A New Approach for Determination of Gel Time of a Glass/Epoxy Prepreg

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ABSTRACT: Gel time of a glass/epoxy prepreg, HexPly®1454, was investigated by a parallel plate rheometer. The prepreg is based on dicyandiamide (DICY)-cured diglycidyl ether of bisphenol A epoxy resin system. It is found that the application of the G'-G'' crossover method for gel time determination is not suitable for this system. A new approach was proposed in which the maximum tan δ is regarded as the gel point. This can accurately define the gel point at various temperatures. The results proved that this point is independent of the applied frequency. The activation energy for the cure reaction of the system was determined via gel time determination of the prepreg at different isothermal temperatures and found to be 75.0 ± 10.2 kJ/mol. This is in good agreement with the activation energy obtained from the dynamic DSC studies. The steady-shear rheology experiment was used to study the viscosity profile and subsequently to determine the gel point and verify the new approach for gel time determination. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1483–1489, 2011

Key words: gel time; prepreg; rheometry; glass fiber; epoxy

INTRODUCTION

From an application point of view, the effective use of any thermosetting system requires one to be able to predict the cure kinetics of the system to consistently obtain the maximum possible glass transition temperature and also to predict the flow behavior of the curing resin, in particular, to precisely locate when the sol–gel transition occurs. Accurate knowledge of the gel time would therefore allow the estimation of the optimal temperature and time for which the sample should be heated before being allowed to set in the mould.[1] The gel time also can be used to determine the activation energy for the cure reaction of the system. The gel point is an irreversible reaction in which the weight-average molecular weight reaches infinity.[2,3] A thermoset polymer at its gel time is in a transition state between a liquid and a solid. At the gel time, the molecular weight distribution is infinitely broad, with molecules ranging from the smallest unreacted chain to the infinite, sample–spanning cluster. 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 differential 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.[2,4]

The gel time can be determined according to the different criteria.[5,6] The commonly used criteria for gel time involve:

- Criterion 1: the gel time is determined from the crossing point between the baseline and the tangent drawn from the turning point of G' curve.[7,8]
- Criterion 2: the gel time is the time required for viscosity to reach a very large value or tends to infinity.[9]
- Criterion 3: the gel time is thought as the time where tan δ equals 1, or G' and G'' curves crossover.[2,3,8,10]
- Criterion 4: the gel time is taken as the point where tan δ is independent of frequency.[11–13]

Measurement of the diverging steady shear viscosity (Criterion 2) is an appealing experiment because of its simplicity. Even the torque on a processing machine might serve as an estimate of the diverging viscosity. It has, however, severe disadvantages that need to be considered[2]:

1. Near liquid–solid transition (LST), the relaxation times become very long, and steady shear flow cannot be reached in the relatively short

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transient experiment. Large strains are the consequence for most reported data.

2. At large strain, the liquid shows shear thinning in some poorly understood fashion. Shearing causes breakage of the fragile network structure near LST, which has been observed as an apparent delay in gelation.

3. LST is found by extrapolation. The actual experiment may also end prematurely sometime before LST if the developing structure in the material is very stiff and the rising stress overloads the rheometer. The diverging viscosity, therefore, does not show the real gel point. The transition may appear early because of torque overload or it may be delayed by chain scission due to large strain. This apparent gel point, however, is still important since it relates to processing applications in which either the machine would clog or the newly formed network structure would break (or both).

Criterion 3 can only be effectively used for some thermoset polymers. The definition of the type of polymers for which this method can be used effectively to identify the gel point was given by the Winter's criterion.[2,3] The Winter's criterion involves the measurement of rheological properties of the resin and relies on the fact that the shear stress relaxation $G(t)$ at the gel point has been found to obey a power-law-type of relationship as follow[13]:

$$G(t) = \sigma t^{-n} \tag{1}$$

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

$$G'(\omega) = \Gamma(1-n)\cos(n\pi/2)\sigma\omega^n \quad \text{i.e.,} \quad G'(\omega) \approx \omega^n \tag{2}$$

$$G''(\omega) = \Gamma(1-n)\sin(n\pi/2)\sigma\omega^n \quad \text{i.e.,} \quad G''(\omega) \approx \omega^n \tag{3}$$

The above equations indicate that G' and G'' will coincide when $n = 1/2$. Also, at the gel point, the loss tangent, tan δ, is independent of the frequency:

$$\tan\delta = G''/G' = \tan(n\pi/2) \tag{4}$$

as such, if tan δ was measured at different frequencies, it coincides at a single point at the gel point 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 $n = 1/2$, 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 crosslinknig agent. Therefore, the only class of network polymers for which the gel point coincides exactly at the crossover would be a stoichiometrically balanced network polymer system at temperatures significantly above its T_g.

