

Determining the Gel Point of an Epoxy–Hexaanhydro-4-methylphthalic Anhydride (MHHPA) System

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ABSTRACT: The DEBGA–MHHPA epoxy system has found increasing applications in microelectronics packaging for which the ability to understand and model the cure kinetics mechanism accurately is crucial. The present article reports on the work done to elucidate accurate knowledge of the gel point by rheological methods. To determine the gel point using the G' – G'' crossover method was found not to be accurate, and the gel point obtained by this method was found to be frequency-dependent. Using the gel point where $\tan \delta$ was found independent of the frequency can accurately define the gel point at different temperatures. At the gel point determined by this method, G' and G'' were found to follow the same power law, demonstrating the accuracy of the method in determining the gel point. The scaling exponent obtained was 0.75–0.79. The activation energy for the cure reaction of the system was determined to be 75.1 kJ/mol by the obtained gel times at different temperatures. The steady-shear rheology test was also used to observe the viscosity change at the gel point. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1248–1256, 2000

Key words: gel point; epoxy; activation energy; cure reaction

INTRODUCTION

Interest in the low-viscosity, highly transparent, and excellent electrical insulation epoxy DEBGA–MHHPA system has received increasing attention due to its application in high-grade LEDs, IC die encapsulation, conductive ink paste, adhesives, etc., in the microelectronics industries as well as in structural components using resin transfer-molding techniques. From an application standpoint, the effective use of any thermosetting system requires one to be able to predict the cure kinetics of the system^{1,2} to consistently obtain the maximum possible glass transition temperature³ and also to predict the flow behavior of the curing resin, in particular, to precisely locate when the sol–gel transition occurs. This is because the

polymer can be easily shaped or processed only before the gel point, where it can still flow and be easily formed with the stresses applied relaxing to zero thereafter. Accurate knowledge of the gel point (GP) would therefore allow estimation of the optimal temperature and time for which the sample should be heated before being allowed to set in the mold. The GP is also useful in that it can be used to determine the activation energy for the cure reaction of the system.

The GP for a crosslinking reaction is defined unambiguously as the instant at which the weight-average molecular weight reaches infinity and, as such, is an irreversible reaction. A crosslinking polymer at its GP is in a transition state between a liquid and a solid.^{4,5} At the GP, the molecular weight (MW) distribution is infinitely broad ($MW/M_n \rightarrow \infty$), with molecules ranging from the smallest unreacted chain to the infinite, sample-spanning cluster. The polymer reaches its GP at a critical extent of crosslinking,

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$\alpha \rightarrow \alpha_{\text{gel}}$.⁶ Before the GP, that is, $\alpha < \alpha_{\text{gel}}$, the polymer is called a sol, because it is typically soluble in an appropriate solvent. Beyond the GP, $\alpha > \alpha_{\text{gel}}$, at least part of the polymer is typically not soluble in most solvents and is called a gel.

A distinction may be drawn between molecular gelation (the phenomenon) and macroscopic gelation (its consequence). Molecular gelation occurs at a well-defined and often calculable stage in the course of chemical reaction, provided that the reaction mechanism is independent of temperature and free of noncrosslinking side reactions. Macroscopic consequences of gelation include a rapid approach toward infinite viscosity and development of elastic properties not present in the pre-gel resin. Kinetically, gelation does not usually inhibit the curing process so the conversion rate remains unchanged. Hence, it cannot be detected kinetically by techniques sensitive only to chemical reactions, such as different scanning calorimetry and thermogravimetric analysis. Molecular gelation may be detected as the point at which the reacting resin becomes just insoluble or defined by means of its rheological method.^{4,7} Macroscopic ways to approximate gelation include the time to reach a specific viscosity^{8,9} and using a back extrapolation to determine the zero equilibrium modulus.

