

Curing studies on epoxy system with fillers

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A dynamic torsional vibration method has been developed and used to investigate the isothermal cure processes of a thermosetting resin containing fillers. The isothermal cure behaviour of an epoxy resin–imidazole–SiO₂ system at various temperatures and various SiO₂ filler loadings was predicted using non-equilibrium thermodynamic fluctuation theory. There was good agreement between the theoretical prediction and experimental curing curves. It has been shown that activation energy of the cure reaction remained almost a constant value of $\Delta H = 76.6 \times 10^3 \text{ J mol}^{-1}$ within the range 0 to 120 phr SiO₂ filler loadings, but SiO₂ filler has a complicated effect on the rate of the cure reaction.

1. Introduction

Fillers added into polymer resin can effectively improve the physical or mechanical properties of matrix materials, including reinforcement, wear resistance, flame retardancy etc. The costs and the volume shrinkage during cure can also be reduced when inorganic fillers are used in thermosetting resin. As the filler content in resin systems is always above 50%, sometimes even more than 100%, their cure behaviour and ultimate mechanical properties are dependent to a large extent on the filler content and degree of cure. However, it is the filler that will change the cure processes of the resin system; one can never use the curing procedure used for pure resin system, and additional measuring is necessary.

A variety of experimental techniques has been developed for studying the cure reaction of the thermosetting resin. They include dynamic mechanical methods [1], methods based on calorimetry [2], chemical analysis, spectroscopy [3] and dielectric measurements [4] of which only dynamic mechanical measurements, especially torsional braid analysis (TBA) [5] used widely for following the curing reaction of pure resin, relate the final mechanical properties of the resin. However TBA becomes difficult to apply when fillers are used in thermosets. To overcome the difficulty we have developed an alternative dynamic mechanical measurement – the dynamic torsional vibration method which was used successfully to study the curing processes of epoxy resin, and later applied to the cure behaviour of resin-based composites [6, 7].

A reasonable kinetic model of curing reaction is necessary to predict the cure behaviour of a curing product during cure. The kinetic model based on the method of calorimetry DSC does not have a direct correlation with the mechanical properties of the curing product. Although both Craig [8] and Mussatti and Macoska [9] have developed a kinetic model for predicting viscosity and modulus during the curing reaction, the application of this model is limited because it does not include the resin-filler interreac-

tion. With this problem in mind, Hsich [10, 11] developed a new kinetic model based on the non-equilibrium thermodynamic fluctuation theory and successfully studied the cure behaviour of a natural rubber–sulphur–carbon black system.

In the present paper Hsich's theory was applied to predict the cure behaviour of epoxy composites containing SiO₂ powder fillers at various temperatures and for various SiO₂ filler loadings. The theoretical prediction was compared with the experimental results obtained from the dynamic torsional vibration method. There is a good agreement between the theoretical prediction and the experimental curves.

2. Theory

The non-equilibrium thermodynamic fluctuation theory proposed by Hsich describes directly the changes of the physical or mechanical properties of the curing system. According to this theory, any chemical relaxation (reaction) can be explained by an irreversible thermodynamic fluctuation theory in which any changes in physical or mechanical properties, during the chemical reaction, can be interpreted and predicted from the mean square fluctuation of thermodynamic ordering parameters ξ . The cure reaction can be considered as a multiple chemical reaction in which each chemical reaction is associated with a thermodynamic ordering parameter ξ . Thus variations in physical or mechanical properties during cure can be expressed as the time correlation of the mean square fluctuation of ordering parameters. There is a similarity between the kinetic process of cure and the molecular structural relaxation process. Thus, the physical or mechanical properties of resin systems during cure can be expressed as

$$\begin{aligned} \frac{G_\infty - G(t)}{G_\infty - G_0} &= \sum_i W_i (\Delta \xi_i)^2 \exp \left[- \left(\frac{t}{\tau_i} \right) \right] \\ &= \sum_i g_i \exp \left[- \left(\frac{t}{\tau_i} \right) \right] \end{aligned} \quad (1)$$

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 , $g_i = W_i(\Delta\xi_i)^2$, W_i are the weight constants and τ_i is the relaxation time of the chemical reaction associated with ordering parameters ξ_i .

