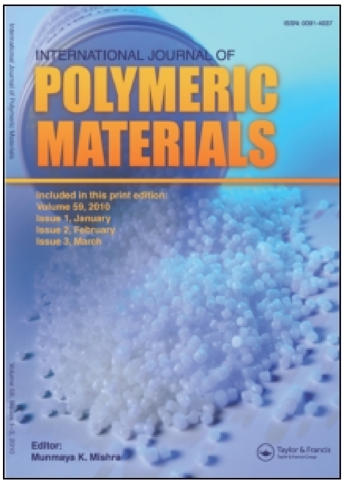

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Curing Behavior, Kinetics and Thermal Properties of o-Cresol Formaldehyde Epoxy Resin Modified by Liquid Crystalline Epoxy Resin

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Curing Behavior, Kinetics and Thermal Properties of o-Cresol Formaldehyde Epoxy Resin Modified by Liquid Crystalline Epoxy Resin

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The curing kinetics of a bi-component system of o-cresol-formaldehyde epoxy resin (o-CFER) modified by liquid crystalline p-phenylene di[4-(2,3-epoxypropyl) benzoate] (p-PEPB), with 4,4-diamino-diphenyl ether (DDE) as a curing agent, was investigated by nonisothermal differential scanning calorimetry (DSC) method. The relationship between apparent activation energy, Ea, and the conversion α *was obtained by the isoconversional method of Ozawa. A molecular reaction mechanism is proposed. The results show that the values of Ea in the initial stage are higher and tend to decrease slightly with the reaction progress. The primary amines have a higher Ea than secondary amines. The average curing Ea of o-CFER/p-PEPB/DDE system is 61.64 KJ/mol. These curing reactions can be described by a model proposed by Šesták and Berggren, which includes two parameters of m and n. Parameters such as reaction orders were evaluated using the Šesták-Berggren (S-B) equation and the following kinetic equation:* $d\alpha/dt = A\exp(-Ea/RT)\alpha^m(1-a)^n$. *The curing behavior of the system was studied by polarized optical microscopy (POM) and torsional braid analysis (TBA). The compatibility of the p-PEPB and o-CFER system is very good. Temperature of mechanical loss peak is higher by 63°C than the common o-CFER epoxy resin, when the weight ratio of p-PEPB with o-CFER is 4:100.*

Keywords: curing kinetics, epoxy resin, liquid crystal, thermal analysis

INTRODUCTION

Epoxy resins are widely applied as engineering thermosets because of their good mechanical and thermal properties [1]. Unfortunately, they also have low fracture toughness. Two common approaches for epoxy

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modifications are introduction of functionalized reactive rubbers or thermoplastics. Reactive rubbers like carboxyl-(CTBN), amine-(ATBN) or epoxy-terminated butadiene acrylonitrile (ETBN) have improved the toughness of epoxy products. However, the blends show adverse effects on glass transition temperature range, stiffness and strength [2–4]. The toughening mechanism of such blends involves a chemically induced phase separation process. On the other hand, toughening epoxy resins with thermoplastics presents significant problems in processing due to the large viscosity difference between the thermoplastics and the epoxy resins.

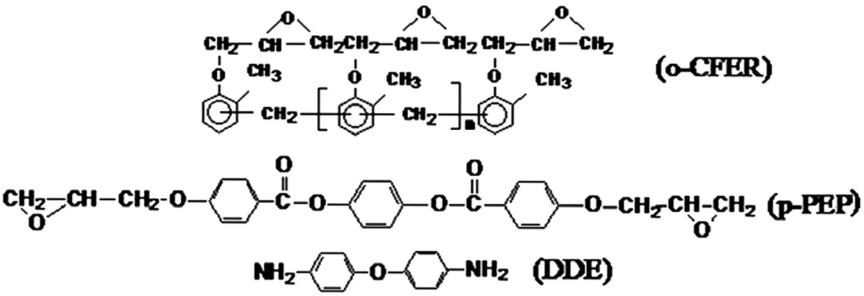
Recently, it has been recognized that these properties of epoxy resins could be greatly enhanced if liquid crystalline (LC)-like structures are incorporated into the epoxy networks [5]. LC materials have great potential as functional molecular systems because of their self-organized dynamic structure. Thermotropic liquid crystalline compounds have become important in the field of advanced materials, such as electronic devices, high-strength fibers and so on [6].

