

Study on Cure Behavior of Epoxy Resin–BF₃–MEA System by Dynamic Torsional Vibration Method

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SYNOPSIS

A dynamic torsional vibration method has been developed and used to investigate the isothermal cure processes of resin system of epoxy resin–boron trifluoride monoethylamine complex—SiO₂, optimizing its cure conditions and estimating the apparent dynamic parameters including gel time and rate of cure reaction and discussing the effect of filler on cure. The cure behavior of resin system has been predicted by the nonequilibrium thermodynamic theory. The theoretical prediction is in good agreement with the experimental results obtained by dynamic torsional vibration method.

INTRODUCTION

Cure of thermosetting resin is one of the key processes for thermosetting adhesives, and also for the process of resin-based composites. The strength of adhesive join and composites are related to the curing process directly. In industry, it is required to judge the cure of the resin systems in order to determine the optimum condition, including cure system, curing temperature, time, etc., and guarantee the quantity of cured resin or articles.

The cure of thermosets is the crosslinking of linear macromolecules having a very complicated mechanism. As soon as the crosslinkings form, the resin will not be solved and melted, which leads quite a bit of difficulty in studying it. Traditionally, chemical analysis, IR, and calorimetry detecting the degree of conversion of reactive groups have been used to study the cure process. However, the increasing of consumption of reactive groups is already not obvious at the last stage of cure. Thus, the sensitivity and function of these analysis techniques will be reduced quite much. But it is the last stage of cure that has a large effect on the physical and mechanical properties of the cured resin. To a large

extent, it will determine the optimum properties of the resulting resin.

Certainly, the cure is related to mechanical strength. In view of the mechanical properties, the cure is the process during which the modulus of the resin gets large. In the last stage of cure, in which the sensitivity of some analysis techniques decrease rapidly, cure degree can be reflected by the mechanical strength obviously. Therefore, with the mechanical methods the cure process can be studied successfully. Torsional braid analysis,¹ the dynamic spring method,² and the dynamic torsional vibration method^{3–6} developed in our group are some of the successful examples.

In this paper we will present the experimental apparatus of the dynamic torsional vibration method, the isothermal cure process, gel time and other apparent dynamic parameters of the epoxy–boron trifluoride monoethylamine complex system, the effect of filler on the cure process, and prediction cure behavior by nonequilibrium thermodynamic fluctuation theory.

EXPERIMENTAL

Dynamic Torsional Vibration Method

Dynamic torsional vibration is a nonresonant forced vibration. The schematic diagram of a homemade

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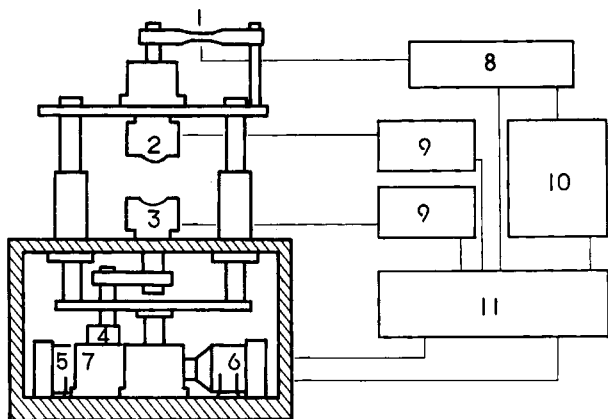


Figure 1 Schematic representation of the dynamic torsional vibration apparatus: (1) strain gauge load cell; (2) upper mold; (3) lower mold; (4) eccentric disc; (5) motor for torsional vibration; (6) motor for closing molds; (7) speed change gear; (8) amplifier; (9) temperature controller; (10) recorder; (11) power supporter.

experimental setup of the dynamic torsional vibration is shown in Figure 1. The lower mold (3) having heater within it and used as the torsional vibrator is filled with the resin materials. When the motor (6) is switched on, the upper mold (2) having a heater within it too comes down, and the molds close with a gap which can be adjusted. The cure temperature is controlled by temperature controllers (8) and (9) connected with molds. Thus the isothermal cure process can be performed. As soon as the molds close, the motor (5) is turned on, and the lower mold starts a torsional vibration at an angle below 1° , which also can be adjusted according to the hardness of cured resin materials, by means of the eccentric disc (4) on the speed change gear (7). The torque amplitude of the torsional vibration is transformed into electric signals by means of the strain gauge load cell (1), amplified through the amplifier (10) and recorded by the recorder (11). The resin system with a different degree of cure has a different viscosity or modulus and a different torque. Therefore, the change in the mechanical properties, i.e., the degree of cure of the resin system, can be monitored and determined by measuring the changes in torque, and continuing curing curves reflecting the whole cure process can be obtained.

