

# 一种双组份液态环氧树脂材料的固化行为

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**摘 要** 将一种液态双酚 A 二缩水甘油醚环氧树脂用曼尼希改型胺进行等温固化, 固化温度范围为 5~60 °C. 采用差示扫描量热法 (DSC) 测试不同固化条件下固化后样品的玻璃化转变温度和剩余反应焓. 结果表明, 玻璃化转变温度  $T_g$  随固化时间的延长而上升,  $T_g$  与转化率之间存在着不依赖于固化温度的一一对应关系. 将  $T_g$  与时间的关系曲线漂移叠合形成固化反应的总曲线, 用时温漂移技术获得了体系唯一的表观活化能 (52.65kJ/mol). 做出包含玻璃化曲线和 iso- $T_g$  曲线的时间-温度-转变 (TTT) 等温固化图.

**关键词** 双组份液态环氧 玻璃化转变温度 等温固化 差示扫描量热

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## CURING CHARACTERISTICS OF A BICOMPONENT LIQUID EPOXY (BLE) MATERIAL

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**ABSTRACT** Isothermal curing of a liquid bisphenol A diglycidyl ether-based epoxy-resin-basin, using a Mannich base of modified amine curing agent, has been performed at four temperature between 5 °C and 60 °C. The samples were isothermally cured for different times and glass transition temperatures ( $T_g$ ) and residual exotherms were determined by Differential Scanning Calorimetry (DSC). The experimental results reveal that  $T_g$  increase with cure time and there is a corresponding relationship between  $T_g$  and conversion which is independent of cure temperature. The master curves were formed by shifting and superposing relationship curves between  $T_g$  and  $t$ . A single apparent activation energy obtained by shift was 52.65kJ·mol<sup>-1</sup>. A Time-Temperature-Transformation (TTT) isothermal cure diagram was carried out to include the time to vitrification and iso- $T_g$  curves.

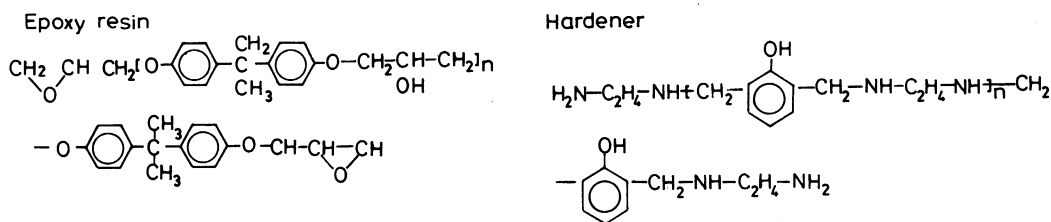
**KEY WORDS** bicomponent liquid epoxy, glass transition temperature, isothermal cure, DSC

## 1. Introduction

In recent years, the research on curing behaviors of epoxy resins has received increasing attention<sup>[1~8]</sup>, many heavy corrosion protection system used for maintenance, as well as binders for building and civil engineering industries are Bicomponent Liquid Epoxy (BLE) formulations. Most of these systems are cured at ambient temperature. The curing process is very important for materials properties. Curing thermosetting materials involves the transformation of low molecular mass liquids into amorphous networks with infinite molecular mass by means of exothermic chemical reactions<sup>[9]</sup>. The state of the samples at any time is dependent on the temperature and the amount of chemical conversion occurred, and can be monitored by the glass transition temperature ( $T_g$ ). As the cure proceeds, there is a considerable increase of the glass transition temperature<sup>[10]</sup>. The fact that  $T_g$  increases nonlinearly with conversion in crosslinking systems makes it more sensitive in the later stages of cure. Moreover,  $T_g$  can be measured accurately and easily throughout the entire range of cure<sup>[11]</sup>. In this work, we examined the variation of  $T_g$  in the relation to the curing reaction.  $T_g$  and the residual exotherm of the reaction was measured by Differential Scanning Calorimetry (DSC). The time-temperature superposition of  $T_g$  vs  $\ln(\text{time})$  provides a kinetically controlled master curve as well as the apparent activation energy of reaction. The activation energy and the data in the master curve can be used to calculate iso- $T_g$  contours prior to vitrification point and the vitrification contour.