At present, many investigators have reported the cure kinetics of epoxy resins and Liquid Crystalline Epoxy Resins, LCER, by isothermal and nonisothermal differential scanning calorimeter (DSC) data [7–11]. The co-cure reaction of neat epoxy resins with LCER can form in situ molecular composites, which can modify the properties of epoxy resins [12]. However, there were no studies about bi-components until now. In this paper, the curing kinetics of the o-CFER/p-PEPB/DDE system is investigated by nonisothermal DSC at different heating rates. The relationship between Ea and α in the overall curing reaction is revealed by the Ozawa's method [13]. Some kinetic parameters are obtained according to the Šesták-Berggren (S-B) equation [14–15]. The molecular mechanism of curing reaction is proposed. The thermal properties of this composite system are investigated by torsional braid analysis (TBA). The morphology of curing materials is examined by polarizing optical microscope (POM).

EXPERIMENTAL

Materials

P-phenylenedi[4-(2,3-epoxypropyl)benzoate] (p-PEPB) was synthesized from hydroquinone, allyl bromide and 4-hydroxy ethyl benzoate according to the literature [16,17]. Its melting point and clearing point are 180 and 250°C, respectively, and it has a nematic texture. The epoxy value is 0.401 mol/100 g. The o-cresol-formaldehyde epoxy



SCHEME 1 The chemical structures of o-CFER, p-PEPB and DDE.

resin (o-CFER) was synthesized according to the literature [18]. 4,4-diaminodiphenyl ether (DDE) was analytically pure grade and supplied by Beijing Chemical Reagent Co., China. The chemical structures of the epoxy resin, DDE and p-PEPB are shown in Scheme 1.

Preparation of o-CFER/p-PEPB/DDE

The samples were mixed homogeneously in needed weight ratios of o-CFER with p-PEPB and heated to the meltpoint, then they were cooled to room temperature, and DDE was added to the systems in a stoichiometric ratio of one epoxy group to one N-hydrogen group. In the kinetic experiment (DSC), the weight ratio of p-PEPB to o-CFER is 4:100. In the torsional braid analysis, the weight ratio of p-PEPB to o-CFER is 2, 4, 6, 8, 10 to 100, respectively.

Characterization of Curing System

Curing reaction was carried out in a differential scanning calorimeter (Diamond, Perkin Elmer Co., USA). The DSC instrument was calibrated with high-purity indium. An approximately 5 mg sample in a standard aluminum pan was individually heated at 5, 10, 15, and 20°C/min from 25 to 300°C under N_2 atmosphere.

The phase behavior of the target compounds was measured by polarizing optical microscope (59XA, Yong-Heng Co., Shanghai, China).

Torsional braid analysis (TBA) was performed using dynamic mechanical spectrometer (GDP-4, Jilin University China) at a heating rate of 2°C min^{-1} from 20 to 220°C.

RESULTS AND DISCUSSION

Optical Texture

The polarized optical microscopy (POM) can identify the mesophases of LC material. The POM was used at every stage of the curing reaction to monitor the change in texture of the sample (the weight ratio of p-PEPB to o-CFER is 4:100). As seen from Figure 1, at a low content of p-PEPB, some little bright spots were observed. Then the bright spots enlarged and increased gradually along with the content of p-PEPB, and took on a structure of sea-island. This result is shows that the mixed system has a phase-separated structure as the content of p-PEPB increases. This is because the liquid crystalline molecules have a stronger tendency of self-aggregation than with o-CFER molecules. The polarized optical micrographs show that the liquid crystalline phase was fixed in the system by the cure process.

Curing Behavior and Activation Energy

The kinetics of curing reaction was measured by the nonisothermal DSC method at heating rates of 5, 10, 15 and 20°C/min. Figure 2