With the normalized condition of $\sum_i g_i = 1$ and the generalization of Equation 1 for a single relaxation process to a continuous distribution of such processes

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

where β is the constant describing the width of the relaxation spectrum.

3. Experimental procedures

3.1. Dynamic torsional vibration method

Dynamic torsional vibration is a non-resonant forced vibration. The schematic diagram of a home-made experimental apparatus of the dynamic torsional vibration is shown in Fig. 1. The lower mould (3) used as the torsional vibrator is filled with the resin materials. When the motor (6) is switched on, the upper mould (2) comes down, and the moulds close with a gap which can be adjusted. At the same time the motor (5) is turned on, and the lower mould starts a torsional vibration at an angle below 1° by means of the eccentric disc (4) on the speed change gear (7). The torque amplitude of the torsional vibration is changed into electrical signals by means of the strain gauge load cell (1), and is recorded by the recorder. The resin system with a different degree of cure has a different 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

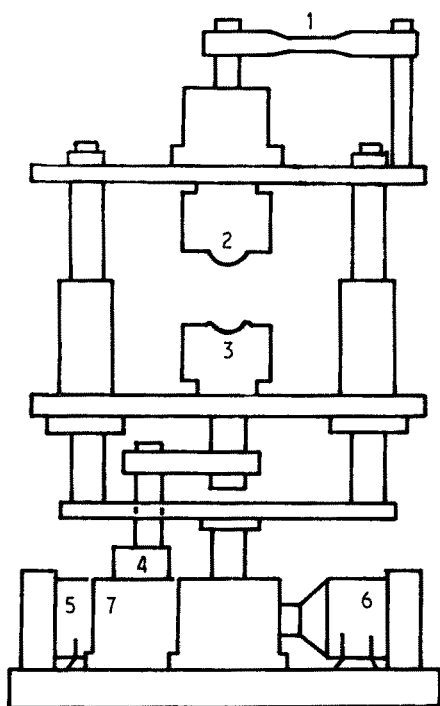


Figure 1 Schematic representation of the dynamic torsional vibration apparatus (1 Strain gauge load cell, 2 Upper mould, 3 Lower mould, 4 Eccentric disc, 5 Motor for torsional vibration, 6 Motor for closing the motor, 7 Speed change gear).

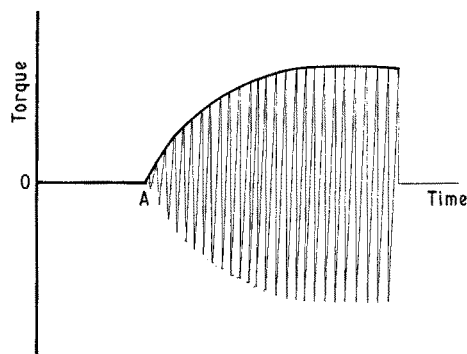


Figure 2 Schematic sketch of the experimental isothermal cure curve. OA is the gel time t_g .

measuring the changes in torque, and continuous curing curves, reflecting whole cure process, can be obtained.

3.2. Materials

The epoxy resin used is a commercial diglycidyl ether of bisphenol A E51 (Shanghai Resin Factory). Imidazole is used as a hardener. The filler is the commercial SiO_2 powder of 600 mesh without any pretreatment. The resin and hardener are mixed in the stoichiometric ratio of 100 parts resin to 4 parts hardener (by weight). Then the mixture is mixed with SiO_2 powder with loadings of 10, 20, 40, 80 and 120 phr respectively. The isothermal curing experiments of the resin systems were carried out at three different temperatures, i.e. 75, 85 and 95°C .