Experimental Curve Analysis

The experimental curve obtained by dynamic torsional vibration apparatus is shown in Figure 2. The abscissa is the curing time and the ordinate is the torque required to turn the resin system by a small

angle, which corresponds to the modulus or viscosity of the resin system, and can be thought of as a relative parameter of the degree of cure. The time of closure of the molds is taken as the starting time of cure, that is, the original point O . In the range OA of the curing time the network structure formed during the cure reaction is not enough to cause forced vibration of the upper mold. As a result, the strain gauge load cell will not have any signal to input, so that the experimental curve is linear corresponding to the abscissa. At the point A , the viscosity of the resin system is high enough (i.e., the network formed is complete enough) for the gelation in the resin system to occur, and the torque appears. The strain gauge load cell inputs some signal. Thus, point A is the gel point and the time corresponding to OA is the gel time t_g for the resin system. After point A the torque increases with the increasing of curing time. The increasing amplitude of the torque (slope of the OB curve) expresses the rate of the curing reaction. The increasing trend of torque tended to steady with increasing curing time, and the equilibrium torque G_∞ is thus reached (point C). The curing reaction is completed and the cup-shaped experimental curve is obtained. The time corresponding to OD is the full curing time and the maximum equilibrium torque CD can be thought of as a relative degree of cure for the resin system. The envelope of the experimental curve corresponds to the change of mechanical behavior of the resin system during cure and represents the isothermal cure curve of the resin system.

The advantage of dynamic torsional vibration method is that it can monitor the cure reaction quantitatively. As soon as the cure reaction is completed, the whole isothermal cure curve can be obtained at the same time.

Materials

The epoxy resin used is a commercial diglycidyl ether of bisphenol A E51 made in Wuxi Resin Factory (China) with the epoxy value 0.48–0.54 and average

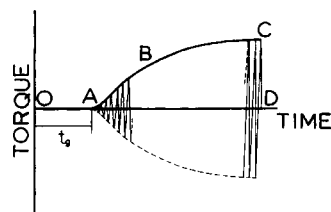


Figure 2 Experimental cure curve analysis. t_g is gel time.

epoxy equivalent 196. Boron trifluoride monoethylamine complex is used as a hardener. The filler is the commercial SiO₂ powder of 600 mesh without any pretreatment. The epoxy resin E51 and boron trifluoride monoethylamine complex are mixed in the stoichiometric ratio of 100 parts resin to 3, 4, and 5 parts hardener, respectively (by weight). While doing the experiments with filler, the mixtures are then mixed with SiO₂ powder with loadings of 10, 20, 40, and 80 phr, respectively, and cured at a temperature of 150°C isothermally.

RESULTS AND DISCUSSION

Isothermal Cure of Epoxy Resin

Figure 3 is the isothermal cure curves of the epoxy-boron trifluoride monoethylamine complex system (3 phr) at 120, 130, 140, and 150°C. The cure curves cured at different temperatures have a similar shape, but obvious differences in their gel times and rates of cure reaction. It is evident from Figure 3 that with increasing cure temperature the gel time decreases in turn, and the rate of cure reaction becomes more and more rapid. Also, the full cure time becomes shorter too. The gelation time obtained from Figure 3 and some related data are listed in Table I.

