of gel time; however, the effects of total strain and component strains is not clear. Considerable care must be exercised in the performance and interpretation of data from this method due to the potential for gel damage and nonlinear viscoelastic effects.

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