The gel time can also be used to calculate the activation energy, the precise determination of which would enable a more accurate kinetic cure model to be available.[14–19] The assumption is that the cure kinetics involves only a single reaction with single activation energy. The value so obtained can be considered to be representative of the multiple reactions in progress. The curing reaction rate can be expressed as a function of conversion and temperature[13]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{5}$$

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

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

where t_α is the time at which the conversion reaches α. Taking the natural logarithm and rearrangement:

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

For a given fixed degree of conversion, the terms in the square brackets are constants.[13] From the isoconversion method which can be applied for gelation, since, effectively $t_\alpha = t_{gel}$

$$\ln t_{gel1} - \ln t_{gel2} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8}$$

From Eq. (8), the activation energy E can be determined by plotting $\text{Ln}(t_{gel})$ against $1/T$.

Further to our previous works[20] on cure characterizations of prepregs by DSC, in this work, the rheological properties of a commercial and widely used prepreg, HexPly®1454, has been investigated. We tried to establish a criterion for gel time determination of prepregs.
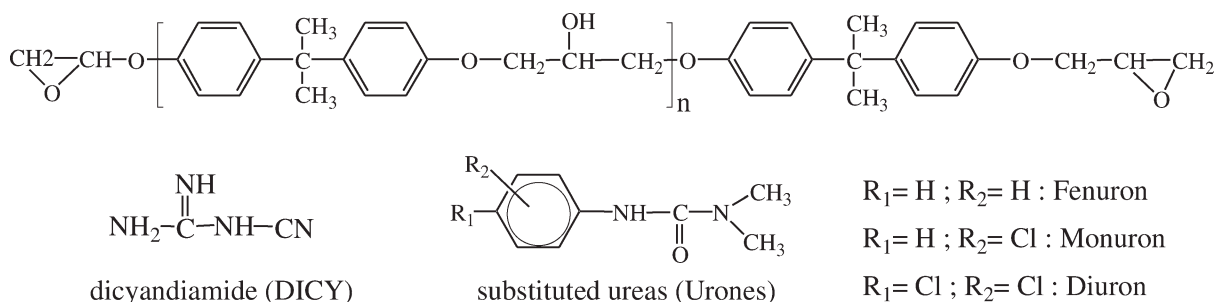
Scheme 1 Chemical structures of diglycidyl ether of bisphenol A, DICY, and urones.

EXPERIMENTAL

Materials

The material used in this study was a glass satin fabric reinforced epoxy prepreg (HexPly®1454), supplied by Hexcel composites. Based on our analysis, the basic formulation of the matrix resin contains the popular 125°C curable DGEBPA/DICY/Urone with 305 g/m² fiber area weight (Satin 8HS) and 49 wt % resin content. The structure of epoxy resin, hardener, and Urones are as shown in Scheme 1.

Experiments

DSC experiment was performed on a NETZSCH DSC 200 F3 instrument in flowing nitrogen environment (50 mL/min). The uncured prepreg sample of 12 ± 2 mg size by considering the content of the resin in the prepreg was placed in an aluminum pan with a pierced lid and placed opposite to the empty reference pan in the DSC chamber. The DSC dynamic heating was then set for temperature range of 25–300°C with heating rate of 2.5°C/min. The sampling time was set to 6 s per point.

All the rheological experiments were conducted on rheometer MCR300 from Physica, 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 test temperature to calibrate the instrument, after which four plies of the prepreg were placed between the plates. The size of each layer of prepreg sample was 25 mm in diameter and about 0.25 mm in thickness. Since one layer of the epoxy prepreg is very thin, four layers of the prepreg with overall thickness of about 1 mm were used as the sample to enhance the accuracy of the measurements. A gap of 1 mm was set for the experiment. The time for loading of the sample was kept to minimum so as to reduce the lag time for the temperature equilibration.