In order to compare the mechanical properties of samples cured at different temperatures, after reaching the equilibrium torque at that temperature, the sample is cooled down to room temperature. It can be seen that the torques at room temperature are not changed so much for these four experimental conditions, suggesting that the cure reaction of the resin system can be completed at the curing tem-

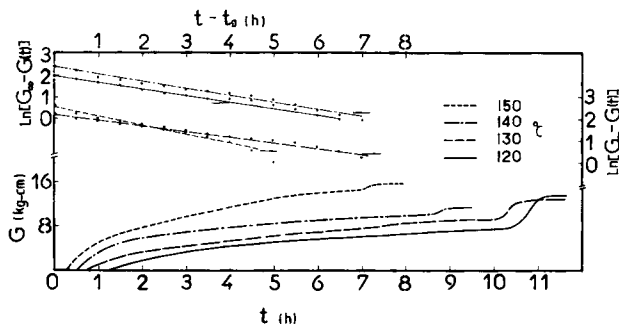


Figure 3 Isothermal cure curves of epoxy resin-boron trifluoride monoethylamine complex system cured at 120, 130, 140, and 150°C, and the plots of $\ln[G_\infty - G(t)]$ against $(t - t_g)$.

Table I Some of Apparent Cure Reaction Dynamic Parameters of Epoxy Resin-Boron Trifluoride Monoethylamine Complex System

Hardener Content (phr)	Cure Temperature (°C)	Gel Time t_g (min)	Activation Energy (kJ/mol)
3	120	75.75	71.4
	130	46.25	
	140	32.00	
	150	20.00	
4	120	70.25	
	130	42.50	
	140	26.75	
	150	18.75	
5	120	60.00	
	130	38.75	
	140	25.00	
	150	17.00	

perature and it is not necessary to have any post-cure procedure.

Figure 4 shows the isothermal cure curves of resin systems with 3, 4, and 5 phr boron trifluoride monoethylamine complex at the curing temperature of 150°C.

Comparing, with all isothermal cure curves, both different curing temperatures and different hardener amounts, the epoxy resin system with 3 phr boron trifluoride monoethylamine complex cured at 150°C should be the best curing system because it has the maximum torque, the shortest gel time (20 min), and fully cured time (about 6.5 h).

Apparent Activation Energy of Resin System

According to Flory's gelation theory,⁷ the chemical conversion at the gel point of the resin system is constant and is not related to the reaction temperature and experimental conditions. As a result, the apparent activation energy of cure reaction E can be obtained from the gel time t_g

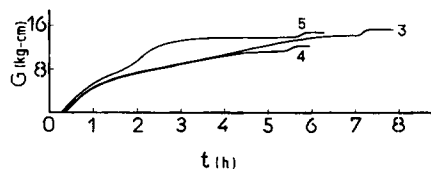


Figure 4 Isothermal cure curves of epoxy resin systems with 3, 4, and 5 phr boron trifluoride monoethylamine complex at the curing temperature 150°C.

$$\ln t_g = C + E/RT \quad (1)$$

where T is the curing temperature, R the gas constant, and C a constant. Figure 5 shows a plot of t_g (see Table I) against $1/T$ for various amounts of hardener of 3, 4, and 5 phr. They are linear lines parallel to each other, suggesting that E of the resin systems with different amounts of hardener is almost the same. The apparent activation energy can be calculated from the slope of the lines and has the value of 71.4 kJ/mol. There was only one datum of activation energy of the epoxy-boron trifluoride monoethylamine complex system in the literature, which was 23 kcal/mol (= 96.3 kJ/mol).^{8,9} The difference between these two data may arise from the different source of the epoxy resin. But the linear lines in Figure 5 suggests that the relationship between gel time t_g and curing temperature T has a good agreement with Flory's theory. Thus, in principle, the gel time at any curing temperature can be predicted by eq. (1) provided that two or three measurements of gel time at different temperatures are made.

Cure Reaction

According to Gaugh,¹⁰ there is a relationship between gel time t_g and the rate constant of cure reaction, k :

$$k \propto (1/t_g)$$

That means the reciprocal of gel time corresponds to the rate of reaction. Thus, the apparent reaction rate can be determined from the relationship between the reciprocal $1/t_g$ and the amount of hardener, c . The plots of $1/t_g$ against c of the epoxy system at testing temperatures are three linear lines (Fig. 6), suggesting that the epoxy resin-boron tri-

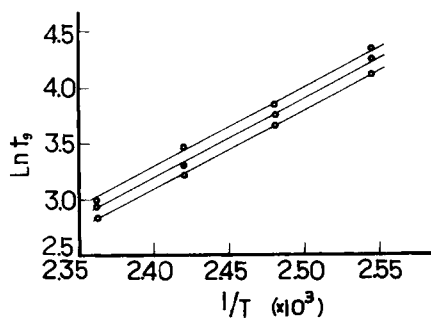


Figure 5 The plot of $\ln t_g$ against $1/T$ for various amounts of hardener of 3, 4, and 5 phr.

