

The Kinetics of B-a and P-a Type Copolybenzoxazine via the Ring Opening Process

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ABSTRACT: The structure of benzoxazines is similar to that of phenolic resin through thermal self-curing of the heterocyclic ring opening reaction that neither requires catalyst nor releases any condensation byproduct. These polybenzoxazine resins have several outstanding properties such as high thermal stability and high glass transition temperature. To better understand the curing kinetics of this copolybenzoxazine thermosetting resin, dynamic and isothermal differential scanning calorimetry measurements were performed. Three models, the Kissinger method, the Flynn–Wall–Osawa method, and the Kamal method, were used to

describe the curing process. Dynamic kinetic activation energies based on Kissinger and Flynn–Wall–Osawa methods are 72.11 and 84.06 KJ/mol, respectively. The Kamal method based on an autocatalytic model results in a total order of reaction between 2.66 and 3.03, depending on curing temperature. Its activation energy and Arrhenius preexponential are 50.3 KJ/mol and 7959, respectively. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 730–737, 2005

Key words: benzoxazine; heterocyclic; ring opening; kinetics; activation energy

INTRODUCTION

The benzoxazine oligomeric products and polybenzoxazine (PBZZ) resins were investigated recently.^{1,2} The benzoxazine can be cured via a thermal ring opening reaction to construct an analogous phenolic structure characterized by a Mannich base bridge ($-\text{CH}_2\text{-NR-CH}_2$).³ Furthermore, the preferred reaction site is the position ortho to the hydroxyl functionality on the aromatic ring. In addition, these PBZZ resins possess several outstanding properties such as near-zero shrinkage after curing,⁴ low water absorption,⁵ and high thermal stability. Furthermore, the PBZZ has a higher glass transition temperature even though it has relatively low cross-linking density.⁶

PBZZ can be formed by the heterocyclic curing via the ring opening process. Hence, controlling the curing conditions of the thermal curing process, such as temperature and time, will result in a notable difference in thermal properties. In this study, we selected B-a type and P-a type benzoxazines to form random co-PBZZ as shown in Scheme 1. The degree of crosslinking depends upon the ratio of B-a/P-a benzoxazine, curing temperature, and time. The kinetics of polymerization was investigated using differential scanning calorimetry (DSC) and Fourier transform in-

frared (FT-IR) spectroscopy during isothermal and dynamic curing processes in this study.

EXPERIMENTAL

Materials

The B-a type benzoxazine based on bisphenol-A, formaldehyde, and aniline and the P-a type based on phenol, formaldehyde, and aniline were synthesized as shown in Scheme 2.⁷ Both bisphenol-A and phenol were purchased from Showa Chemical Co. of Japan. Formaldehyde and aniline were purchased from Aldrich Chemical Co.

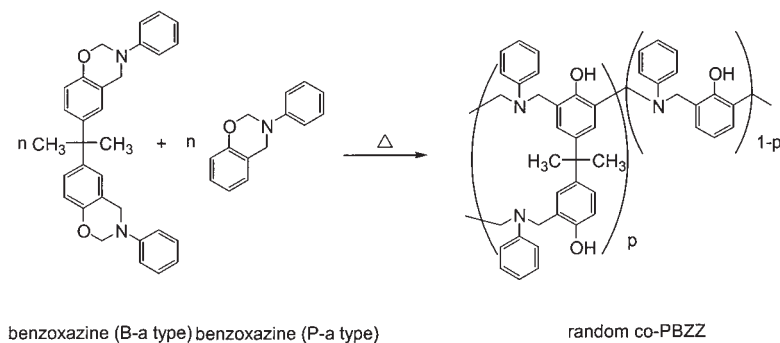
Reactants preparations

A blend of B-a type and P-a type co-PBZZ with equal molar composition was prepared by solution blending. The monomer mixture was stirred and dissolved in acetone. The solution was allowed to evaporate slowly at 50°C under vacuum for 1 day and the sample was used for isothermal and dynamic curing experiments. Afterward, the sample was further post-cured at different curing temperatures for 4 h under vacuum to ensure total curing of the co-PBZZ.

Differential scanning calorimetry

Calorimetric measurements were performed using a TA Instruments differential scanning calorimeter (DSC-2010). Both isothermal and dynamic-heating ex-

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Scheme 1

periments were conducted under a nitrogen flow of 25 mL/min.