RESULTS AND DISCUSSION

Dynamic heating DSC experiment was performed to select the proper isothermal temperatures for determining the gel times of the glass/epoxy prepreg by rheometer. Figure 1 shows the dynamic DSC graph of the epoxy prepreg at the heating rate of 2.5°C/min. As shown in the graph, the curing of the prepreg starts at around 105°C with a peak at 129°C and finally complete at 170°C. The heat of cure reaction, 113.6 J/g, is determined by the area under the peak and via plotting a linear baseline.

Being known the initial, peak, and final cure temperature taken from the dynamic DSC run, seven specific temperatures (100, 110, 115, 120, 125, 130, and 135°C) were selected for isothermal runs in gel time determination by rheometer. Preliminary tests were conducted to determine the optimum instrumental parameters such as the frequency, gap between two plates, and the strain. The optimized experimental conditions are the maximum strain of 0.18%, a gap of about 1 mm, and a frequency of 1 Hz. For isothermal measurements, the sample chamber was preheated to the predetermined temperature and kept at that temperature for half an hour. The sample was then put into the chamber and measurement was started.
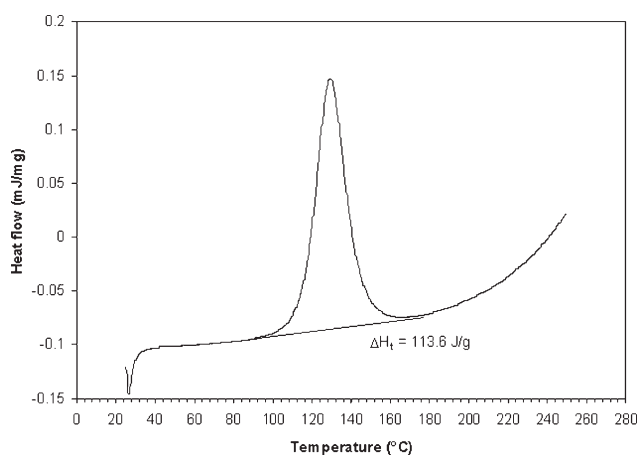