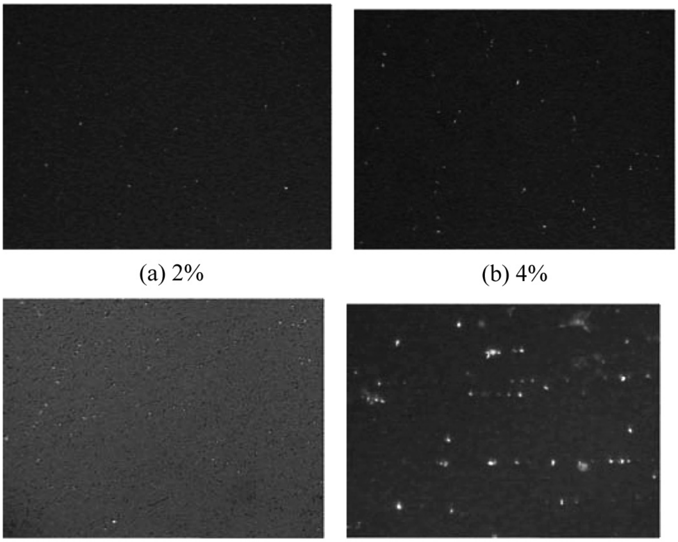

(a) 2%
(b) 4%
(c) 6%
(d) 10%

FIGURE 1 POM photographs of cured o-CFER/p-PEPB/DDE. (a) 2%; (b) 4%; (c) 6%; (d) 10%.

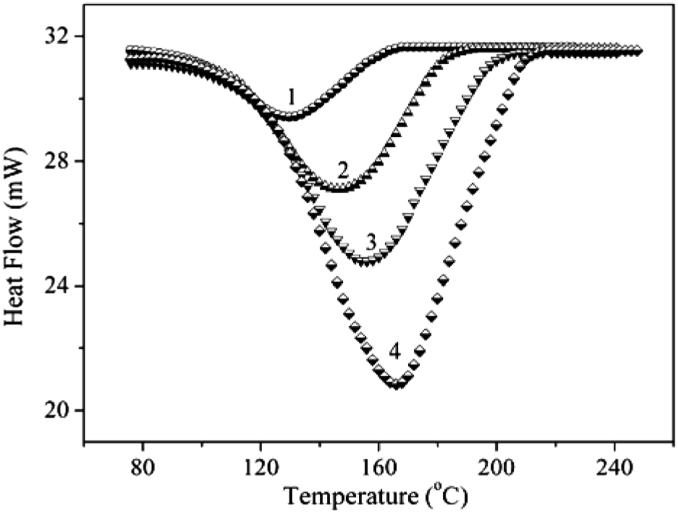


FIGURE 2 DSC curves of o-CFER/p-PEPB/DDE at different heating rates. Heating Rate: 1:5°C/min; 2:10°C/min; 3:15°C/min; 4:20°C/min.

shows the DSC curves for o-CFER/p-PEPB/DDE recorded at the different heating rates. As seen from Figure 2, the initial curing temperature (T_{ci}), the peak temperature (T_{cp}) and the finishing temperature (T_{cf}) increased with the heating rate, and the temperature range of the reaction broadens. The DSC curve of the o-CFER/p-PEPB/DDE is very smooth and only has one curing peak, which indicates that the compatibility of this system is very good.

It can be observed from Figure 2, that increased heating rate leads to decreased cure time. Simultaneously, on increasing the heating rate, the curing curves for the tested specimens are shifted to higher temperatures.

The plots of the initial temperature (T_{ci}), the peak temperature (T_{cp}), the finishing temperature (T_{cf}) vs. heating rate (β) are presented in Figure 3, respectively. From the heating rate $\beta = 0$, we can obtain the gel point of cured-system, T_{gel} is 96.5°C, curing temperature T_{cu} is 118.7°C, final temperature T_f is 140.5°C. The linear correlation coefficients R are between 0.9941 and 0.9960.

For the nonisothermal curing process, the equation for isoconversional method can be expressed in several ways. Equation (1) is known as Ozawa's method [7,9,13], which can be applied to different conversion α of the curing process. Figure 4 shows the ln β vs. $1/T$ plots in the interval of $0.05 \leq \alpha \leq 0.95$. Thus, for a given α, the apparent activation

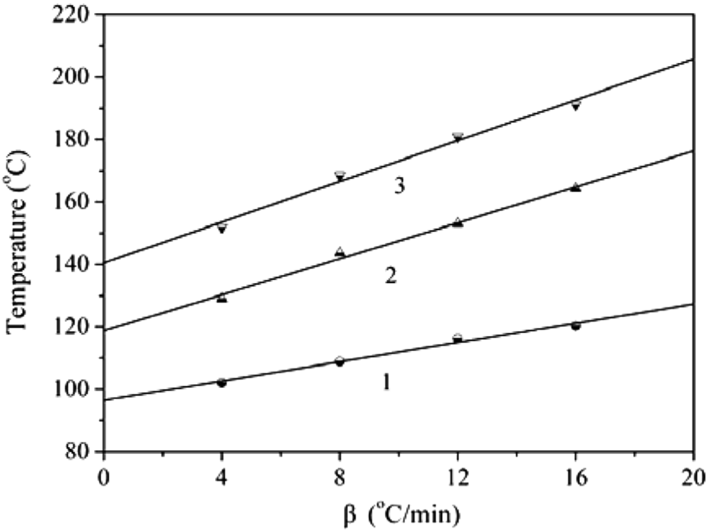


FIGURE 3 T-β curves of p-PEPB/o-CFER/DDE cured-system.