Isothermal curing

The sample (equal molar ratio of B-a and P-a type benzoxazine) was placed in the Al cell at room temperature and the temperature was then raised quickly to a preset temperature for each isothermal experimental. The instrument will achieve stability about 60 s after reaching the setting temperature and data will be recorded immediately. When the DSC exothermic peak reaches the baseline level, the isothermal curing process is complete and the heat of reaction can be measured by integrating the exothermic peak area. Thereafter, the sample is cooled to 30°C and reheated from 30 to 300°C at a rate of 10°C/min to determine the residual heat of the unreacted portion. These isothermal curing curves can be used to evaluate kinetic parameters of the curing reaction.

Dynamic curing

A nonisothermal experiment was carried out at 1, 5, 10, or 20°C/min from 30 to 300°C and integrated the area

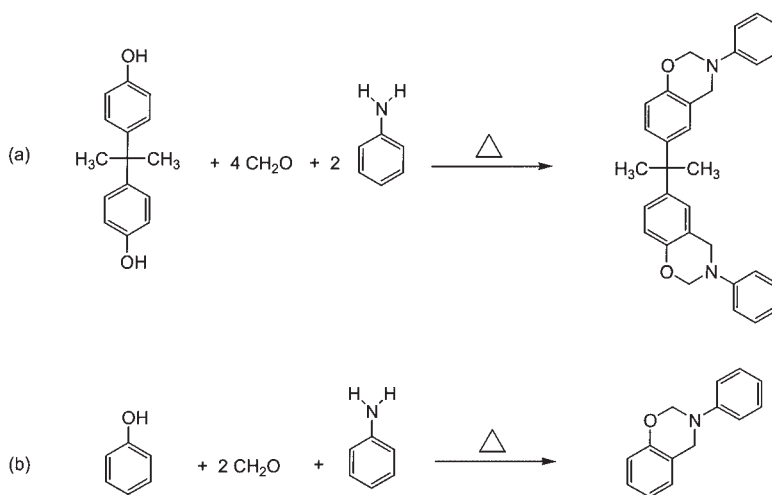
of exothermic peak. We assume that the total recorded heat of reaction represents the total heat evolved from complete curing at different curing rates.

Glass transition temperatures measurement

The samples was cured at 160, 180, 190, 200, or 210°C for 4 h in an oven to ensure total curing of the co-PBZZ. Then, all samples were preheated with a scan rate of 20°C/min from 30 to 260°C and maintained at 260°C for 2 min. The measurement was made using a 5- to 10-mg sample on a DSC sample pan after the cell was quickly cooled to 30°C from the melt of the first scan. The second scan rate was 20°C/min from 30 to 300°C and T_g was taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquids and glass lines.

Infrared spectroscopy

FT-IR measurement was recorded on a Nicolet Avatar 320 FT-IR spectrophotometer. A total of 32 scans were collected with a spectral resolution of 1 cm⁻¹. Infrared



Scheme 2

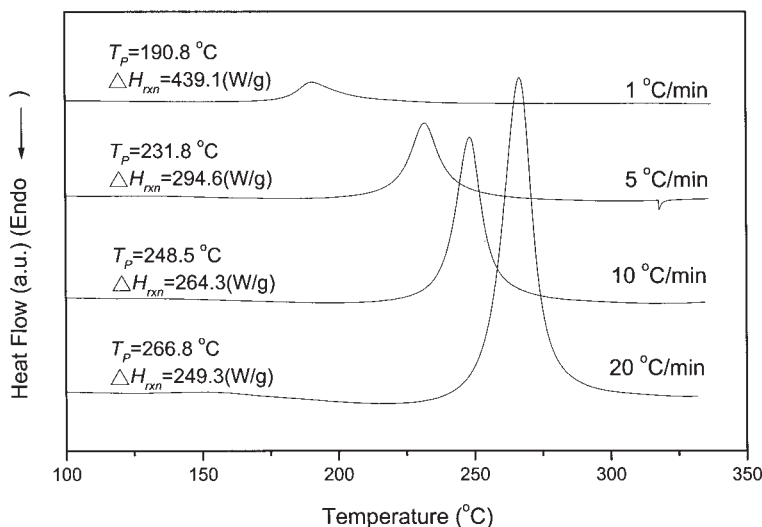


Figure 1 Dynamic DSC exothermic curves at different scan rates.

spectra of the copolymers were obtained using the conventional KBr method. The film used in this study was thin enough to obey the Beer–Lambert law. The sample chamber was purged with nitrogen during process of measurement to maintain the sample film drying.