## 2. Experimental Procedures

Epoxy resin for this study was a diglycidyl ether of bisphenol A (DGEBA;E44, Wuxi Resin Factory, Epoxy equivalent mass = 230) cured with a Mannich base of modified amine (TSY, Shenyang Chemical Group Institute, amine value = 460 mg/KOH). The chemical structures of the reactants are



The reaction was stoichiometric with one epoxy group reacting with one amine hydrogen. The chemicals were mechanically well mixed at about  $-10\text{ }^{\circ}\text{C}$  for 10 min to obtain a homogeneous mixture. After mixing, the mixture was immediately put into small sealed glass bottles and then store in a refrigerator maintained at  $-70\text{ }^{\circ}\text{C}$  to prevent further reaction. The conversion during mixing is neglected in this paper. The initial conversion after mixing was determined by chemical titration to be less than 1%. A Perkin-Elmer instrument (DSC) was used to measure the glass transition temperature and the residual exotherm ( $\Delta H_r$ ) of the reaction after the material was

subjected to isothermal curing for prespecified times. The small glass bottle with the mixture was taken out of refrigerator and allowed to reach room temperature around 15 min (in order to prevent moisture condensation onto the surface of the cold material). Approximately 10~15mg of mixture was transferred into a DSC aluminum pan and then sealed by crimping around the edge. Sample sealed in the pan was isothermally cured for prespecified time from 0.2 to 200hr. The isothermal curing was performed at 5 °C, 25 °C, 40 °C and 60 °C respectively. After curing, each specimen was quenched from cure temperature to -50 °C at a programmed rate of 320 °C /min and then subjected to a temperature scan from -50 °C to 230 °C at 10 °C /min to determine the  $T_g$  of the material after cure and  $\Delta H_r$  of the remaining reaction. Some samples cure time of which greater than 10 h were cured in an isothermal oven. The specimen was taken out of the oven freely recovered from oven to room temperature, immediately transferred to the DSC unit at 30 °C, quenched to -50 °C, and then rescanned in the DSC. This procedure did not introduce significant error because the time needed for recovering and removing a sample (within 5 min) was insignificant in comparison with the cure time.

### 3. Results and Discussions

The glass transition appears as an endothermic shift in the heat flow over a temperature interval. In this work  $T_g$  was measured as the halfway point of the step-transition. The fractional conversion is calculated from the residual enthalpy  $\Delta H_r$  of the partially cured resin and the total enthalpy of reaction ( $\Delta H_T$ ) corresponding to one unreacted mixed sample:

$$X = (\Delta H_T - \Delta H_r) / \Delta H_T \quad (1)$$

#### 3.1 Experimental $T_g$ versus residual heat of reaction

Fig.1 show that both  $T_g$  and  $\Delta H_r$  change regularly with cure time.  $T_g$  increases while  $\Delta H_r$  decreases until the reactants are fully consumed. However  $T_g$  is more sensitive to changes in conversion and can be measured more accurately. It can be found from Fig.1 that in the later stages of cure  $T_g$  shows noticeable increase and  $\Delta H_r$  is almost unmeasurable.  $\Delta H_r$  is used to calculate the extent of reaction according to equation (1). Fig.2 show that the result for each cure temperature covers a wide range of  $T_g$  and clearly overlap those for other cure temperature. It is demonstrated that, for this epoxy-amine system, there is an unique one to one relationship between  $T_g$  and the fractional conversion, independent of cure temperature.

#### 3.2 Effect of the curing condition on the glass transition temperature

During the isothermal curing at  $T_{cure}$ , the  $T_g$  of the system increases with the cure time due to the increase of the network crosslinking density. Beyond the vitrification time,  $T_g$  becomes higher than the curing temperature. Samples which had vitrified for prolonged cure time underwent sub- $T_g$  physical annealing at the temperature of cure. Thus, a structural relaxation process or physical aging in the amorphous phase occurs. Upon the first DSC scanning up from -50 °C through  $T_g$ , these samples exhibited an endothermic peak in the glass transition interval and these phenomena has been found in this work, shown in Fig.3. The operational definition of  $T_g$  was also illustrated.

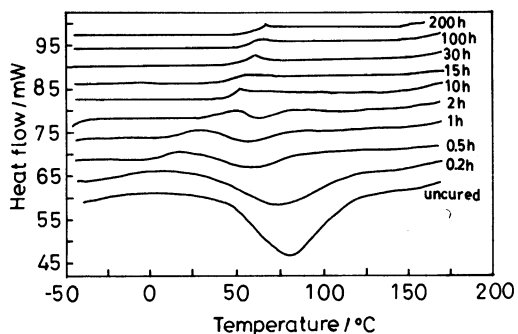


Fig.1 Heat flow of samples cured at 40 °C for different time versus temperature

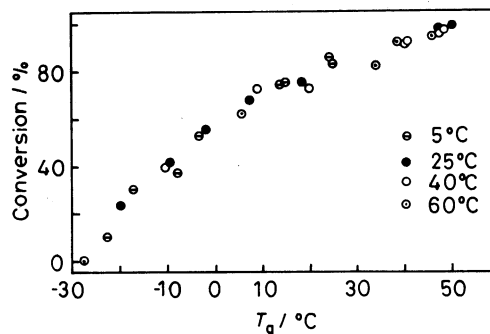


Fig.2 Fractional conversion versus  $T_g$  of partially materials cured at different cure temperatures

In order to eliminate the endothermic annealing peaks, Wisanrakkit recommended that specimens were quickly quenched from temperature just above the endothermic peaks and then immediately rescanned. This procedure did not introduce significant change in the estimate of the chemical conversion of the sample [12].