4. Results and discussion

4.1. Experimental curve

The experimental curve obtained is shown in Fig. 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 of the materials, and is a measurement of the degree of cure. The time of closure of the moulds is taken as the starting time, that is zero. The network structure formed during the curing reaction in the range OA of the curing time is not enough to cause turning, so that the experimental curve is linear corresponding to the abscissa. The viscosity of the resin system is high enough at point A i.e. the network formed is complete enough for the gelation in the resin system to occur, and the torque appears. 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, and the increasing amplitude of the torque expresses the rate of the curing reaction. The change torque tended to stabilize with increasing curing time, and the equilibrium torque G_∞ is thus reached. The curing reaction is completed. The envelope of the experimental curve corresponds to the change in mechanical behaviour of the resin system during cure, and represents the isothermal cure of the resin system.

4.2. Isothermal cure curves of the pure epoxy resin

The isothermal cure curves of pure epoxy-imidazole system at temperatures 75, 85, 95°C are shown in

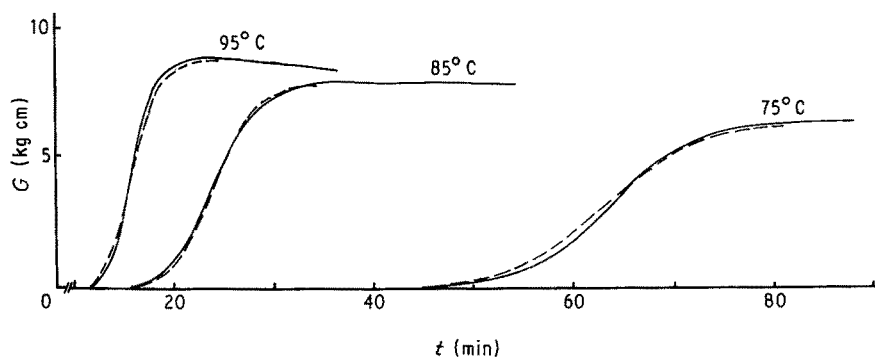


Figure 3 Isothermal cure curves of epoxy resin-imidazole system with 0 phr SiO_2 filler at temperatures 75, 85 and 95°C. — experimental; --- theoretical.

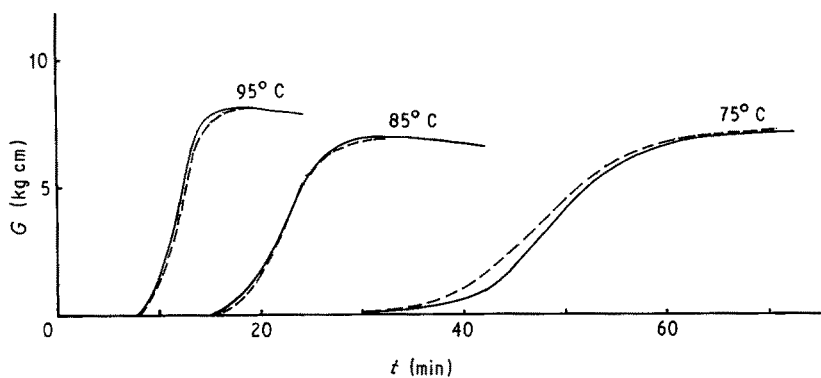


Figure 4 As Fig. 3, but with 10 phr SiO_2 filler.

Fig. 3. The curves are similar in shape at different temperatures, but the gel times and the increasing amplitude of torque are notably different.

The gel time t_g decreases with increasing cure temperature. The slope of the cure curves, after the gel point, is proportional to the rate of cure reaction of the resin system, so that the rate of reaction increases with increasing cure temperature. The gel times of the pure resin system at three different temperatures obtained from Fig. 1 are listed in Table I.

4.3. Isothermal cure curves of the epoxy resin system containing SiO_2 filler powder

The isothermal cure curves of the epoxy resin system containing SiO_2 filler with loadings of 10, 20, 40, 80 and 120 phr, respectively, at three different tempera-

tures 75, 85, 95°C are shown in Figs 4 to 8. The isothermal cure curves of the systems with or without SiO_2 are also similar in shape. The changes in gel times and the rate of reaction with increasing temperature are the same as for the pure epoxy resin. Obviously, the initial torque is equal to zero ($G_0 = 0$) because the cure curve within the time range of 0 to t_g is a linear curve which is identical to the abscissa. G_∞ is the equilibrium value of the torque. For some of cure curves having a maximum (e.g. the cure curve of 95°C), the value of the maximum torque is taken as G_∞ .