RESULTS AND DISCUSSION

Scanning DSC studies

Figure 1 shows the DSC exothermic peaks from different dynamic heating rates^{8,9} at 1, 5, 10, and 20°C/min, respectively. A faster heating rate results in a higher maximum temperature (T_p) since the sample has a shorter time to react and to release the heat of reaction. In addition, lower the heating rate results in larger exothermic heat per unit weight, as expected, and results are summarized in Figure 1. The amount of exothermic heat from the slowest heating rate at 1°C/min can be considered the total heat released to completely cure the sample and the total heat (ΔH_{rxn}) is obtained is 439.1 (W/g). The $(dH/dt)_{iso}$ can be calculated from the trace of the isothermal DSC curve. The reaction rate ($d\alpha/dt$) at a preset curing temperature can be obtained by Eq. (1):

$$\frac{d\alpha}{dt} = \frac{(dH/dt)_{iso}}{\Delta H_{rxn}} \quad (1)$$

Figure 2 shows the reaction rates of co-PBZZ as a function of curing time for different curing temperatures. All samples were cured without the addition of any catalyst, and only a single exothermic peak was observed in all DSC curves. In other words, this heterocyclic ring opening curing reaction simply involves a single exothermic chemical process. As expected, at

a higher curing temperature the curing rate ($d\alpha/dt$) is higher and the curing time period is shorter. Figure 3 illustrates conversion (α) versus isothermal curing time at various curing temperatures. When the curing temperature rises from 160 to 220°C, the conversion increases¹⁰ from 0.35 to 0.93. Figure 4 shows plots of reaction rate versus conversion for different curing temperatures. The maximum reaction rate occurs between 20 (180°C) and 38% (220°C) of conversion. This

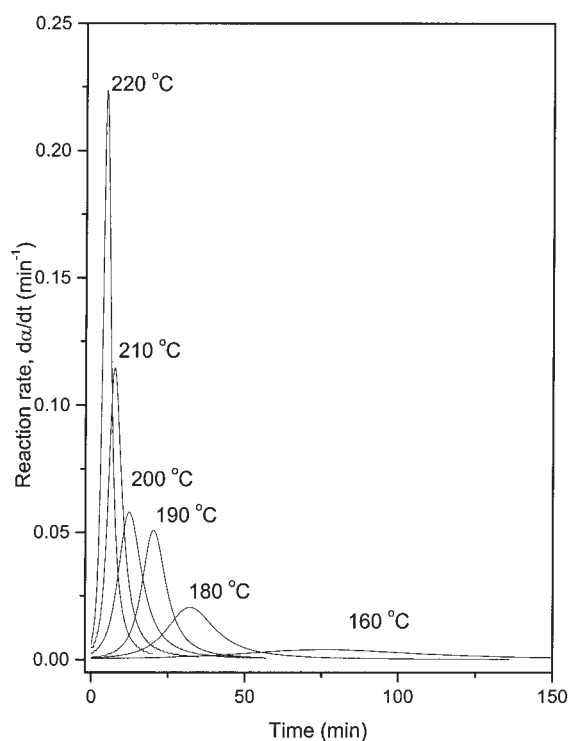


Figure 2 Reaction rate versus isothermal curing time at different curing temperatures.

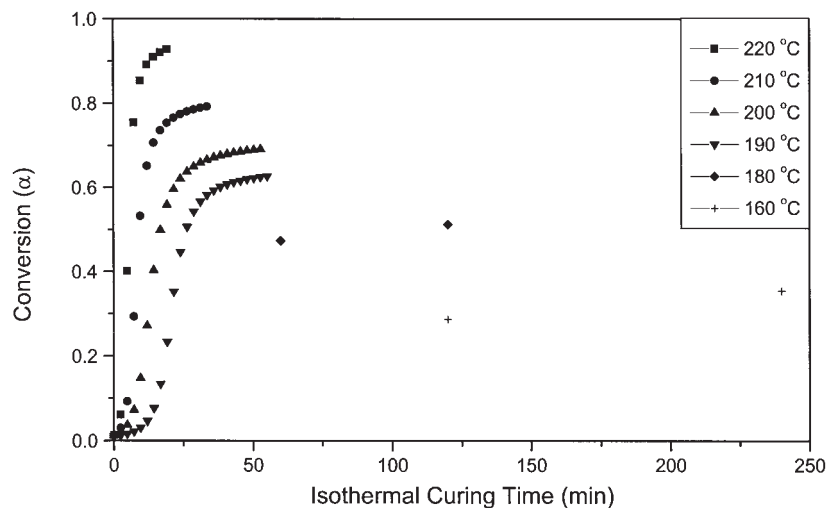


Figure 3 Conversion versus isothermal curing time at different curing temperatures.