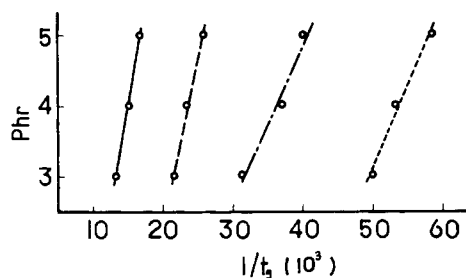


Figure 6 The plot of reciprocal of gel time against initial concentration of hardener, c : (—) 120°C; (---) 130°C; (- · -) 140°C; (· · ·) 150°C.

fluoride monoethylamine complex system is apparently in agreement with the first-order reaction before the gel time t_g .

After gel time t_g , the apparent rate of curing reaction can be considered as follows: The torque, i.e., modulus of the resin system, increases with increasing curing time after t_g . The increasing amplitude of the torque expresses the rate of the curing reaction. The increasing trend of torque tended to steady with increasing curing time, and the equilibrium torque G_∞ is reached and the curing reaction completed. Thus the torque $G(t)$ can be considered as the relative degree of cure. From this point, if the cure is a first order reaction, it should be

$$\frac{d[G_\infty - G(t)]}{[G_\infty - G(t)]} = -k dt$$

i.e.,

$$\ln[G_\infty - G(t)] = -k(t - t_g) + C$$

The plot of $\ln[G_\infty - G(t)]$ against $(t - t_g)$ of the system is shown in Figure 3 too. It can be seen that the plot is almost linear lines. The situation is the same for both other curing temperatures and other hardener contents. That means that the cure of the epoxy-boron trifluoride monoethylamine complex system after gel time is apparently and approximately also a first-order reaction.

Effect of Filler on Cure

The epoxy-boron trifluoride monoethylamine complex is widely used as matrix of the resin-based composite in which some fillers, either powder or fiber, are added. In general the filler content in the resin system is always above 50%, sometimes even more than 100%. Adding of the filler will affect the cure behavior of the resin system very much. Therefore, the ordinary cure conditions (curing temper-

ature and time) will not be suitable for the resin system with filler; it will be necessary to study the effect of filler on cure.

The isothermal cure curves of the resin systems with or without filler SiO₂ are similar in shape, but the change in gel time t_g for various filler loadings is more complex. Table II shows the gel time t_g of the epoxy resin E51-boron trifluoride monoethylamine complex (100 : 5 by weight) containing SiO₂ powder filler with loadings of 10, 20, 40, and 80 phr, respectively, at a temperature of 150°C. With increasing filler loadings the gel time decreases first, reaches a minimum value at the SiO₂ filler loading of 20 phr, and then increases again. But, generally speaking, the gel times t_g of the resin systems with filler are smaller than those of the resin system without filler.

As mentioned before, the gel time is related to the rate of reaction. Decreasing of the gel time implies increasing of the cure reaction rate, which means that the adding of SiO₂ filler causes the acceleration of the cure reaction, which can be further proved by comparing the slopes of cure curves after gel time t_g . The effect of filler on cure reaction rate is the combining result of the following two factors: Introduction of filler reduces reaction concentration of resin, and decreases the reaction rate, but it also introduces a new surface. Absorption of even the catalyst of the surface may cause the reaction rate to increase. When the filler loading is less 20 phr, the mechanism of the accelerating reaction rate is dominant; the reaction rate, in general, is accelerational. However, when the filler loading is more than 20 phr SiO₂ powder, the trend is toward the decreasing of concentration beyond any possible absorption or catalyst. As a result, the whole reaction rate becomes slower. Therefore, the rate of cure reaction should be related to the nature of the surface of the filler SiO₂ powder. In fact, after treatment of the filler SiO₂ by the coupling agent there is not any minimum rate at some SiO₂ filler loading for the epoxy-SiO₂ system.¹¹