The most common rheological tests for detecting the GP involve the measurement of an equilibrium modulus^{10,11} or the divergence of the steady shear viscosity.^{11–15} Measurement of the equilibrium modulus is particularly difficult since one needs to measure the equilibrium modulus when it is exactly zero to determine the GP. The modulus value at this point remains below the detection limit for a considerable amount of time, thereby reducing the accuracy of the method significantly. While the method of measuring the diverging steady shear viscosity can only locate the GP approximately, it has the advantage that the experiment is relatively simple. The approximate location of the GP for this method involves measuring the diverging steady shear viscosity of the curing sample during its curing process. Typically, the shear viscosity increases as gelation commences, although in some cases where the heat of reaction is sufficient to increase the resin temperature, the viscosity might actually decrease initially.¹⁵ As the gelation process proceeds, the viscosity value would rise exponentially and provide a clear demarcation in a linear plot of the viscosity against the time of cure. The

method has been found to work with relative accuracy for several epoxy systems.^{8,9,12,16,17}

A third but less common method to determine the GP is to use the crossover point of the shear moduli, G' and G'' ,^{16–24} although this can only be effectively used for some polymers. The definition of the type of polymers for which this third method can be used effectively to identify the GP was given by the Winter's criterion.^{4,5} The Winter's criterion involves the measurement of rheological properties of the resin and relies on the fact that the stress relaxation at the GP has been found to obey a power-law-type of relationship as follows:

$$G(t) = \sigma t^{-n}; \quad \alpha = \alpha_{\text{gel}} \quad (1)$$

where the stress of the gel, σ , depends on the flexibility of the molecular chains and crosslinks and on the crosslink density at the GP. n is the relaxation exponent and typically has values in the range $0 < n < 1$. From the power law, the frequency dependence of the dynamic shear moduli at the GP can be deduced to be

$$G'(\omega) = \Gamma(1 - n)\cos(n\pi/2)\sigma\omega^n$$

i.e., $G'(\omega) \sim \omega^n$ (2)

$$G''(\omega) = \Gamma(1 - n)\sin(n\pi/2)\sigma\omega^n$$

i.e., $G''(\omega) \sim \omega^n$ (3)

The above equations indicate that G' and G'' will coincide when $n = \frac{1}{2}$. Also, at the GP, the loss tangent, $\tan \delta$, is independent of the frequency:

$$\tan \delta = G'/G'' = \tan(n\pi/2) \quad (4)$$

As such, if $\tan \delta$ was measured at different frequencies, it coincides at a single point at the GP but only at temperatures significantly above the glass transition temperature (T_g) of the crosslinking polymer. Stoichiometrically balanced network polymer systems have been found to relax with $n = \frac{1}{2}$, with a stoichiometrically unbalanced system having $n < 0.5$ for systems with an excess of a crosslinking agent and $n > 0.5$ for systems with an inadequate amount of a crosslinking agent.^{4,5} Therefore, the only class of network polymers for which the GP coincides exactly at the crossover would be a stoichiometrically balanced network polymer system at temperatures significantly above its T_g .

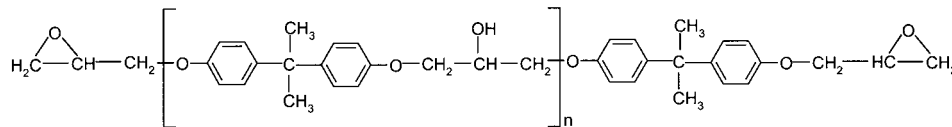


Figure 1 Structure of DGEBA epoxy.

The Winter criterium⁴ for the GP necessitates the measurement of the dynamic moduli at different frequencies. This is done by using a multiwave rheology approach, where a compound wave form is applied to the curing sample. The multiwave test superimposes a number of dynamic frequencies at specified strains into a multiple-frequency signal that is transferred through the sample. The response is measured and deconvoluted by Fourier transformations into the separate responses of the individual frequencies. The advantage of the multiwave test is that a response (e.g., G' , G'') can be measured instantaneously as a function of the frequency, and, thus, the response is not influenced by the time of testing, as in a dynamic frequency sweep. The multiwave method to determine the GP has been successfully used,²⁵⁻²⁷ and it has been shown that the validity of the data obtained using the multiwave technique has been verified by comparing it with continuous time sweeps conducted at the same temperature. The time sweep results apparently showed excellent concurrence with the data from the multiwave experiment.²⁵

