

Study on Cure Behavior of a Model Epoxy System by Means of TTT Diagram

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Abstract: Curing behavior of a model epoxies system (E-54/AG-80) with DDS as hardener was studied in this paper. Round disk compression mode DMA was executed to study the gel behaviors at different temperatures to determine the relationship between gel time (t_{gel}) and temperature. The cure kinetics was studied by dynamic DSC analysis. Parameters were obtained for establishing a phenomenological cure reaction model. The relationship between glass transition temperature (T_g) and cure degree (α) was also analyzed by both isothermal and dynamic DSC method based on DiBenedetto equation, which gave a mathematical description of T_g as a function of both time and temperature. Consequently, characteristic temperatures such as T_{g0} , $t_{gel}T_g$ and $T_{g\infty}$ were determined. Finally, the Time-Temperature Transition (TTT) diagram was designed based on the data and equations.

Key words: epoxy resin; cure behavior; TTT diagram

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Due to their high strength, modulus and fracture toughness as well as good adhesion and thermal resistance^[1], epoxy resins as matrices are widely used in aeronautics, astronautics, transportation, sports and other industry. Standard epoxy resins are usually based on DGEBA (diglycidyl ether of bisphenol A), which needs active hydrogen or other active groups to open two epoxy rings. Four-functional epoxy like TGMDA (tetraglycidyl methylene dianiline) is often used for high-performance epoxy matrix composites because of its relatively higher cross-linking density over DGEBA. TGMDA can serve at higher temperatures than DGEBA. However, due to the higher cross-linking density, TGMDA is intrinsically brittle. A practical solution for optimizing the properties is to use a bi-component blend of DGEBA and TGMDA. It was expected that the blend epoxy system could provide higher strength, modulus, fracture toughness and higher temperature resistance. It was the intension of this paper to study the curing behavior of the bi-component epoxy system of DGEBA and TGMDA.

Time-Temperature Transition (TTT) diagram

was originally developed to describe the phase transition behavior of steels. TTT concept was also used for description of the complete curing behavior of epoxies as function of temperature and time^[2,3]. A typical TTT diagram of reactive thermosetting systems is characterized by three transition temperatures of $T_{g\infty}$, T_{g0} and $t_{gel}T_g$, and three transition lines. $T_{g\infty}$ denotes the glass transition temperature when the resin is fully cured. T_{g0} is defined as a temperature at which the state of epoxy is changed from non-gelled glass to liquid solution, and $t_{gel}T_g$ is a critical temperature at which the gelation and vitrification of the polymer occurs simultaneously. Gelation line is defined by a group of points at which the covalent bonds of epoxy begin to connect among the linear chains, forming regions of large networks. When the gelation develops, the state of epoxy is changed from a liquid solution to a rubber state, so the viscosity increases drastically. Vitrification occurs when the glass transition temperature of the curing resin increases to the current resin temperature, forming a S-shape line. At this point, the rate of the cure reaction is significantly reduced since further cross-linking requires

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diffusion of molecules through the network. The vitrification line is usually obtained by cure kinetic simulation.

In this study, a methodological procedure was developed to establish cure kinetic model and gelation model by generating and using a series experimental data. The models and the data were then used to form TTT diagram of the model bi-component epoxy system. And it was hoped that the TTT diagram can provide a useful tool for process optimization of epoxy matrix composites.

1 Experimental

1.1 Materials

The model system used in this study was a combination of a two-functional epoxy DGEBA (E-54, Wuxi Resin Factory, Jiangsu province, China) and a four-functional epoxy TGM DA (AG-80, Shanghai Institute of Synthetic Resins) with DDS as the curing agent. They were mixed at a ratio of E-54: AG-80: DDS = 2: 3: 2.

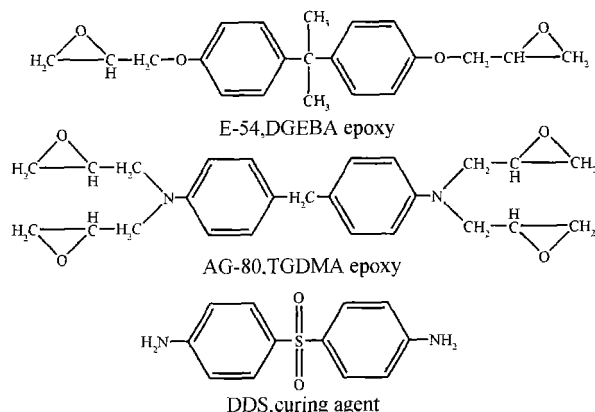


Fig. 1 Chemical structure of the materials in this study

1.2 Blending Procedures and Sample Preparation

The bi-component epoxy system was first mixed and dissolved in THF by stirring at room temperature, forming a homogenous solution. A vacuum pump was employed to extract the solvent out of the resin system for 72h. The prepared resin was preserved at 20 °C.