energy Ea can be obtained from linear regression according to Eq. (1).

$$\ln\beta = A' - 1.052\frac{Ea}{RT} \tag{1}$$

where A' is the pre-exponential factor of Arrhenius equation, T is the temperature (K), R is the gas constant (8.314 J·mol/K), β is heating rate, $A' = \lg AEa/g(\alpha)R - 3.315$, $g(\alpha) = \int_0^\alpha d\alpha/f(\alpha) = A/\beta\int_0^T \exp(-Ea/RT)dT$, $f(\alpha)$ is a temperature-dependent kinetic model function.

According to the relationship of α–T and the Ozawa equation, from the plots of ln β vs. $1/T$, the Ea at any conversion α can be calculated, the linear coefficients are all included between 0.9991 and 0.9999, and it shows that the curing systems well obey Ozawa's kinetic model. The average Ea of o-CFER/p-PEPB/DDE system is 61.64 KJ/mol. Figure 5 shows the variation of Ea in the interval of $0 \leq \alpha \leq 1$. As seen from Figure 5, the Ea values change with various α because the mechanism of the curing reaction for epoxy/amine is complex due to gelation, vitrification and phase change of the LC system in the curing reaction process. The values of Ea decrease a little in the final stage of reaction.

The molecular mechanism of the curing reaction is a primary reason. As seen from Figure 5, the value of Ea in the initial stage is higher

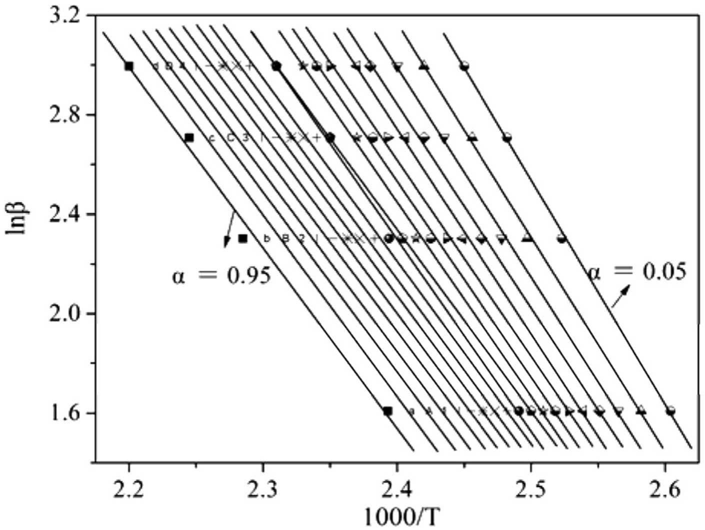


FIGURE 4 $\ln \beta - 1/T$ plots in the interval of $0.05 \le \alpha \le 0.95$.

than those of any other time. With the reaction progression, the *Ea* tends to decrease slightly, which is a result of reaction mechanism. In the initial stage, the hydroxyl group does not exist in the o-CFER/p-PEPB/DDE system or only in trace amounts, and the