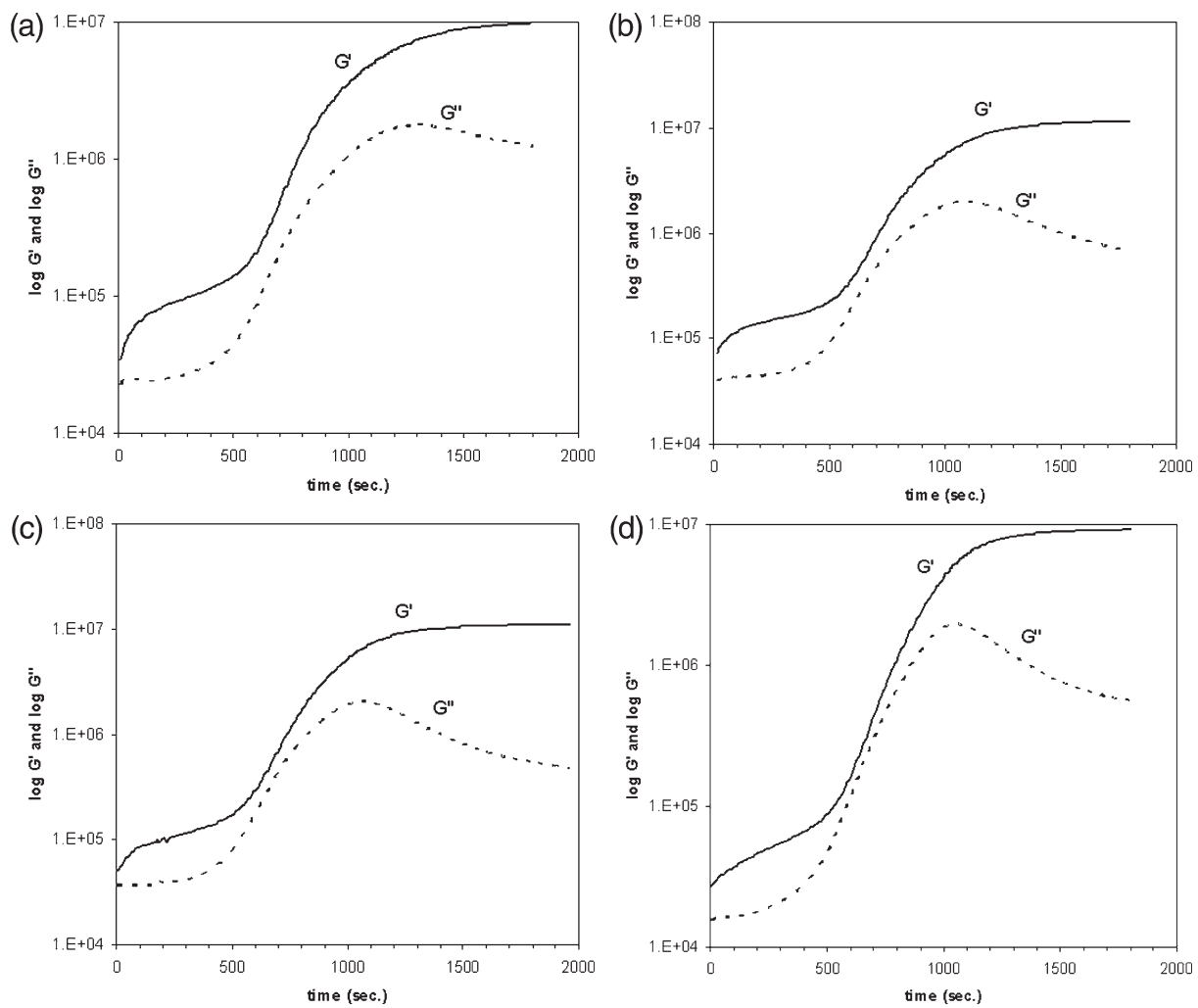**Figure 1** Dynamic DSC cure diagram of the glass/epoxy prepreg at the heating rate of 2.5°C/min.

Figure 2 Evolution of the storage (*G′*) and loss (*G″*) modulus for a glass/epoxy prepreg system obtained at different frequencies (a) 1 Hz, (b) 5 Hz, (c) 10 Hz, (d) 20 Hz isothermally cured at 120°C.
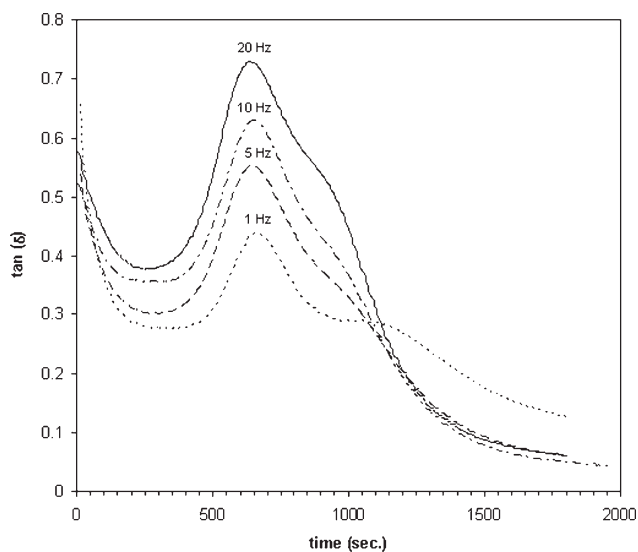