result confirms that the curing process follows an autocatalytic model with maximum reaction rate between 20 and 40% conversion.¹¹

Kinetic analysis

Kinetic analysis can be performed mostly using three kinetic models:¹² the Kissinger¹³ and Flynn–Wall–Ozawa¹⁴ methods are suitable for dynamic kinetic anal-

ysis, while the Kamal method¹⁵ is suitable for isothermal kinetic analysis (autocatalytic model).

The extent of reaction, α , is proportional to the heat generated during the reaction. The reaction rate is a function of conversion, which can be expressed by the general law as shown in Eq. (2),

$$\frac{d\alpha}{dt} = k(T) f(\alpha), \quad (2)$$

where t is the time, $k(T)$ is the rate constant, and $f(\alpha)$ is a function of dependence of conversion. By integrating the above equation, a new equation can be obtained as follows:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = k(T)t, \quad (3)$$

where $g(\alpha)$ is the integrated form of the conversion-dependent function.

Dynamic kinetic method

Nonisothermal analysis can include the single heating rate method and the multiple heating rate method. The single heating method measures the curing process based on only a single constant rate cycle suitable for the n th-order reaction. Furthermore, these multiple heating rate methods are applicable for both n th-order and autocatalytic reactions. Two such multiple heating rate methods were proposed by Kissinger¹³ and Flynn–Wall–Ozawa.¹⁴ These two methods were used in this study instead of other nonisothermal methods

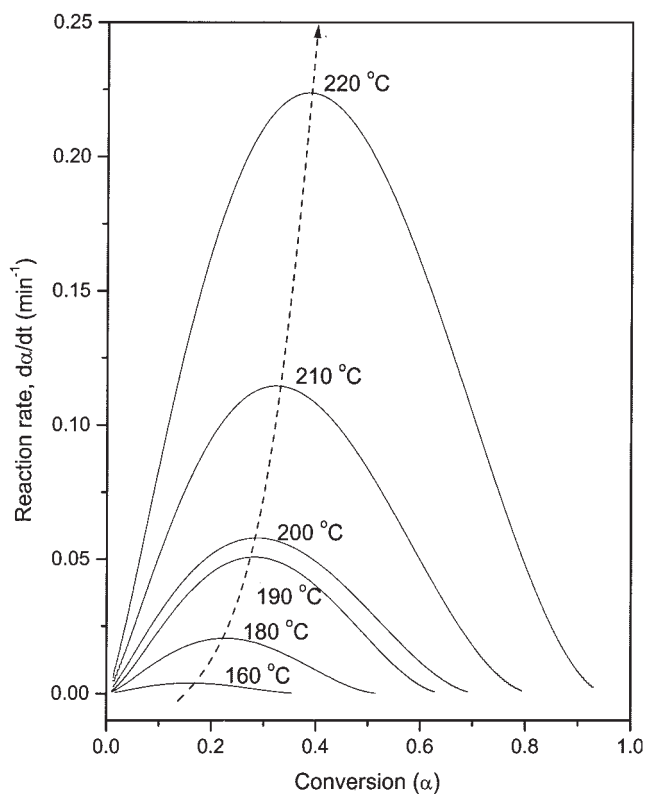


Figure 4 The tendency of reaction rate versus conversion.