It can be noted that gel time t_g decreases with increasing temperature at constant SiO_2 filler loadings, but the change in gel time t_g for various filler loadings at constant temperature is more complex. Generally speaking, the gel times t_g for the powder filler SiO_2 are smaller than for those without the filler.

TABLE I

SiO_2 filler loading (phr)	T (°C)	t_g (min)	τ (min)	τ_0 (10^{-11} min)	ΔH (10^3 J mol $^{-1}$)	β
0	75	45.25	20.50	6.33	76.6	2.70
	85	15.75	9.50			
	95	11.25	5.25			
10	75	30.25	19.50	5.96	76.6	2.55
	85	15.25	9.00			
	95	7.75	5.00			
20	75	21.00	17.50	5.41	76.6	1.98
	85	11.75	7.88			
	95	9.50	4.75			
40	75	24.00	22.30	7.19	76.6	2.07
	85	12.75	10.13			
	95	7.75	6.25			
80	75	26.75	28.00	8.46	76.6	2.16
	85	10.75	13.25			
	95	8.00	7.00			
120	75	40.00	26.75	8.46	76.6	2.35
	85	14.25	13.75			
	95	7.50	7.00			

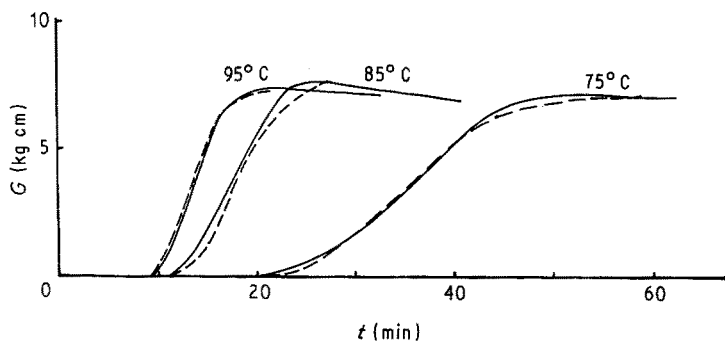


Figure 5 As Fig. 3, but with 20 phr SiO₂ filler.

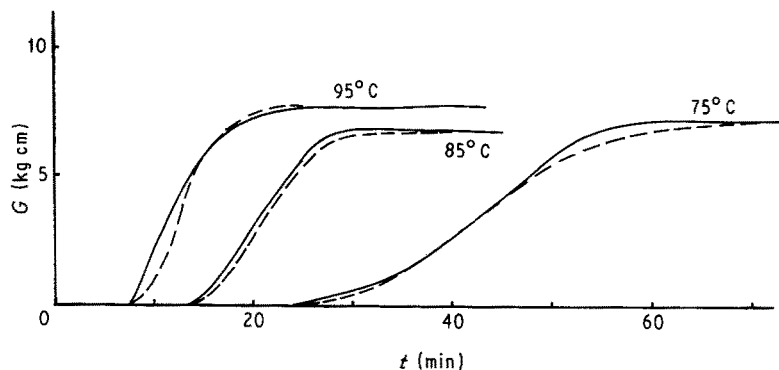


Figure 6 As Fig. 3, but with 40 phr SiO₂ filler.

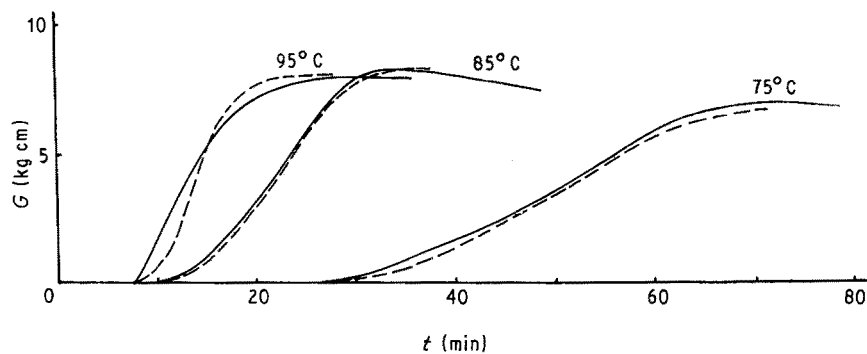


Figure 7 As Fig. 3, but with 80 phr SiO₂ filler.