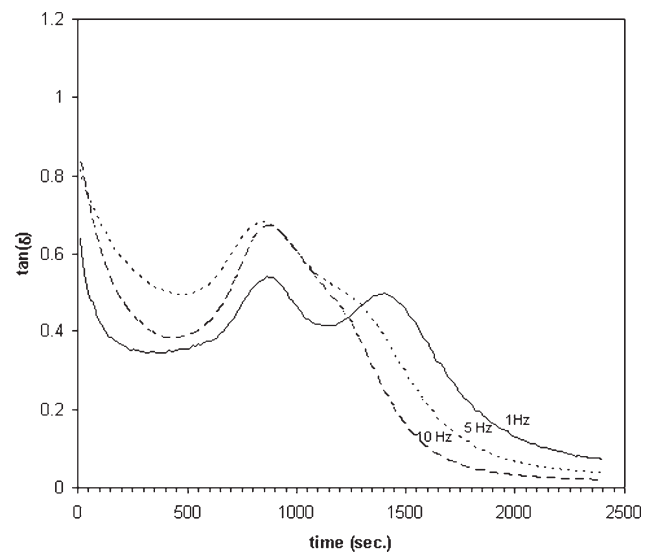**Figure 3** Variation of tan δ during the curing of glass/epoxy prepreg at 120°C.

Figure 4 Variation of tan δ during the curing of glass/epoxy prepreg at 115°C at different frequencies.
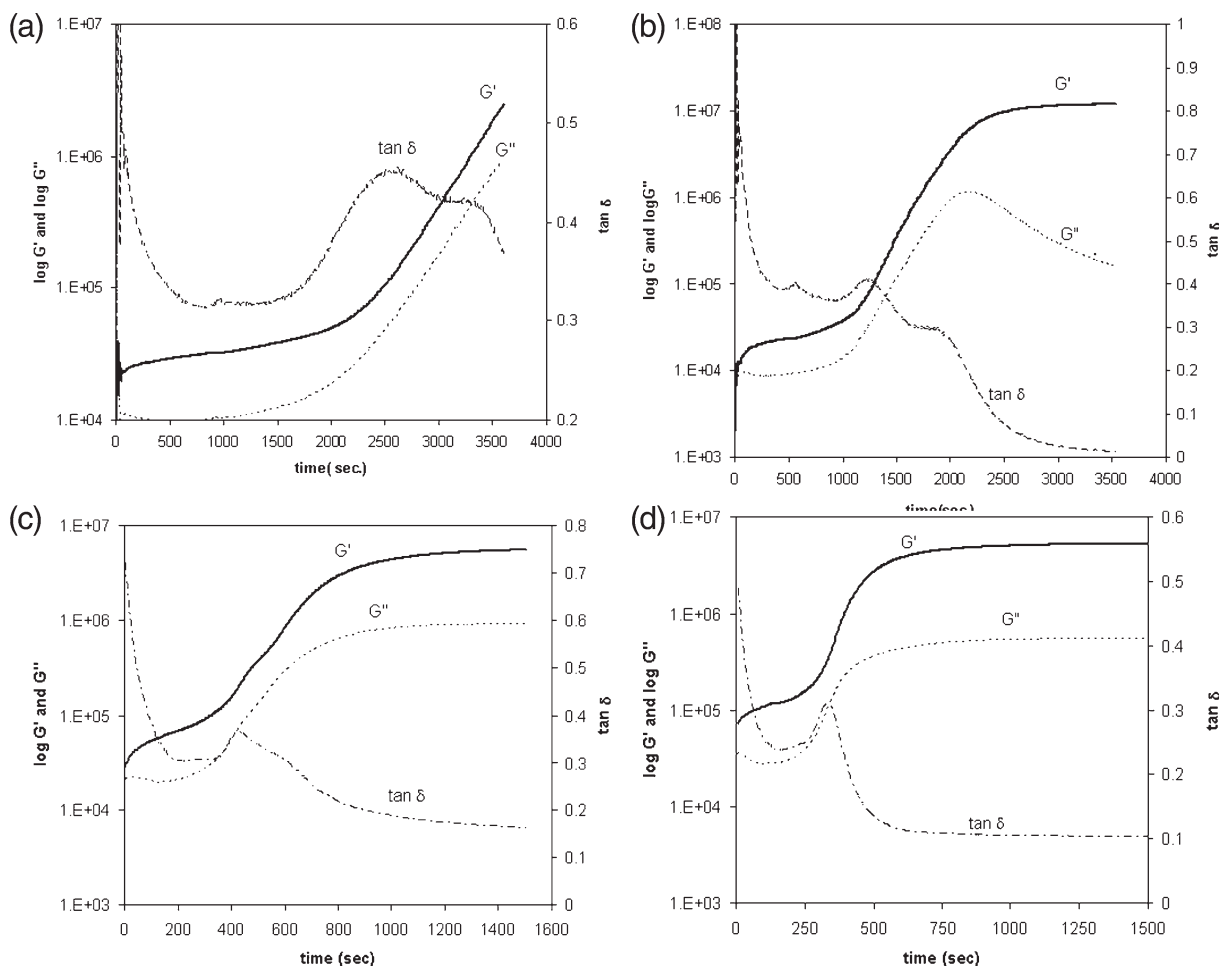
Figure 5 Variation of G', G'', and tan δ during the curing of glass/epoxy prepreg at (a) 100, (b) 110, (c) 130, and (d)135°C.