For thermal mechanical analysis (DMA, in compression mode), round disk samples of a diameter of 15mm were prepared by using the resin with glass fabric as carrier according the test specification.

1.3 Analysis

A differential scanning calorimeter (DSC Q10, Thermal Analysis & Rheology Instruments Inc.) and a dynamic mechanical analyzer (DMA Q800, Thermal Analysis & Rheology Instruments Inc.) were used to study the transition behavior of the system.

DSC Q10 was used in both dynamic and isothermal modes to determine the glass transition temperature. The fresh resin was scanned from - 50 °C to 300 °C to determine T_{g0} , the peak temperature T_{peak} and the total enthalpy ΔH_{total} . Then, the sample was scanned for the second time to obtain $T_{g\infty}$. In the isothermal mode, enthalpies (ΔH_t) were measured at a specific isothermal temperature with different time. Then the sample was executed by a followed dynamic mode from room temperature to 300 °C, the residual enthalpies (ΔH_{res}) and $T_g(T, t)$ were determined to calculate the degrees of conversion $\alpha(T, t)$ according the following equation

$$\alpha(T, t) = 1 - \frac{\Delta H_{res}}{\Delta H_{total}} \times 100\% \quad (1)$$

Because of the wide range of temperatures, the calorimeter was calibrated using standard indium and zinc. The weight of the samples was 3~7mg. All the experiments were carried out under a nitrogen atmosphere with a 50mL/min mass control.

A round disk compression clamp with the upper disk of 15mm diameter and the bottom one of 40mm of DMA Q800 was applied to detect the gel behavior of the system. Isothermal conditions were applied at 130, 140, 150, 160, 170, 180 °C, respectively. The crossing points of the storage modulus and the loss modulus was defined as gel points, while the time corresponding to the points was defined as gel time (t_{gel}).

The overall activation energy for the cure reaction process can be obtained from gel time data, assuming that all reactions during the curing process can be modeled though differential equation containing only one unique apparent activation energy, according to the following equation^[3]:

$$\frac{d\alpha}{dt} = A_0 \exp^{-\frac{E_a}{RT}} f(\alpha) \quad (2)$$

where A_0 stands for a constant for each degree of

conversion, E_a the apparent activation energy for the overall curing reaction, T the isothermal curing temperature, and $f(\alpha)$ a temperature-independent function of conversion. Integration of Eq. (2) from $\alpha=0$ to $\alpha=\alpha_{gel}$, and taking natural logarithms results in

$$\ln(t_{gel}) = \ln\left(\frac{\int_0^{\alpha_{gel}} \frac{d\alpha}{f(\alpha)}\right) + \frac{E_a}{RT} \quad (3)$$

The first item of the right-hand side is time independent, so the upper equation can be written as the following form:

$$\ln(t_{gel}) = A + \frac{E_a}{RT} \quad (4)$$

In Eq. (4), A is a new constant and E_a are unknown parameters. Taking $\ln(t_{gel})$ as y axis and $1/T$ as x axis, a linear fitting can be made to calculate the parameter A and E_a as the intercept and slope, respectively. Putting the two calculated parameters back to Eq. (4), the gelation function will be made for the reac-

tive system.

2 Results and Discussions

2.1 Gelation Study

Gelation is a transition phenomenon characterized by beginning of cross-linking reaction for reactive polymers. It depends on the stoichiometry, reactivity, and functionality of the reactants^[3]. Prior to the gelation, the resin is usually a low-viscous homogenous liquid whereas after the gelation, it exhibits a rubbery viscoelastic behavior and the viscosity increases drastically. The gel time (t_{gel}) is the time when gelation occurs. This time can be experimentally determined using DMA. Results measured on the bi-component epoxy system are shown in Fig. 2. The isothermal conditions were 130, 140, 150, 160, 170, 180 °C, respectively.