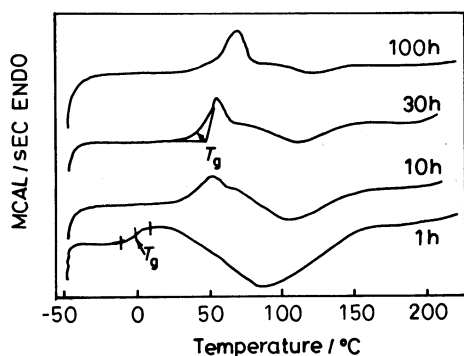


Fig.3 DSC scan of samples isothermally cured at 25 °C for different time

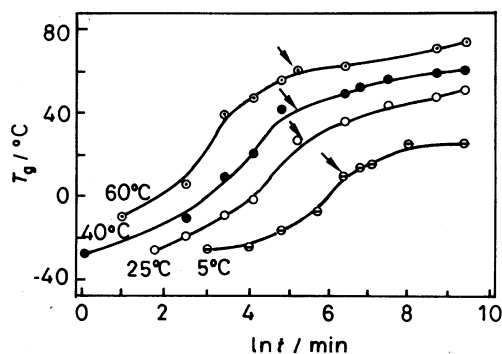


Fig.4  $T_g$  versus time at different cure temperatures

### 3.3 Time dependent of $T_g$

The variation of  $T_g$  obtained in this work with time is shown in Figure 4. Neglecting the contribution of diffusion control, the variation of  $T_g$  with cure time and temperature can be described as:

$$F(T_g) = \ln k(T) + \ln t \quad (2)$$

For a kinetically controlled reaction, all isothermal  $T_g$  versus  $\ln(\text{time})$  curves can be superimposed by simply shifting along the  $\ln(\text{time})$  axis relative to a fixed reference temperature to form a master curve (Fig.5). Note that the vitrification points at different cure temperature are designed on the master curve by arrows. The fact that the isothermal vitrification points for all cure

temperature lie on the master curve indicates that prior to vitrification, the reaction is primarily kinetically controlled.

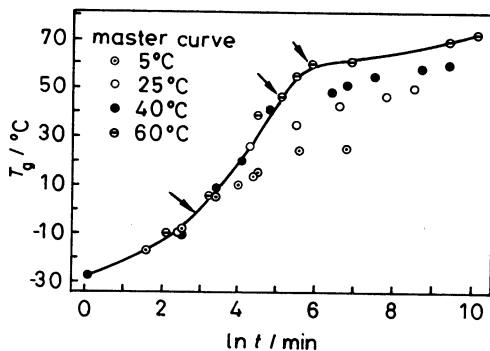


Fig.5 Superposition of curves for  $T_g$  versus  $\ln t$  to form a master curve ( $T_{ref} = 40\text{ }^\circ\text{C}$ )

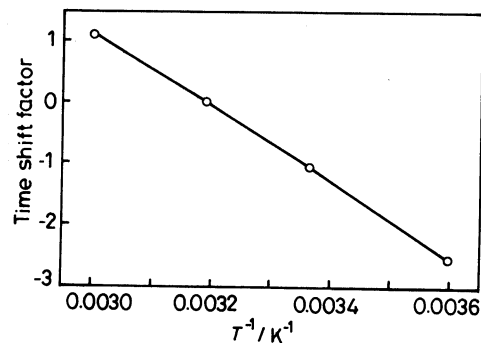


Fig.6 Arrhenius plot of the shift factors versus  $1/T$

### 3.4 Activation Energy

Equation (2) describes the variation of  $T_g$  with cure time and temperature. Let  $T_g$  vary with time  $t_1$  for cure temperature  $T_1$ , and with time  $t_2$  for cure temperature  $T_2$ , then