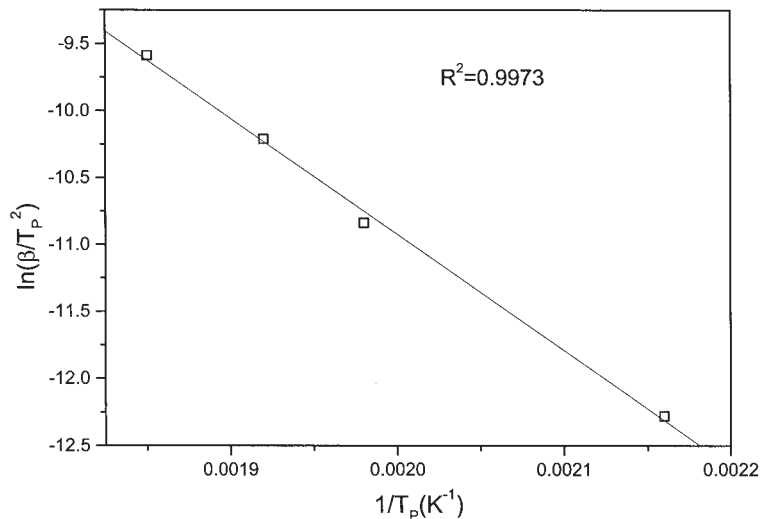


Figure 5 Plots for determination of the activation energy of curing reaction by the Kissinger method.

because they do not require prior knowledge of the reaction mechanism to quantify kinetic parameters.

where $\beta = dT/dt$ is a constant heating rate, T_p is the maximum exothermic temperature, and R is the universal gas constant. By plotting

(a) The Kissinger method

Based on the Kissinger method, the activation energy can be obtained while the maximum reaction rate

$$\ln\left(\frac{\beta}{T_p^2}\right)$$

versus

$$\frac{1}{T_p}$$

is zero under a constant heating rate condition. The resulting relation can be expressed by Eq. (4)

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \tag{4}$$

which gives the activation energy without a specific assumption of the conversion-dependent function, we calculated the slope as shown in Figure 5.

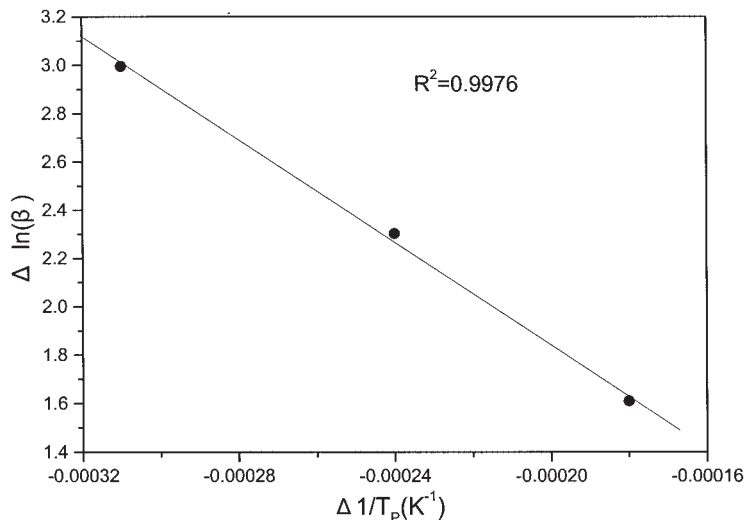


Figure 6 Plots for determination of the activation energy of curing reaction by the Flynn–Wall–Ozawa method.

Therefore, the value of E_a of 72.11 KJ/mol was obtained.

(b) Flynn–Wall–Ozawa method

The Flynn–Wall–Ozawa method is another widespread method used to describe the dynamic kinetic analysis without any assumptions on the conversion-dependence function. Its general expression can be represented by Eq. (5).

$$E_a = \frac{-R}{1.052} \frac{\Delta \ln \beta}{\Delta(1/T_p)} \quad (5)$$

By plotting $\Delta \ln \beta$ versus $\Delta(1/T_p)$ we can obtain the slope value equal to

$$\frac{\Delta \ln \beta}{\Delta(1/T_p)}$$

by the least-squares technique to improve the linear approximation on the temperature integration term at Figure 6. Thus, the activation energy of $E_a = 84.06$ KJ/mol was obtained.

Isothermal kinetic analysis (autocatalytic model)

The autocatalytic model is a phenomenological approach developed by Kamal. Since the system is autocatalytic, the reaction rate can be described by the following general expression for autocatalyzed systems:

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n, \quad (6)$$

where α is the reaction conversion, k is the kinetic rate constant, m and n are the kinetic exponents of the reaction, and $m + n$ is the overall reaction order.