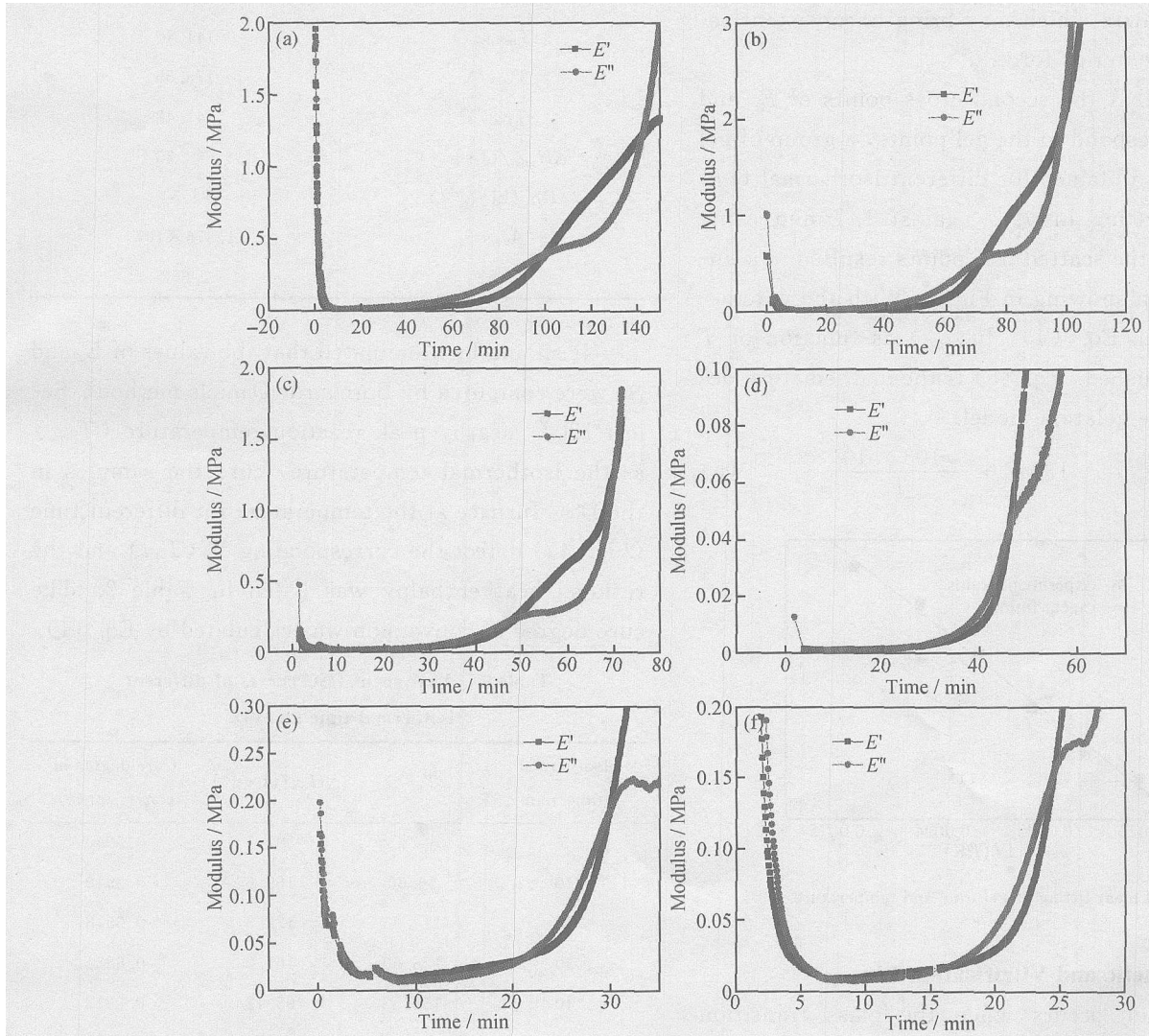


Fig. 2 DMA gelation test diagram at different isothermal temperatures

(a) $T = 130$ °C; (b) $T = 140$ °C; (c) $T = 150$ °C; (d) $T = 160$ °C; (e) $T = 170$ °C; (f) $T = 180$ °C

As indicated, both the storage modulus (E') and the loss modulus (E'') curves decrease sharply at the initiation, followed by a steady stage until a slight increase. Then, the two curves cross two times with each other. At the cross points, the epoxy rings are opened by the hydrogen of amine driving by heat, inducing the molecule chains increasing gradually, and the chains link locally to form fine phases, corresponding to E' and E'' deviating of the base line or even to the first cross point. It indicates that the fine phases connect each other, meaning gelation, when both E' and E'' increase drastically.

It is noteworthy that there is an unclear second step on each E'' curve, this is maybe caused by the reaction type of the system which we still unknown, or even associating with sample preparation because an interface exists between the glass fiber and the uncured resin matrix which may bring inconsistent response to the exterior force.