Figure 2 shows the results obtained for the glass/epoxy prepreg, plotting the storage modulus (G') and the loss modulus (G'') during the cure process at isothermal temperature of 120°C at different frequencies of 1, 5, 10, and 20 Hz. It can be seen that during the initial cure period, the storage modulus is greater than the loss modulus. The elastic nature of the epoxy prepreg dominates its viscous behavior. In the final cure stage, the storage modulus is much greater than the loss modulus. The epoxy prepreg becomes mostly an elastic solid. Under isothermal conditions, the storage modulus increases with the advancement of the cure process, and it finally reaches a plateau. In contrast, the loss modulus increases due to the increment of the molecular weight through polymerization, reaches a maximum, and then decreases. G'' first increases as the viscosity does increase, mainly due to polymerization and networking, with the cure process till the viscosity attains almost an infinity value where the molecular relaxations are extremely slow. Consequently, the reason it decreases is simply that the viscous effects
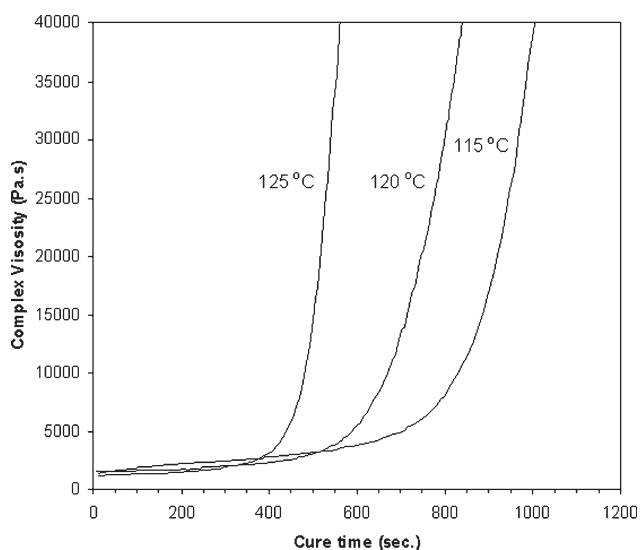

Figure 6 Steady shear viscosity changes during isothermal cure of the glass/epoxy prepreg at various temperatures.

	Isothermal cure temperatures (°C)						
	100	110	115	120	125	130	135
Gel time (sec)	2520	1250	880	640	450	420	320
ln (t_{gel})	7.832	7.131	6.780	6.462	6.109	6.040	5.768
$1/T$, K^{-1}	0.00268	0.00261	0.00258	0.00254	0.00251	0.00248	0.00245

are no longer operative and the material is put into a solid state (only elastic behavior is observed).

Near the gel point, with increasing the frequency, G'' curve approaches the G' curve, but does not cross it and finally they become parallel. Figure 2 clearly shows that the G'-G'' crossover does not occur at the frequency ranges used and thus the Criterion 3 can not be used for gel time determination.

Figure 3 shows the results of a multi wave experiment for the glass/epoxy prepreg, plotting the values obtained for the tan δ versus cure time at 1, 5, 10, and 20 Hz at 120°C. It can be seen that for this system the criterion 4, the point at which tan δ becomes independent of the frequency, occurs far beyond the gel point at around 1200 s, and it is not possible to define the gel time by this criterion.