The gel time can also be used to calculate the activation energy,^{17,26-30} the precise determination of which would enable a more accurate kinetic cure model to be available.² The assumption is typically made that the cure kinetics involves only a single reaction with a single activation energy. While this is often not the case, the single activation energy value so obtained can be considered to be representative of the multiple reactions in progress. The kinetic reaction can thus be expressed by an Arrhenius-type equation:

$$\frac{d\alpha}{dt} = kf(\alpha) = A \times \exp\left(-\frac{E}{RT}\right) \times f(\alpha) \quad (5)$$

where α is the conversion; k , the conversion rate constant, which is assumed to be a function of temperature based on an Arrhenius-type equation; $f(\alpha)$, a function of conversion; A , the Arrhenius frequency factor; E , the activation energy; R , the Boltzmann constant; and T , the curing temperature. Rearranging eq. (5) and integrating,

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \times \exp\left(-\frac{E}{RT}\right) \times \int_{t=0}^{t=t_\alpha} dt = A \times \exp\left(-\frac{E}{RT}\right) \times t_\alpha \quad (6)$$

where t_α is the time at which the conversion reaches α . Taking the natural logarithm,

$$\ln\left(\int_0^\alpha \frac{d\alpha}{f(\alpha)}\right) = \ln(A) - \frac{E}{RT} + \ln(t_\alpha) \quad (7)$$

or

$$\ln t_\alpha = \frac{E}{RT} + \left[\ln\left(\int_0^\alpha \frac{d\alpha}{f(\alpha)}\right) - \ln(A) \right] \quad (8)$$

For a given fixed degree of conversion, the terms in the square brackets are constants. By

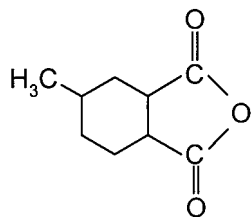


Figure 2 Structure of hexahydro-4-methylphthalic anhydride.

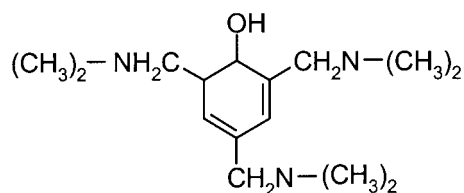
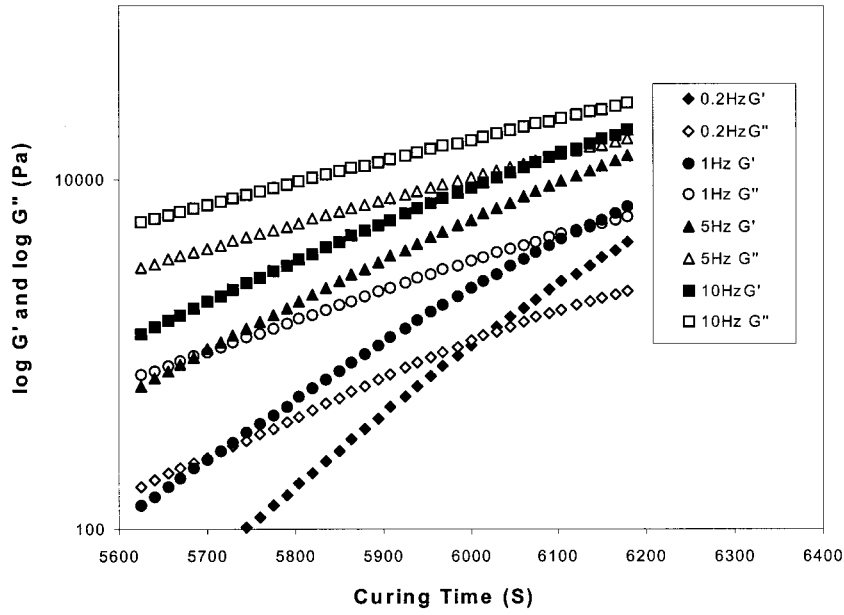
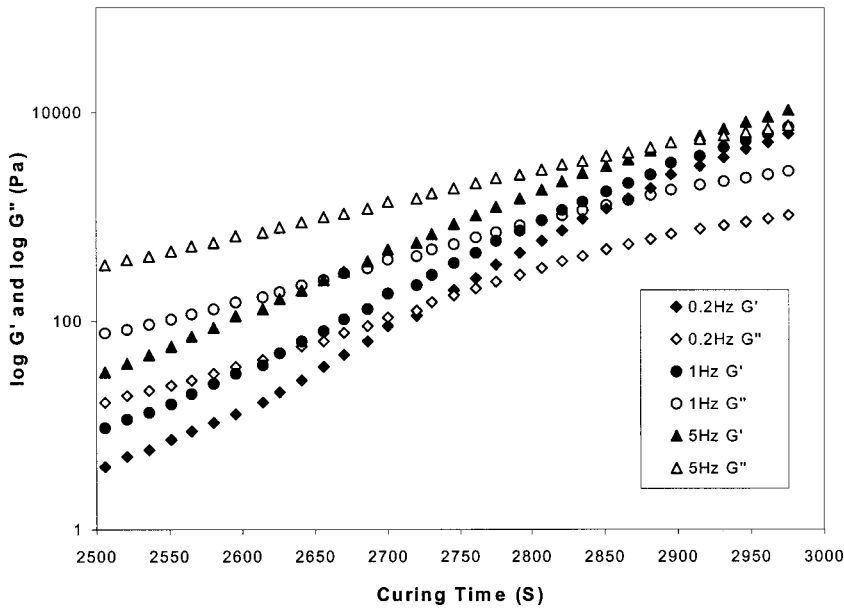