Defining that the second cross points of E' and E'' curves correspond to the gel points, a group of gel time (t_{gel}) was obtained for different isothermal temperatures. Plotting $\ln(t_{gel})$ against $1/T$ and using Eq. (4) to fit the scatted test points resulted in a linear relationship showing in Fig. 3. With the parameter A and E_a in Eq. (4), $\ln(t_{gel})$ as function of T could be established. Eq. (5) is the mathematical description of the gelation model.

$$\ln t_{gel} = -13.42 + \frac{9.103 \times 10^3}{T} \tag{5}$$

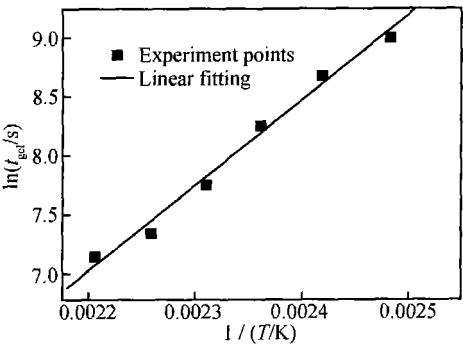


Fig. 3 Linear fitting of gel-time and temperature

2.2 Cure Kinetic and Vitrification Line

Vitrification occurs when the glass transition temperature of the curing resin increases to the current resin temperature. The rate of the cure reaction

is significantly reduced because the gelled network counteracts diffusion of molecules. What should be concerned is that the final physical phase depends on the temperature at which the process has been held at. At vitrification point the resin will not necessarily be 100% cured, some amount of the non-reacted components will still remain, and the reaction will continue very slowly from this point.

All the information of the resin system collected from the first scan and the second scan of the fresh resin by DSC was listed in Table 1, including the results calculated by the software, which developed by Thermal Analysis & Rheology Instruments Inc.

Table 1 Information form DSC analysis

Subjects	Values
$T_{g0}/^{\circ}\text{C}$	-19.41
$T_{g\infty}/^{\circ}\text{C}$	220.97
$T_{\text{initial}}/^{\circ}\text{C}$	141.40
$T_{\text{peak}}/^{\circ}\text{C}$	173.55
$T_{\text{final}}/^{\circ}\text{C}$	241.48
$\Delta H_{\text{total}}/(\text{J}\cdot\text{g}^{-1})$	563.35
$E_a/(\text{kJ}\cdot\text{g}^{-1})$	87.54
A_0/s^{-1}	1.376×10^7
n	1.602

It should be illuminated that the values of E_a and A_0 were computed by Borchardt-Daniels method. Select 180 $^{\circ}\text{C}$ nearby peak reaction temperature (T_{peak}) as the isothermal temperature, cure the samples in the DSC furnace at the temperature for different time (Fig. 4), detect the corresponding $T_g(T, t)$ and the residual heat enthalpy was listed in Table 2. The cure degree of conversion was calculated by Eq. (1).

Table 2 Analysis of DSC curves of different isothermal time at 180 $^{\circ}\text{C}$

Isothermal time/min	$T_g/^{\circ}\text{C}$	$\Delta H_{\text{res}}/(\text{J}\cdot\text{g}^{-1})$	Cure degree of conversion(α)
5		392.1	0.3040
10	56.60	169.6	0.3949
20	114.33	178.5	0.6518
30	126.50	167.2	0.6831
40	158.53	95.12	0.8312
60	179.23	83.40	0.8520
80	197.93	55.0	0.8854

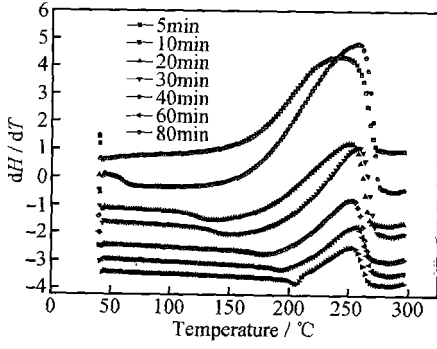


Fig. 4 DSC curves of different isothermal time at 180 °C

Because the relationship between T_g and conversion is independent of the isothermal cure temperature^[3], we can use empirical DiBenedetto equation (Eq. 6) to fit the scattering points of T_g and α to gain a relationship of the two, where λ is taken as an adjustable structure-dependent parameter between 0 and 1. Fig. 5 shows a fit of T_g versus α using the DiBenedetto equation, in this equation, λ is found to be $\lambda = 0.715$.

$$T_g = T_{g0} + \frac{(T_{g\infty} - T_{g0})\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (6)$$