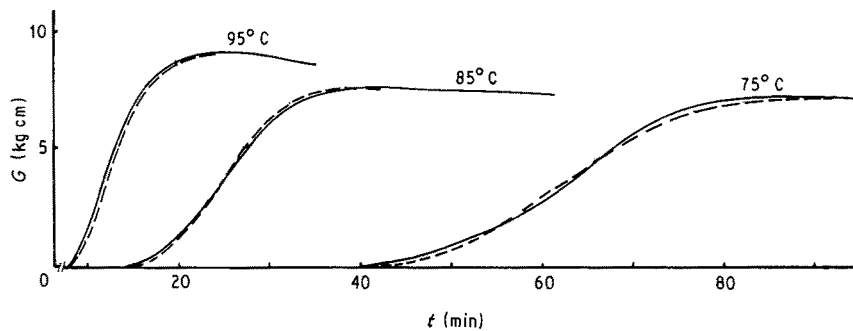


Figure 8 As Fig. 3, but with 120 phr SiO₂ filler.

4.4. Relaxation time and activation energy

As seen from the cure curves 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 cure property of the resin systems during cure in which t_g and G_∞ can be read directly from the experimental cure curve.

In order to obtain the relaxation time τ , let $t = t_g + \tau$, thus

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

From a measurement of the time corresponding to $0.63G_\infty$ in the experimental cure curve, the relaxation

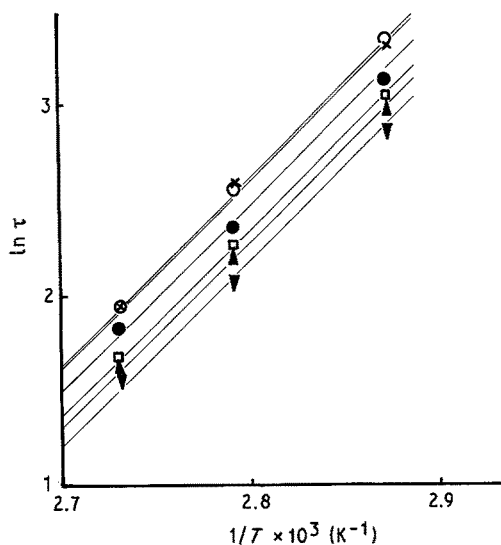


Figure 9 The $\ln \tau$ against $1/T$ plots (\square 0 phr, \blacktriangle 10 phr, ∇ 20 phr, \bullet 40 phr, \times 80 phr, \circ 120 phr).

time τ can be obtained from Equation 4

$$\tau = t - t_g$$

The values for the relaxation time τ at various temperatures and various SiO_2 filler loadings obtained in this way are listed in Table I.

The relationship between the relaxation time τ and the cure temperature T is in accordance with Arrhenius equation

$$\ln \tau = \ln \tau_0 + \frac{\Delta H}{RT} \quad (5)$$

where ΔH is the apparent activation energy of the cure reaction, which can be obtained from the slope of $\ln \tau - 1/T$ plot (Fig. 9).

The $\ln \tau - 1/T$ plots, at various SiO_2 filler loadings, are almost parallel lines, so that the activation energy ΔH has the same values of $76.6 \times 10^3 \text{ J mol}^{-1}$, meaning that the SiO_2 fillers have an insignificant effect on the activation energy. This fact is in accordance with the other results [11, 12].