Figure 3 shows a peak in tan δ curve near the gel point. The peak is independent of the frequency and occurs at the same time. As such, it is possible to define the time at which this peak occurs to be the gel time of the system. Figure 4 shows similar results for the glass/epoxy prepreg cured at 115°C. Again, the peak of tan δ at different frequencies occurred at the same time (about 880 ± 20 s). This behavior was also observed at other isothermal temperatures 100, 110, 125, 130, and 135°C. Figure 5 shows G', G'', and tan δ curves for the curing at 100, 110, 130, and 135°C. It can be seen that the peak in tan δ ocurred in the gel point region.

Determination of gel time by the peak of tan δ in dynamic mechanical thermal analysis (DMTA) was reported before,[21–23] however, based on our knowledge, determination of gel time by this criterion in rheometry experiments has not been published anywhere.

To see if this behavior can be used for gel time determination, we use Criterion 2 that is a simple method of determining the approximate location of the gel time involves measuring the diverging steady shear viscosity of the curing sample. Figure 6 shows this method, where it can be seen that the viscosity of the prepreg increases exponentially due to the abrupt change of the molecular weight at the gel point. By plotting a tangent line before and after the significant increase in viscosity, one can obtain the gel time as 850 s for the curing at 115°C, 650 s for the curing at 120°C, and 450 s for the curing at 125°C. However, it can be observed that the determi-

nation of the exact location of the gel time, particularly for measurements taken at lower temperatures can be imprecise.

It is evident that the peak in tan δ, which is independent of frequency, coincides with the data obtained form criterion 2, and this can be used as a new criterion for gel time determination of this glass/epoxy prepreg system.

From the graphs shown in Figures 3 and 4, and similar experiments at 100, 110, 125, 130, and 135°C, the gel times of the glass/epoxy prepreg were obtained and the results are summarized in Table I.

Gelation is a phenomenon which will happen at a given constant degree of conversion. Equation (8) can be used to obtain the value of the activation energy. Figure 7 shows the plot of the Ln(gel time) versus $1/T$. These data are also included in the Table I. According to Eq. (8), the slope of the line is equal to (E/R), where E is the activation energy of the cure reaction, and R is the gas constant. From the graph in Figure 7, the activation energy of the system was determined to be 75.0 ± 10.2 kJ/mol. This is in good agreement with the value obtained by others, proving the accuracy of this method.
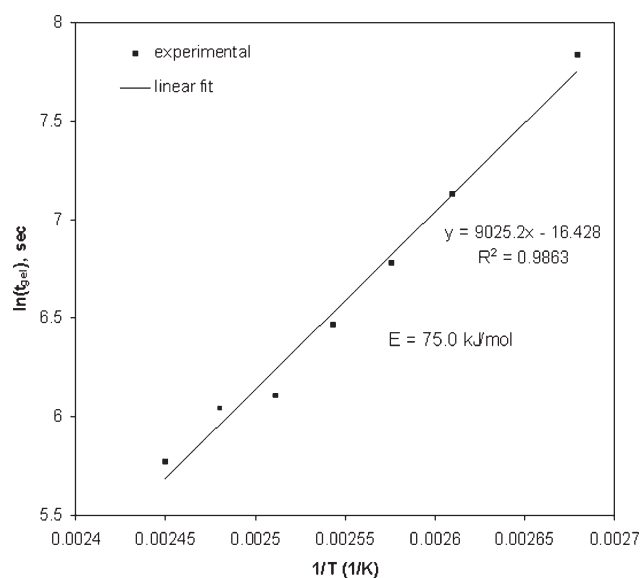

Figure 7 Logarithmic plot of gel time (t_{gel}) versus 1/T to obtain the activation energy.

CONCLUSIONS

Gel time of a glass/epoxy prepreg, HexPly®1454, which is based on DICY-cured diglycidyl ether of bisphenol A epoxy resin system was investigated by a parallel plate rheometer. It was found that the G'-G'' crossover method is not applicable for this system, and instead of this, peak point in tan δ curve can accurately define the gel point at different temperatures and frequencies. This point is independent of frequency. The activation energy of the system was determined to be 84.8 kJ/mol. This is in good agreement with the value obtained by multiple-heating-rate DSC method (75.0 ± 10.2 kJ/mol), proving the accuracy of the proposed method.

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