Theoretical Prediction of Cure Behavior

Hsich's nonequilibrium thermodynamic fluctuation theory^{12,13} directly describes the changes of physical or mechanical properties of the curing system during cure. According to this theory, the physical or mechanical properties of the resin system during cure can be expressed as

$$\frac{G_\infty - G(t)}{G_\infty - G_0} = \exp[-(t/\tau)^\beta] \quad (2)$$

Table II The Effect of SiO₂ Filler Loading on the Gel Time, Cure at 150°C

SiO ₂	(phr)	0	10	20	40	80
t_g	(s)	110	95	90	98	106

where G_0 and G_∞ are the initial and final physical or mechanical properties during cure, respectively, $G(t)$ is the property at time t , τ the time parameter (relaxation time) of the reaction system, and β the constant describing the width of the relaxation spectrum. In our experiment the mechanical property is just torque. As seen from the isothermal cure curve in Fig. 2, G_0 is zero; the torque begins to appear only after the gel time t_g . Equation (2) describing the cure curve after t_g should be

$$\frac{G_\infty - G(t)}{G_\infty} = \exp\left[-\left(\frac{t - t_g}{\tau}\right)^\beta\right]$$

or

$$G(t) = G_\infty \left\{ 1 - \exp\left[-\left(\frac{t - t_g}{\tau}\right)^\beta\right] \right\} \quad (3)$$

Equation (3) describes the changes in torque of the resin system during cure in which t_g and G_∞ can be read directly from the experimental isothermal cure curve.

In order to obtain the relaxation time r , let $t = t_g + r$; thus

$$\begin{aligned} G(t = t_g + r) &= G_\infty (1 - e^{-1}) \\ &= 0.63G_\infty \end{aligned} \quad (4)$$

From a measurement of the time corresponding to $0.63G_\infty$ in the experimental isothermal cure curve, the relaxation time τ can be obtained from eq. (4):

$$\tau = t - t_g$$

Having determined τ , eq. (3) is reduced to an equation with a single parameter only. A method of nonlinear least squares is used to fit eq. (3) to all experimental cure curves. The values of β at various curing temperatures can be determined using the line of best fit. With this β value, the torque $G(t)$ for any time, i.e., the theoretically predicted value, can be calculated according to the eq. (3) provided that the gel time t_g and the relaxation τ are already known. The theoretical cure curves are also plotted

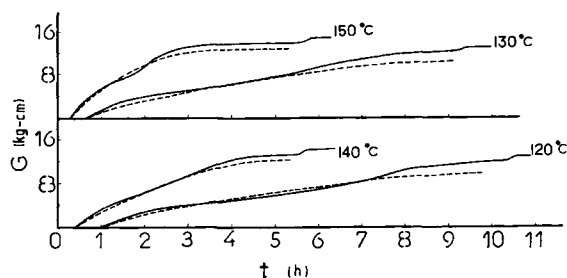


Figure 7 Theoretical prediction and experimental determination of cure behavior of the resin system with 5 phr hardener cured at 120, 130, 140, and 150°C: (—) experimental; (---) calculated.

in Figure 7 as broken lines. The theoretical prediction shows good agreement with the experimental curves for various curing temperatures. The situation was the same for the resin systems with various hardener amounts and various filler loadings.

The nonequilibrium thermodynamic fluctuation theory was originally used to study the vulcanization of the natural rubber-carbon black system.¹² We used it to predict the cure behavior of the epoxy resin-imidazole-SiO₂ system successfully.⁶ Thus, provided that the parameter τ and β are obtained from limit experimental measurements, the whole cure behavior can be predicted for the given resin system. The previous papers³⁻⁶ and results here have shown that the prediction of cure properties theoretically by nonequilibrium thermodynamic fluctuation theory is successful. Partially, the nonequilibrium thermodynamic fluctuation theory directly relates the curing parameters (time, temperature, composition) to the physical or mechanical properties of resin system. Therefore, it is more practice than the cure theory based on the calorimetry.

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