Figure 3 Structure of 2,4,6-tris(dimethylaminomethyl)phenol.



(a)



(b)

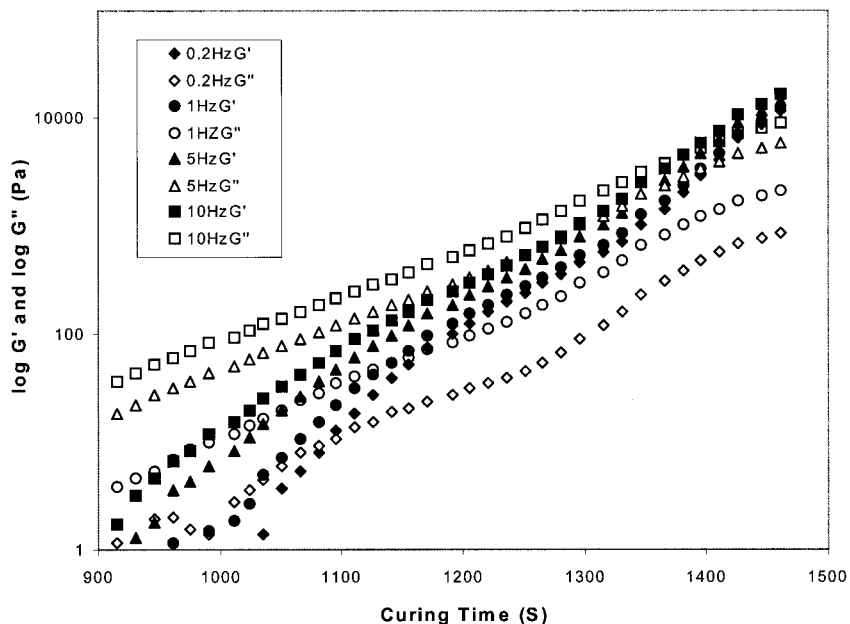
Figure 4 Evolution of the storage (G') and loss (G'') moduli for an epoxy-anhydride system obtained by a multiwave technique: (a) isothermal cure at 80°C; (b) isothermal cure at 90°C; (c) isothermal cure at 100°C.