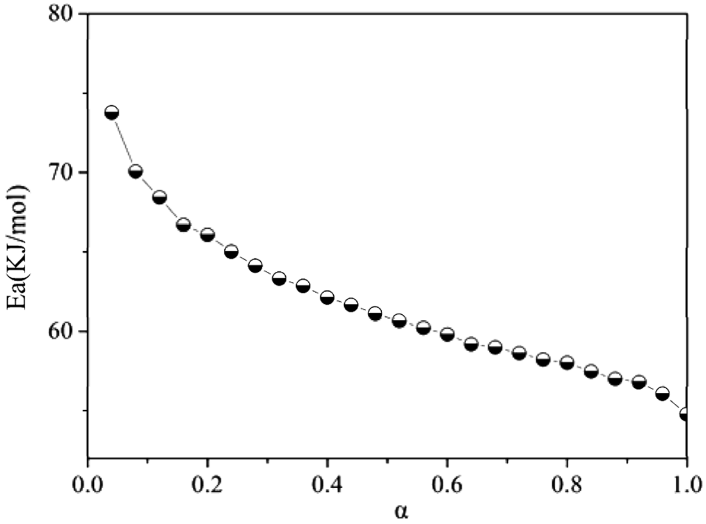
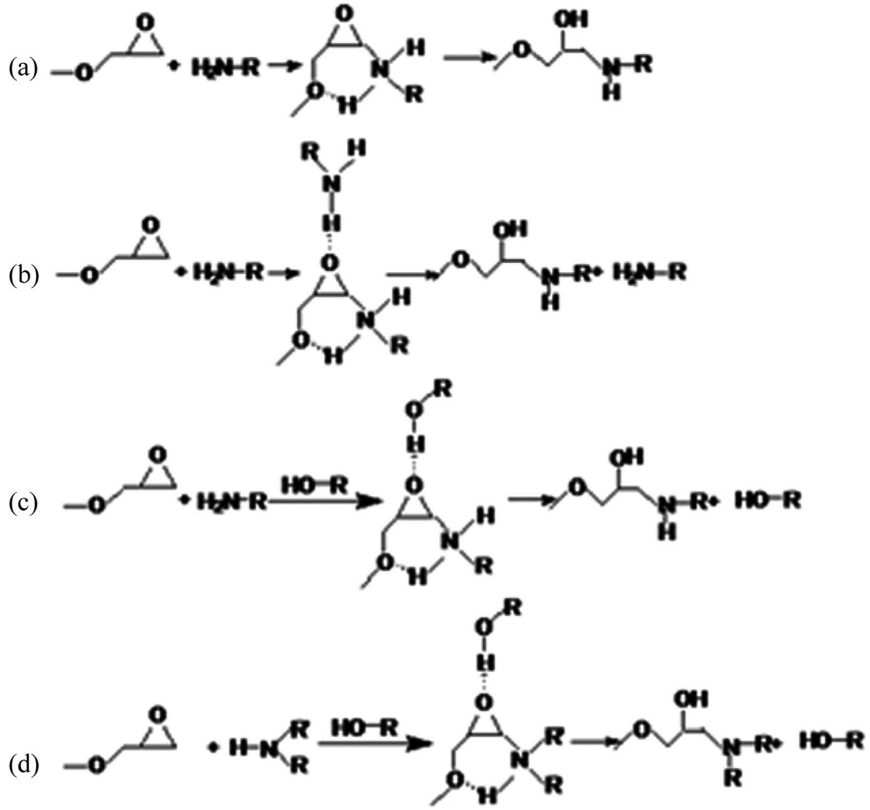


FIGURE 5 Relationship of *Ea* vs. α for the sample.

reaction occurs between the epoxy group and primary amine which has a different transition state than the hydroxyl catalyzed reaction. These transition states are shown in Scheme 2 (a)–(d). *Ea* for both uncatalyzed (a) and self-promoted reaction (b) pathways are higher than hydroxyl catalyzed (c), because of larger steric effects [19]. It is noteworthy that the curing reaction of an epoxy group with amine generates a hydroxyl group, so that the reaction is accelerated as the reaction progresses and the reaction pathway is changed to (c). On the other hand, in early stages, the primary amine reacts first, however, the secondary amine controls the reaction in the middle and final stages. There are lower *Ea* values and higher rate constants for secondary amine than those of primary amine around the hydroxyl



SCHEME 2 Transition states of the three reaction pathways. (a) uncatalyzed, (b) self-promoted, (c) alcohol-catalyzed, (d) second amine reaction of alcohol-catalyzed.

groups [20,21]. Therefore, with the reaction progress the Ea tends to be decrease.