$$F(T_g) = \ln k(T_1) + \ln(t_1) = \ln k(T_2) + \ln(t_2) \quad (3)$$

$$\ln(t_1) - \ln(t_2) = \ln k(T_2) - \ln k(T_1) \quad (4)$$

The shift factor,  $A(T)$ , can be used to calculate apparent activation energy of the reaction, since equation (4) provides the relationship between the time shift factors and the rate constants  $A(T) = \ln(t_{ref}) - \ln(t_T) = \ln K(T) - \ln K(T_{ref}) = -E/RT + E/RT_{ref}$ . The shift factors relative to  $40\text{ }^\circ\text{C}$  is listed in table I, plotting the master curve shift factor against reciprocal temperature ( $1/T$ ) yield a straight line with a slope  $-E/R$  (Fig.6). The apparent activation energy then obtained is  $52.56\text{ kJ}\cdot\text{mol}^{-1}$ . It is well known that the system activation energy less  $60\text{ kJ}\cdot\text{mol}^{-1}$  of which can react rapidly at ambient temperature. The result also suggest for the present system that there is only one overall reaction mechanism with a single apparent activation energy.

Table 1 Shift factor relative to  $40\text{ }^\circ\text{C}$  for different cure temperature

Cure Temperature/ $^\circ\text{C}$	Shift Factors $A(T) = \ln(t_{ref}) - \ln(t_T)$
5	-2.55
25	-1.05
40	0
60	1.10

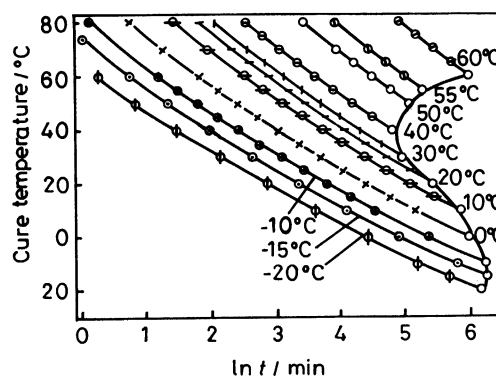
Table 2 contains the apparent activation energies obtain by time-temperature shift of  $T_g$  with the values for other epoxy system.

**Table 2** Activation energies for epoxy systems obtained by  $T_g$ -shift

System	Activation Energy/ $\text{kJ}\cdot\text{mol}^{-1}$	Reference
DGEBA-DETA	67.08	15
Epoxy Novolac-DDS	61.32	13
DGEBA-TMAB	63.84	14
DGEBA-anhydride-imidazole		
100/90/1.5	63.85	10
100/50/1.5	69.30	10
DGEBA-Mannich amine	52.56	this work

### 3.5 Construction of the Vitrification Curve and Iso- $T_g$ Contours in the Isothermal TTT Diagram

The reaction activation energy determined in the previous section can be used for constructing an iso  $T_g$  contour. The relationship between times to reach a fixed  $T_g$  at different cure temperature for a kinetically controlled reaction given by equation (4) recast as  $-Ea/RT_1 + \ln(t_{Tg,1}) = -Ea/RT_2 + \ln(t_{Tg,2})$ , where  $t_{Tg,1}$  is the time needed to reach a given  $T_g$  at cure temperature  $T_1$  and  $t_{Tg,2}$  is the time needed to reach the same  $T_g$  at cure temperature  $T_2$ . With the reaction activation energy, each point on the master curve provides a necessary date point to reach a particular  $T_g$  at  $T = 40^\circ\text{C}$ , which can be used for the calculation of an iso- $T_g$ . Vitrification points for all possible values of  $T_g$  constitute the vitrification curve in the TTT diagram. Fig.7 shows the vitrification curve and different iso- $T_g$  contours. The maximum time to vitrification at low temperature can be considered to be due to opposing influences of the temperature dependencies of the viscosity and the reaction rate constant. The minimum time to vitrification at high temperature is a consequence of the opposing influences of the increasing reaction rate constant and the decreasing concentration of reactants at vitrification with increase of temperature. From a practical point of view, the calculation procedure provides a convenient ways for calculating the entire vitrification curve from limited short-time data at high cure temperature.



**Fig.7** Calculated isothermal TTT diagram showing iso- $T_g$  and vitrification curve

## 4. Conclusions

For present BLE system, there is a unique one-to-one relationship between  $T_g$  and conversion which is independent of the cure temperature. A master curve at a reference cure temperature (40

℃) was obtained by plotting time-temperature shift of the  $T_g$  versus  $\ln(t)$  at different temperature. An activation energy for the reaction equal to  $52.65\text{kJ}\cdot\text{mol}^{-1}$  was calculated. The single activation energy suggests that only one overall reaction mechanism dominates the curing reaction of the present BLE system. The isothermal vitrification points at all cure temperatures lie on the master curve, which indicates that the reaction prior to vitrification is only kinetically controlled. In the TTT cure diagram, the master curve, together with the calculated activation energy is used as a basis for a simple calculation of vitrification curves and iso- $T_g$  contours are presented.

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