However, in practice, the curing reaction will cease when the reaction conversion reaches the maximum value (α_{\max}). Then, Eq. (6) must be corrected and changed into Eq. (7).^{16–18}

$$\frac{d\alpha}{dt} = k\alpha^m(\alpha_{\max} - \alpha)^n \quad (7)$$

(when $\alpha = \alpha_{\max} \Rightarrow \frac{d\alpha}{dt} = 0$),

where α_{\max} is based on different curing temperatures. To rearrange and take the nature logarithm of Eq. (7), Eqs. (8) and (9) are obtained. We use the iteration method to calculate the approximate values of m , n , and k according to Eqs. (8) and (9). When $n_{i+1} - n_i < 0.01$, the iteration will be stopped. Then, the values

TABLE I
The Values of m , n , and k and Total Order of Different Curing Temperature

Curing temp. (°C)	m	n	k (1/min)	$m + n$
220	1.36	1.67	2.19	3.03
210	1.26	1.70	1.70	2.96
200	1.35	1.55	1.25	2.90
190	1.27	1.46	1.18	2.73
180	1.15	1.52	0.75	2.67
160	1.23	1.43	0.39	2.66

of m , n , and k of different curing temperatures are obtained. The results are listed in Table I.

$$\ln \left(\frac{(d\alpha/dt)}{(\alpha_{\max} - \alpha)^n} \right) = \ln k + m \ln \alpha \quad (8)$$

$$\ln \left(\frac{(d\alpha/dt)}{k\alpha^m} \right) = n \ln(\alpha_{\max} - \alpha) \quad (9)$$

In additional, the rate constant, k , may be described by the Arrhenius expression,¹⁶

$$k = Ae^{-E_a/RT}, \quad (10)$$

where A is the Arrhenius preexponential factor (or frequency factor), E_a is the energy of activation, R is the universal gas constant, and T is the absolute temperature.

Taking the nature logarithm of Eq. (10), we obtain Eq. (11). We plot $\ln k$ versus $1000/T$ for different isothermal curing temperatures; data are shown in Figure 7. The activation energy of $E_a = 50.3$ KJ/mol and $\ln A = 8.982$ ($A = 7959$) is obtained.

$$\ln k = \ln A - E_a/RT. \quad (11)$$

Comparing the three kinetic models, the values of the activation energy can be obtained from both dynamic and isothermal analysis. Hence, it is appropriate to calculate the activation energy and kinetic parameters including m , n , and k using the Kissinger, Flynn–Wall–Ozawa, and Kamal methods in this system.

Glass transition temperature analysis

Figure 8 shows traces of DSC thermograms of B-a and P-a type co-PBZZ under various curing temperatures for 4 h. Under all conditions, the polymer blend gives only a single glass transition temperature because of similar structure. In addition, by increasing the curing temperature, the T_g also increases with until 190°C or above. Then, the T_g will remain at a near-constant value,¹⁹ which is about 173°C. In other words, the

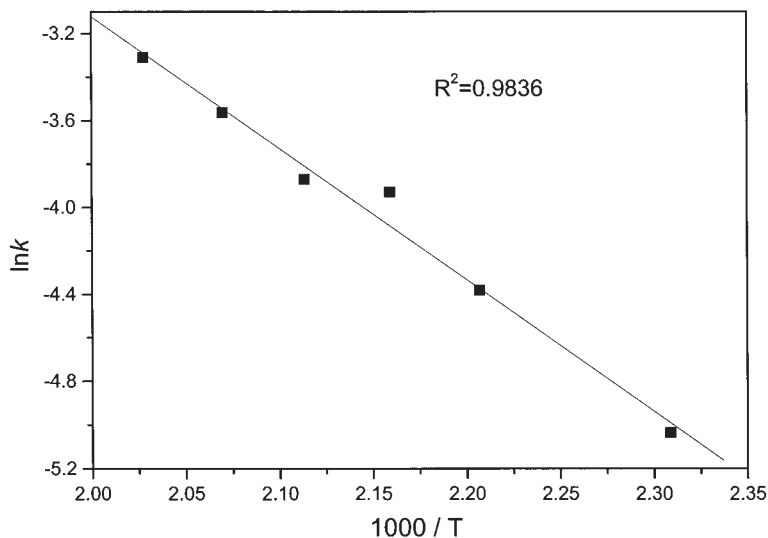


Figure 7 Plots of $\ln k$ versus $1000/T$ for determination of the activation energy and Arrhenius preexponential of the curing reaction by the isothermal method.

different curing temperatures affect the degree of curing and result in different glass transition temperatures until the maximum T_g is reached at 173°C .