assuming $t_{\alpha 1}$ and $t_{\alpha 2}$ be the time to reach the same conversion at two different curing temperatures T_1 and T_2 , respectively,

$$\ln t_{\alpha 1} - \ln t_{\alpha 2} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (9)$$

This then is the isoconversion method which can be applied for gelation, since, effectively, $t_{\alpha} = t_{gel}$. From eq. (9),

$$\ln t_{gel1} - \ln t_{gel2} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (10)$$



(c)

Figure 4 (Continued from the previous page)

From eq. (10), the activation energy E is then determined by plotting $\ln(t_{\text{gel}})$ against $1/T$. The results of the activation energy by this method for other types of epoxy systems have shown good agreement with the results by other methods, for example, compared to DSC isothermal methods for a commercial epoxy–DICY system³¹ and for complex epoxy–DICY systems by DSC and TBA methods.³²

EXPERIMENTAL

The epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBA; Epikote 828, Shell Chemicals, Singapore, $n = 0.2$, $M_w = 383$); the structure is as shown in Figure 1.

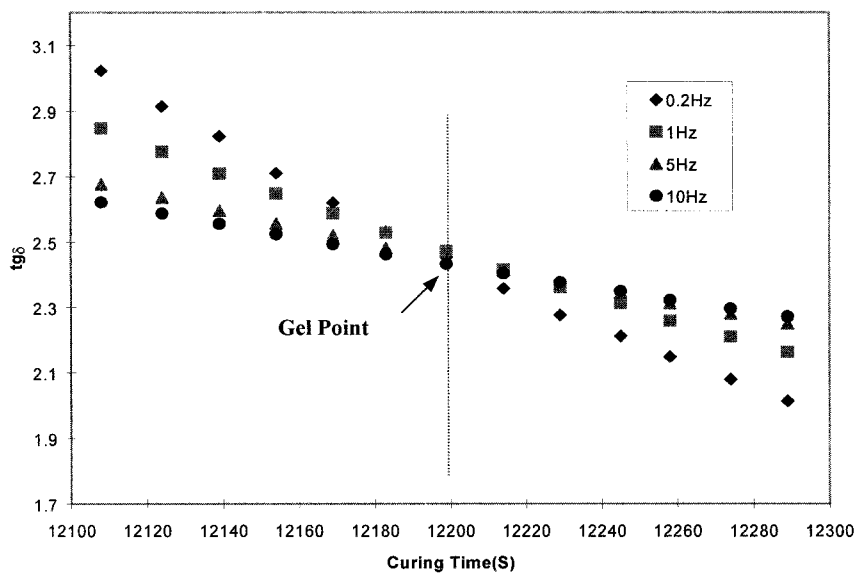
The hardener of our system is hexahydro-4-methylphthalic anhydride (MHHPA) (Aldrich, Milwaukee, WI, USA). Its structure is as shown in Figure 2. The tertiary amine catalyst used is 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30) (Fig. 3). The epoxy, hardener, and catalyst were mixed according to different ratios.

All the rheological experiments performed in this project were conducted with a Rheometric Scientific ARES rheometer, using a 25-mm disposal aluminum parallel plates system which was