Cure Kinetics of o-CFER/p-PEPB/DDE

The basic assumption for the application of DSC technique to the thermosets is that the rate of the kinetic process $(d\alpha/dt)$ is proportional to the measured heat flow $\phi = dH/dt$

$$r = \frac{d\alpha}{dt} = \frac{\phi}{\Delta H} \tag{2}$$

where ΔH is the enthalpy of the curing reaction, α is extent of reaction or conversion and r is defined as the curing rate. The reaction rate of the curing process in the kinetic analysis can be described as follows:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{3}$$

where $f(\alpha)$ is a temperature-dependent kinetic model function, $K(T)$ is a temperature-dependent reaction rate constant and follows an Arrhenius equation:

$$K(T) = A\exp\left(\frac{-Ea}{RT}\right) \tag{4}$$

As is known, the Ozawa equation [1] can be applied to different degrees of conversion. According to Málek's viewpoint, the values of Ea can be used to find the appropriate kinetic model which best describes the conversion function of the curing system [14]. The most suitable kinetic model can be evaluated with the functions $y(\alpha)$ and $z(\alpha)$ according the Eqs. (5) and (6) as follow:

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)\exp(x) \tag{5}$$

$$z(\alpha) = \pi(x)\left(\frac{d\alpha}{dt}\right)T/\beta \tag{6}$$

where x is a reduced activation energy $(x = Ea/RT)$,and $\pi(x)$ is the expression of the temperature integral, which can be well approximated using the fourth rational expression as in Eq. (7)

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{7}$$

The $y(\alpha)$ function is proportional to $f(\alpha)$ function, being characteristic for a given kinetic model. The shape and the maximum of both $y(\alpha)$ and $z(\alpha)$ function for several models, are normalized within (0, 1) range. The maximum α_M of the $y(\alpha)$ function and α_P^∞ of the $z(\alpha)$ function suggest the choice of the most suitable kinetic model characterizing the curing process [9,14].

Using the value of Ea and knowing the kinetic model, the pre-exponential factor A is calculated according to Eq. (8)

$$A = -\frac{\beta x_p}{Tf'(\alpha_p)}\exp(x_p) \tag{8}$$

where $f'(\alpha)$ is the differential form of the kinetic model $df(\alpha)/d\alpha$, α_p is the conversion corresponding to the peak on DSC curve.

The average value of Ea was used to calculate both $y(\alpha)$ and $z(\alpha)$ functions, using Eqs. (6) and (7). Figures 6 and 7 show the variation of $y(\alpha)$ and $z(\alpha)$ values with conversion α for the sample at different heating rates. The values of both $y(\alpha)$ and $z(\alpha)$ were normalized within the (0, 1). From Figures 6 and 7, the value of α_M and α_P^∞ (the value of α while $y(\alpha)$ or $z(\alpha)$ at the maximum value of DSC peak, respectively) can be obtained. Both α_M and α_P^∞ are used to choose the kinetic model which is correct for the system studied [14].

The values of α_p, α_M and α_P^∞ for the sample are listed in Table 1. As can be seen, the values of α_M are lower than the value of α_p, whereas

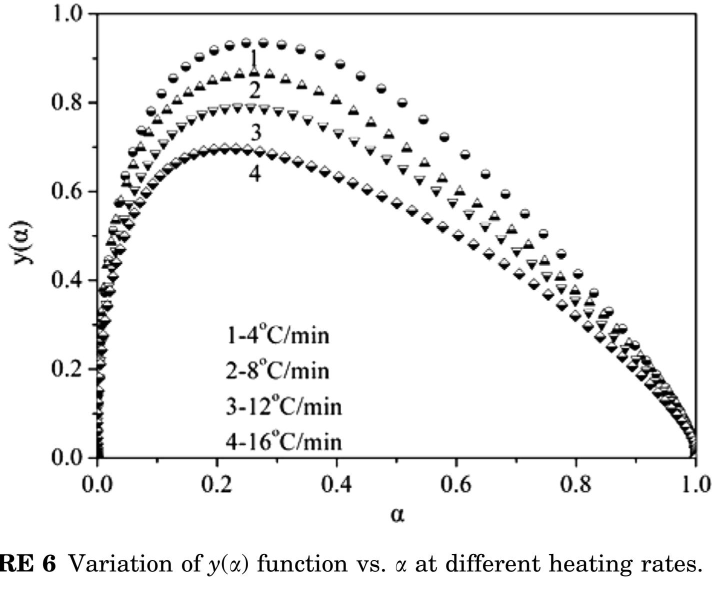


FIGURE 6 Variation of $y(\alpha)$ function vs. α at different heating rates.