Fourier transfer infrared spectroscopy analysis

The FT-IR spectra^{20,21} of B-a type and P-a type benzoxazine copolymers after different temperature treat-

ments were recorded and are shown in Figure 9a. The bands of 748 and 691 cm^{-1} , corresponding to the monosubstituted benzene, are still present even after high-temperature curing. On the contrary, the characteristic absorption band of the oxazine ring at 947 cm^{-1} disappeared, and the absorption at 1495 cm^{-1} from the trisubstituted benzene ring and at 1236 cm^{-1} from the CH_2 wagging both decreased. However, a new absorption band appeared at 1478 cm^{-1} due to the tetrasubstituted benzene ring mode. Besides, the absorptions at 1030 and 1230 cm^{-1} corresponding to the symmetric and asymmetric C-O-C bonds of the benzoxazine, disappear after the curing process. Furthermore, a broad hydroxyl bond is formed because of the ring opening process as shown in Figure 9b. Based

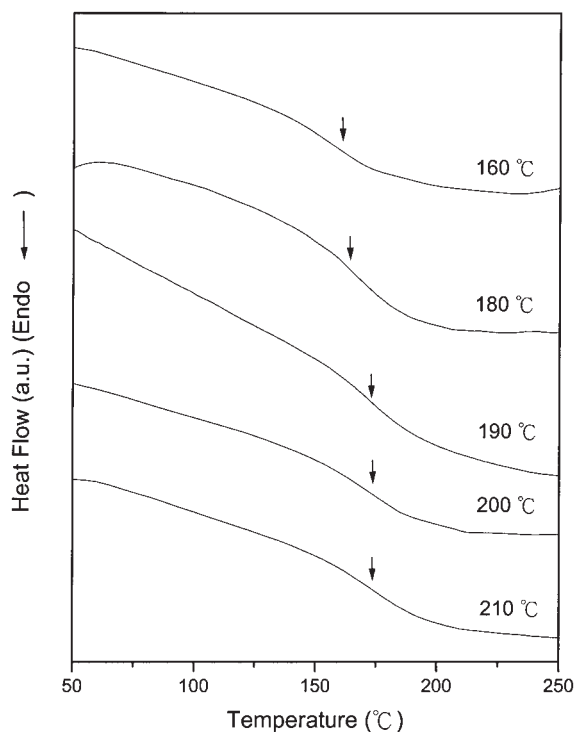


Figure 8 The DSC curves at different curing temperatures for 4 h.

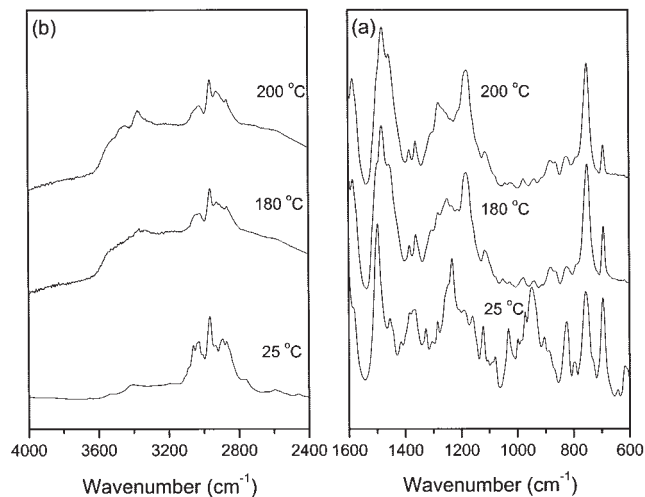


Figure 9 FTIR spectra recorded at room temperature between (a) 600 and 1600 cm^{-1} and (b) 2400 and 4000 cm^{-1}

on DSC and FT-IR results, the ring opening reaction indeed occurs as shown in Scheme 1.

CONCLUSION

Based on the DSC results, the equal molar mixture of B-a type and P-a type co-PBZZ is completely miscible in the amorphous phase and gives a single glass transition temperature. The product T_g depends upon the ratio of B-a/P-a benzoxazine, curing temperature, and curing time. The maximum T_g is about 173°C. The isothermal curing process of the co-PBZZ precursor involves an autocatalytic-type curing mechanism. In the dynamic experiments, the activation energy is 72.11 KJ/mol based on the Kissinger method and 84.06 KJ/mol based on the Flynn–Wall–Ozawa method. Furthermore, in the isothermal experiments, the activation energy and Arrhenius preexponential are 50.3 KJ/mol and 7959 based on the Kamal method, and the total order of reaction is between 2.66 and 3.03, depending on the isothermal curing temperature.

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