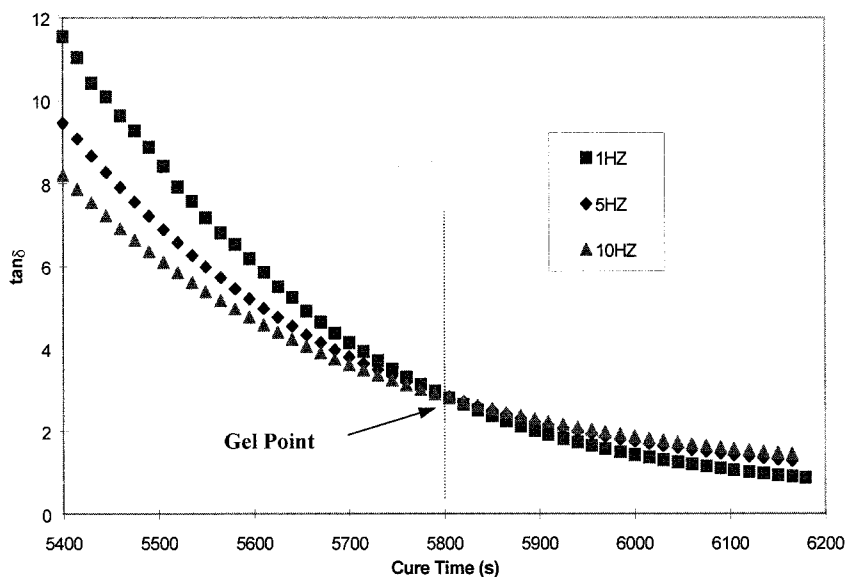
enclosed within a convection oven. The oven was supplied with air for heating. The temperature of the sample was measured by insertion of a thermocouple inside the rheometer shaft, to within 1 mm of the bottom plate surface. The plates were zeroed at the temperature of the test, after which the uncured epoxy system was placed between the plates. The time for loading the sample was kept to a minimum so as to reduce the lag time for temperature equilibration. A gap of 1 mm was used for the multiwave and the steady-state shear tests. The multiwave experiment was run with a fundamental frequency of 0.2 Hz. A total of four wave forms (0.2, 1.0, 5.0, and 10.0 Hz) were used to create the composite strain input. The steady-state shear viscosity, η , of the reacting mixture during the isothermal cure of the epoxy–anhydride was also determined at a rotation speed of 0.1 cycle/s. The low rotation speed was used to avoid a disturbance movement during curing.

RESULTS AND DISCUSSION

To illustrate how the $G'–G''$ crossover point may not define the GP for some systems, this is illustrated experimentally using a DGEBA–anhydride



(a)

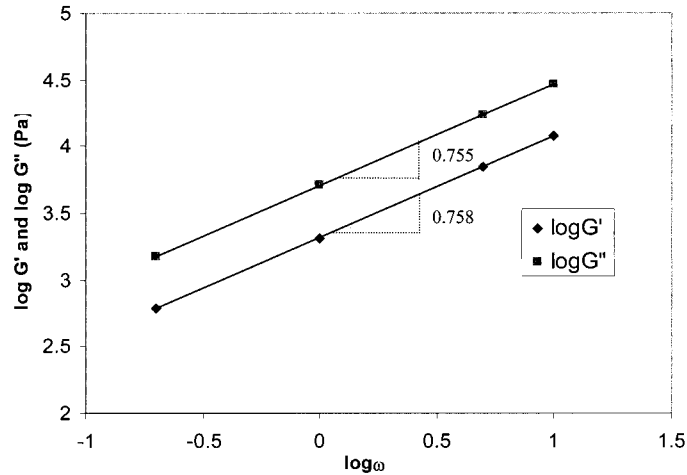


(b)

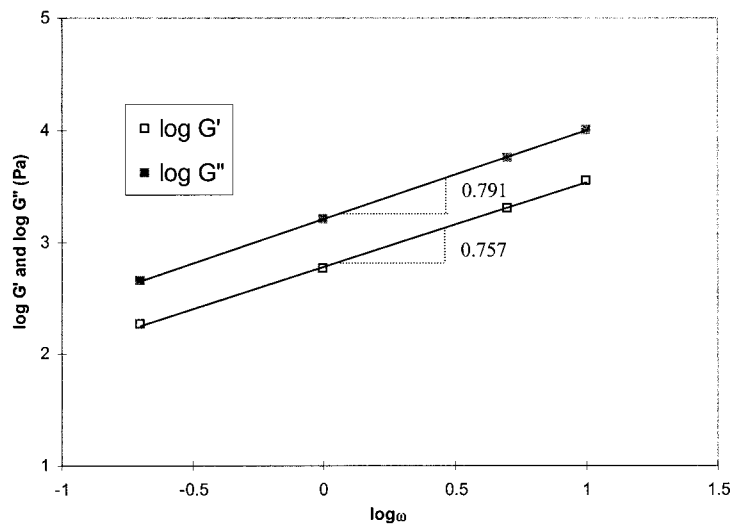
Figure 5 (a) Variation of $\tan \delta$ during cure of an epoxy-MHHPA system at 70°C; (b) variation of $\tan \delta$ during cure of an epoxy-MHHPA system at 80°C.