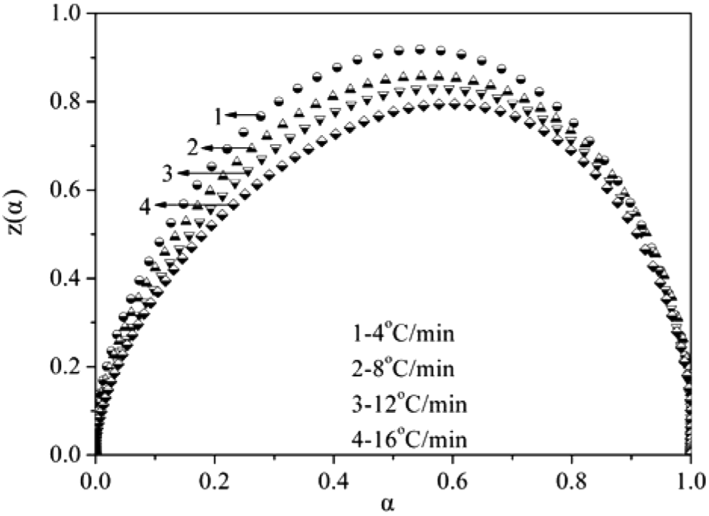


FIGURE 7 Variation of $z(\alpha)$ function vs. α at different heating rates.

α_P^∞ exhibits values lower than 0.632. In accordance with the results of Málek on the kinetics of the curing reaction of thermosets under non-isothermal conditions [14], the studied curing system can be described using the two-parameter autocatalytic kinetic model of Šesták-Berggren following Eqs. (9) and (10) [14,15,21]:

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{9}$$

$$\ln\left[\left(\frac{d\alpha}{dt}\right)e^x\right] = \ln A + n\ln[\alpha^p(1-\alpha)] \tag{10}$$

The kinetic parameter n is obtained from the slope of the linear dependence $ln[(d\alpha/dt)e^x]$ vs. $ln[\alpha^p(1-\alpha)]$ (from Eq. (3)), and $m = pn$, where p is equal to $\alpha_M/(1-\alpha_M)$. Table 2 lists some kinetic parameters evaluated for the proposed Šesták-Berggren kinetic model.

TABLE 1 α_p, α_M and α_P^∞ Values Evaluated with the DSC Data

Heating rate (°C/min)	α_p	α_M	α_P^∞
5	0.5098	0.2775	0.5450
10	0.5172	0.2621	0.5172
15	0.5662	0.2341	0.5662
20	0.5771	0.2126	0.6032

TABLE 2 Kinetic Parameters Evaluated for the Sample

Heating rate (°C/min)	*Ea* (KJ/mol)	ln A	Mean	*p*	*n*	Mean	*m*	Mean
5	61.64	22.04	21.83	0.38	0.97	0.95	0.37	0.31
10		22.03		0.36	1.11		0.39	
15		21.76		0.31	0.93		0.28	
20		21.48		0.27	0.79		0.21	

The correctness of the kinetic model proposed using the Šesták-Berggren equation was verified by plotting $d\alpha/dt$ vs. temperature T (experimental points) with theoretical curves (full lines), using the data listed in Table 2. Figure 8 presents a comparison of experimental and theoretical values for the sample. As seen from Figure 8, a good agreement can be seen between the calculated theoretical curves and those experimentally determined. In other words, the two-parameter Šesták-Berggren model can give a good description for the studied curing system, and the kinetic equation of the system can be described as follows:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{Ea}{RT}\right)\alpha^m(1-a)^n$$

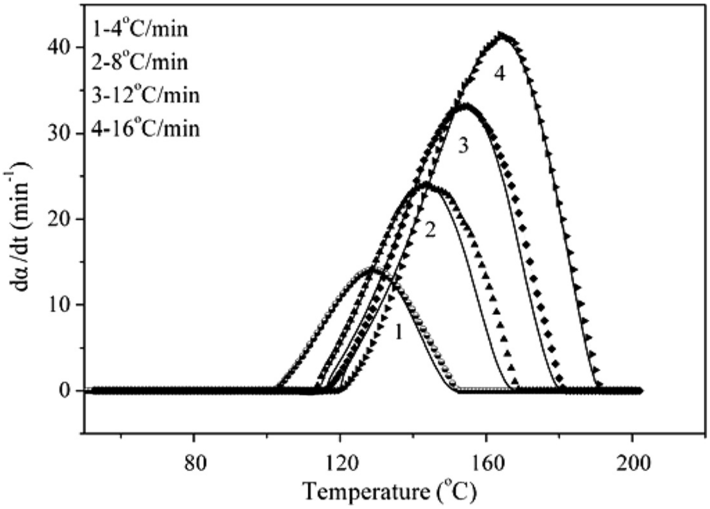


FIGURE 8 Comparison of experimental (symbols) and calculated (full lines) DSC curves for the sample.