4.5. Rate of reaction

τ_0 obtained from the section on the ordinate of the $\ln \tau - 1/T$ plot decreases at first, then increases with increasing SiO_2 filler loadings (Fig. 10). The reciprocal of τ_0 at the constant ΔH and T expresses the rate of cure reaction of the resin system, so the curing rate of the resin system increases at first, then decreases, and there is a maximum of 20 phr SiO_2 filler loading.

A combination of two factors influence the effects of SiO_2 filler on the curing rate of the resin system. The addition of the SiO_2 filler reduces the concentration of the resin reactants, and the rate of reaction is reduced. On the other hand, the filler additives at the same time introduce a new surface, which may have absorption, or even catalysis, and therefore accelerate the curing reaction. The mechanism of acceleration is dominant while SiO_2 filler loading is less than 20%. However, reduction of the reactant concentration in the resin system will exceed any possible absorption or catalysis of the filler surface when SiO_2 filler loadings are greater than 20%, and hence the total curing rate

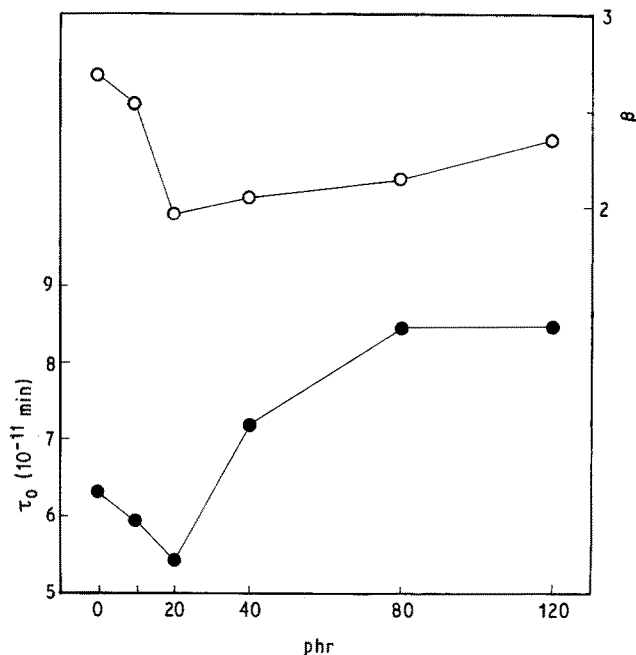


Figure 10 Dependence of τ_0 (\bullet) and β (\circ) on SiO_2 filler loadings.

becomes slow. Thus the rate of reaction is dependent on the nature of the filler surface. In fact, if SiO_2 fillers are treated with a coupling agent, the maximum curing rate for certain SiO_2 filler loadings in epoxy- SiO_2 system will not be observed [12].

4.6. Theoretical prediction

If τ has been determined, Equation 3 is reduced to only a single parameter β equation. A method of least squares is used to fit Equation 3 to all experimental cure curves. The values of β at various filler loadings can be determined using the line of best fit, and these values are listed in Table I (see also Fig. 10). With this β value, the torque $G(t)$ for any time, i.e. the theoretically predicted value, can be calculated according to Equation 3 provided that the gel time t_g and the relaxation time, τ , are already known. The theoretical curves (broken lines) are also plotted in Figs 3 to 8. The theoretical prediction shows a good agreement amongst the experimental cure curves for various filler loadings at various temperatures tested.

5. Conclusions

The conclusions are as follows.

- (1) The dynamic torsional vibration method developed for the cure study of pure resin can also be used to monitor quantitatively the isothermal curing processes of the resin system containing SiO_2 powder filler.
- (2) The non-equilibrium thermodynamic fluctuation theory can successfully describe and predict the mechanical properties of the resin system with or without SiO_2 powder filler during the curing processes.
- (3) The effect of the filler loading on the activation energy ΔH is insignificant. The activation energy of the epoxy-imidazole- SiO_2 system remains almost a constant value of $\Delta H = 76.6 \times 10^3 \text{ J mol}^{-1}$ within the range of 0 to 120 phr SiO_2 filler loadings.
- (4) In general, the adding of SiO_2 filler reduces gel times and increases the rate of cure reaction of the resin system.

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