system. Figure 4 shows the results obtained for the DGEBA-anhydride epoxy system, plotting the obtained storage modulus (G') and the loss modulus (G'') during the curing process at isothermal temperatures of 80, 90, and 100°C. Figure 4 clearly shows that the crossover of G' and G'' of the epoxy/anhydride system changed with the frequency at all curing temperatures. Within the frequency range studied, the G' , G'' crossover points occurred later with increasing frequency,

indicating that, for the epoxy system being tested, the occurrence of the G' - G'' crossover is a frequency-dependent event. If the crossover is used to define the GP, the GP so defined would be frequency-dependent. This is, of course, contrary to the definition that the GP should depend only on the temperature and be independent of the frequency. As such, for this epoxy/anhydride system, it is not accurate to use the G' - G'' crossover to define the GP.



(a)



(b)

Figure 6 The frequency spectrum of G' and G'' at the GP of different temperatures: (a) 70°C; (b) 80°C.

Figure 5 shows the results of a multiwave test for the DGEBA/MHHPA system, plotting the values obtained for the $\tan \delta$ versus cure time at 0.2, 1, 5, and 10 Hz at 70 and 80°C. The results clearly show that the G' and G'' curves of different frequencies intersect at only one point, at which $\tan \delta$ becomes independent of the frequency. As such, it is possible to define the time at which this occurs to be the gel time for the system.

From the graphs shown in Figure 5, the gel time of the DGEBA/MHHPA system is about 12,200 (± 50) s at 70°C cure and 5800 (± 50) s at 80°C cure. The reason for using relatively low cure temperatures to determine the gel time is

because at higher temperatures the time to reach the gel time decreases considerably to a length which would render the measured cure time relatively inaccurate.

Comparing the GPs obtained from Figure 5 to those which were obtained from Figure 4, it is seen that for the same curing temperature the crossover always happens later than at the GP. The GP occurs earlier than the crossover when the relaxation exponent $n > \frac{1}{2}$. According to eqs. (2) and (3), the relaxation exponent n can be obtained by plotting a graph of $\log G'$ and $\log G''$ versus $\log \omega$. By combining the 80°C multiwave test result [Figs. 5(a) and 4(a)], we can get the

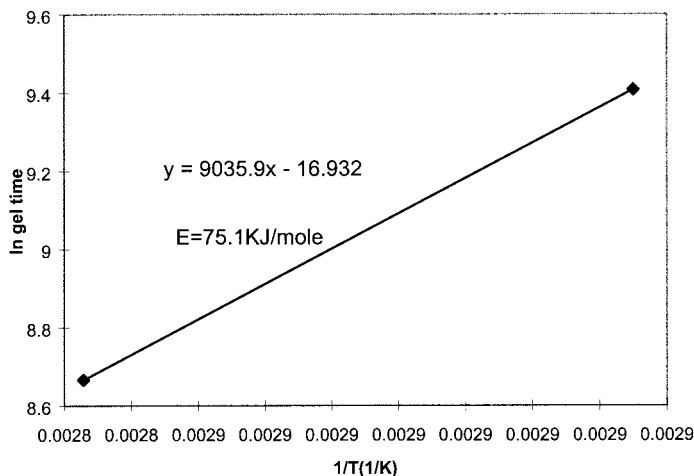


Figure 7 Semilogarithmic plot of gel time versus ($1/T$) where the temperature T is expressed in Kelvin.

variation of dynamic moduli with frequency at the GP.

Figure 6 plots the values of $\log G'$ and $\log G''$ against $\log \omega$ at the GP for curing at 70 and 80°C. The values of the slopes obtained for $\log G'$ and $\log G''$ at 70°C are 0.758 and 0.755, respectively, while the values are 0.791 and 0.757 at 80°C, respectively. Based on eqs. (2) and (3), these values represent the relaxation exponent, n , confirming that the relaxation exponent of the epoxy-anhydride system $n > \frac{1}{2}$.