Mechanical Loss and Glass Transition Temperature T_g

Because the glass transition temperature (T_g) can be used effectively to monitor the molecular motion and curing reaction, the torsional braid analysis (TBA) can be used to determine the T_g of the thermosetting system, and it is particularly useful at high conversion and after vitrification because of the nonlinearity of T_g vs. conversion α [22]. Generally, there is a one-to-one relationship between the T_g and mechanical loss peak temperature T_p. The higher T_p, the higher is T_g, which depends upon the curing conditions, such as the amount of crosslinking agent, cure temperature and time. With these curing conditions varying, the T_p and T_g of the system will be changed, so that, T_g has been used directly as a parameter in the analysis of reaction kinetic models, which can be determined by TBA [22,23]. Figure 9 is the TBA graphs of cured systems. As seen from Figure 9, the mechanical loss peak temperature T_p changes with changing content of p-PEPB. The maximal mechanical loss peak temperature T_p is 146.4°C at the content of p-PEPB of 4 parts in 100 parts sample p-PEPB and it is higher by about 63°C than pure o-CFER system. This might suggest that, in the presence of polymer networks, the rigidity of the segments and the macroscopically uniaxial orientation of LC molecules are playing an important role in causing the T_g to increase, and it is also related to a higher T_m of p-PEPB. But when the content of the

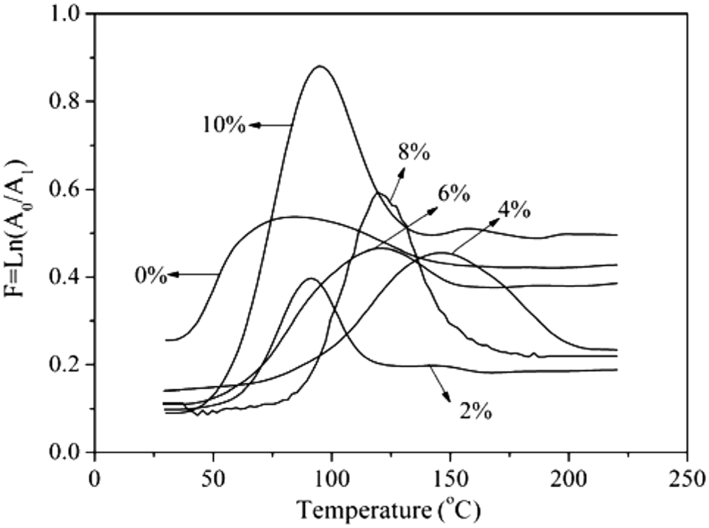


FIGURE 9 $\ln(A_o/A_i)$ of epoxy resin with different content of p-PEPB.

TABLE 3 Mechanical Loss Peak-Temperature T_p of Cure-system for Different p-PEPB Contents (wt%)

Differentp-PEPB content (wt%)	0	2	4	6	8	10
T_{pp} of $\mathrm{Ln}(A_o/A_i)$ (°C)	83.1	91.2	146.4	121.4	120.8	95.0

p-PEPB is higher than 4 parts, the LC molecules self-aggregation and phase separation will occur and the T_g decreases again, as shown in Figure 9. The changes of loss peak T_p with content of p-PEPB are shown in Table 3.

CONCLUSIONS

The o-CFER and p-PEPB can be co-cured when DDE is used as a curing reagent. The curing kinetics of o-CFER/p-PEPB/DDE mixed system can be described by Ozawa's equation. The average *Ea* of the system is 61.64 KJ/mol. The *Ea* values change with the α, and the values of *Ea* in the initial stage are higher than those of any other time. This shows that primary amines have a higher *Ea* than second amines, and the alcohol-catalyzed reaction has a lower E*a*.

The two-parameter (m, n) autocatalytic Šesták-Berggren model is the most adequate to describe the cure kinetics of the studied system. The reaction orders n and m for o-CFER/p-PEPB/DDE are 0.95 and 0.31, respectively.

The co-cure of p-PEPB with epoxy resins can increase the T_g of the resins.

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