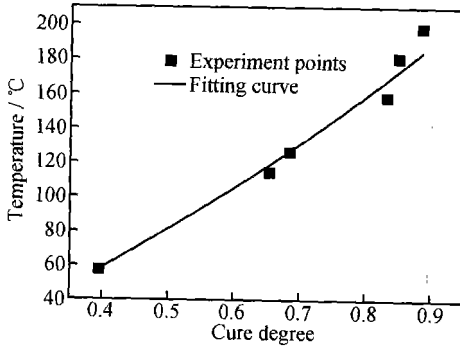


Fig. 5 Relationship between cure degree and temperature using DiBenedetto Equation

Note that Eq. (6) gives a relationship between T_g and conversion, while a relationship between curing degree (α) and (T, t) can be written as Eq. (7), derived from Eq. (2). Then a relationship between T_g and (T, t) can be gained by returning Eq. (7) to Eq. (6). According to the definition of glass transition temperature, let $T_g = T$ in the new equation (Eq. 8), a corresponding time (t_{vir}) can be solved. Plot a curve of T versus t_{vir} , a “S” model vitrification line can be ultimately diagramed, as showed in Fig. 6.

$$\alpha = 1 - [1 - (1 - n)A_0 \exp(-\frac{E_a}{RT})]^{(\frac{1}{1-n})} \quad (7)$$

$$T_g = T_{g0} +$$

$$\frac{(T_{g\infty} - T_{g0})[1 - \{1 - (1 - n)A_0 \exp(-\frac{E_a}{RT})\}^{(\frac{1}{1-n})}]}{1 - (1 - \lambda)[1 - \{1 - (1 - n)A_0 \exp(-\frac{E_a}{RT})\}^{(\frac{1}{1-n})}]} \quad (8)$$

2.3 TTT diagram

The TTT diagram was plotted from the contours of the logarithmic time to gel and to vitrify as a function of the reaction temperature (Fig. 6), which was based on gelation model (Eq. 5) and vitrification model (Eq. 8). The intersection of gelation line and vitrification line, $_{gel}T_g$, was found to be $_{gd}T_g = 70.2^\circ\text{C}$, corresponding a long gel time (134.7 h), which was a relatively long time to manufacture process. Isoconversion curves have been determined by numerical integration of the kinetic model accounting differential coefficient. Isoconversion curves corresponding to $\alpha = 0.3$, 0.4539 and 0.7 are plotted. The isoconversion curve 0.4539 is the fitting result of gelation scattering points.

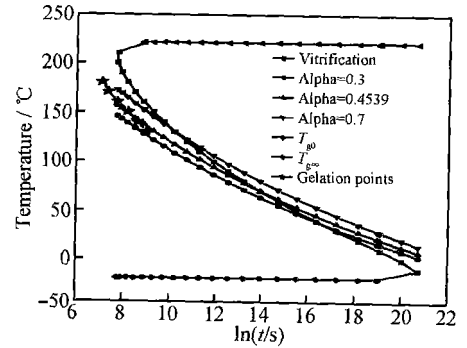


Fig. 6 Time-temperature transition diagram of the epoxy resin

The values of the three characteristic temperatures T_{g0} , $_{gd}T_g$ and $T_{g\infty}$, were found to be -19.41 , 70.2°C and 220.97°C respectively. This diagram shows the different stages during the cure process. According the TTT diagram, the glass transition temperature of a thermosetting resin increases with the extent of conversion. When T_g reaches the value of isothermal cure temperature, the material vitrifies. In the vicinity of vitrification, the segmental mobility of the macromolecule chains decreases, and the overall rate of reaction may controlled by the limiting diffusion of reaction species^[4-8]. Between T_{g0} and $_{gel}T_g$, the solution is a liquid state, which is convenient for flow. Crosslinking initiates from gel line

to the vitrification, where a transition to a glassy solid is made. The reaction is very slow thereafter. Between T_{g1} and $T_{g\infty}$, the solution ends the possibility of flow. Crosslinking continues at a good rate until vitrification.

3 Conclusions

The cure kinetics of a bicomponent high performance epoxy resin was studied by dynamic DSC analysis, and the parameters of the cure reaction were obtained to establish a phenomenological model. The relationship between glass transition temperature (T_g) and cure degree (α) was analyzed with isothermal plus dynamic DSC method based on DiBenedetto equation, a mathematical description of T_g as a function of both time and temperature was suggested. Round disk compression mode DMA was employed to study the gelation at different temperatures, the relationship between gel time and temperature was obtained. The conversion at gelation was turned out to be $\alpha = 0.4539$, while the temperature at which vitrification line and gelation line transected was found to be $T_{gd} = 70.18^\circ\text{C}$. The Time-Temperature-Transition (TTT) diagram was plotted based on the works above, which served as a tool for process optimization in advanced composites manufacture.

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(上接第 56 页)

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