According to Winter's theory, for this kind of network polymer, the G' and G'' do not coincide with the GP, but, in fact, the GP would occur earlier than the crossover. The experiments have thus verified the validity of the model Winter proposed. The similar values in the slopes of the two lines also indicate that, at the GP, G' and G'' follow the same power law, demonstrating the accuracy of the method in determining the location of the GP. From Figure 6, it can be seen that the relaxation exponent is independent of the curing temperature. The scaling exponent that was obtained is similar to the value obtained for epoxy systems (0.7 ± 0.5) in other work.³³

Gelation is a phenomenon which will happen at a given constant degree of conversion. Equation (10) can be used to obtain the value of the activation energy. Figure 7 shows the plot of $\ln(\text{gel time})$ versus ($1/T$). The two gel times used are the gel times at 70 and 80°C obtained earlier. According to eq. (10), the slope of the line is equal to (E/R) , where E is the activation energy of the crosslinking reaction and R is the universal gas constant. From the graphs in Figure 7, the activation en-

ergy of the system tested by this method was determined to be 75.1 kJ/mol. This result is comparable to the value (71.3 kJ/mol) obtained by the multiple-heating-rate method, showing the relative accuracy of the method. After so obtaining the value for the activation energy of the DGEBA/MHHPA system, eq. (10) can be used to estimate the gel times of any temperature.

A simple method of locating the approximate location of the GP involves measuring the diverging steady shear viscosity of the curing sample and has been shown to be viable by some researchers.^{8,9,11,13,25} The method is illustrated in Figure 8, where it can be observed that the viscosity of the system increases exponentially due to the abrupt change of the molecular weight at the GP. However, it can be seen that the determination of the exact location of the GP, particularly for measurements taken at lower temperatures, can be rather imprecise.

CONCLUSIONS

Determination of the GP by using the $G'-G''$ crossover method was not found to be accurate, and the GP obtained by this method was found to be frequency-dependent. The GP for a DGEBA/MHHPA epoxy system was accurately determined, using the point where $tg\delta$ was independent of the frequency at different temperatures. At the GP determined by this method, the G' and G'' were found to follow the same power law, demonstrating the accuracy of the method in determining the GP. The scaling exponent obtained

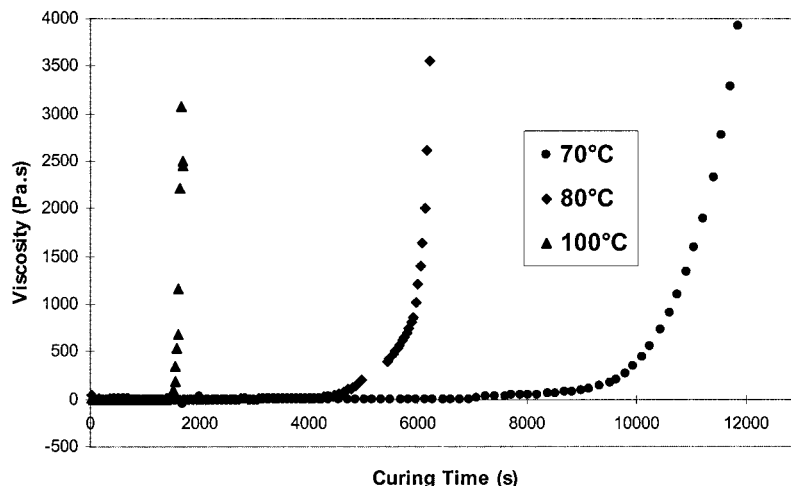


Figure 8 Steady shear viscosity change during isothermal cure.

was 0.75–0.79 and found to be independent of curing temperatures. The activation energy for the cure reaction of the system was determined to be 75.1 kJ/mol using the obtained gel times at different temperatures. The shear divergence method can observe the viscosity change during the GP, but this method was not precise enough to define the GP, especially for lower temperatures.

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