Research Article
Study on Curing Kinetics of Heat-resistant Flexible Polyamide Modified Epoxy Resin Adhesive

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Abstract: In order to study the effects of numerous variables affecting the reaction rate of heat-resistant flexible modified epoxy resin adhesive, the curing kinetics of polyamide modified epoxy resin was studied. The heat-resistant flexible modified epoxy resin adhesive cured at room-temperature was prepared with epoxy resin, polysulfide rubber and organosilicone as adhesive component, polyamide as main curing agent and addition of different modified filler and the curing agent containing benzene ring structure. The curing kinetics of polyamide modified epoxy resin was studied by Differential Scanning Calorimetry (DSC) at different heating speeds and the characteristic temperatures of the curing process were analyzed and confirmed. the kinetics parameters of activation energy was calculated using Flynn-Wall-Ozawa equation and Kissinger equation, respectively, then the kinetic model of curing reaction was built as $\frac{d\alpha}{dt}$ = 4.38×10^7 exp (-57740/RT) (1-α)$^{0.93}$, the results show that the two-parameter model is adequate to represent the curing reaction process, the model can well describe the curing reaction process of the studied resin. The DSC curves obtained using the experimental data show a good agreement with that theoretically calculated. The research results will provide theoretical basis for the choice of manufacturing process and the optimization of processing window.

Keywords: Curing kinetics, epoxy resin, heat-resistant, modification, organosilicone, polyamide

INTRODUCTION

Epoxy resins are widely used in diverse areas such as molding compounds, surface coating and painting materials, microelectronic encapsulated materials, printed circuit boards and adhesives owing to their satisfactory mechanical properties, including suitable weather, chemical and thermal resistance (Horie *et al*., 1970; Acitelli *et al*., 1971). The glass transition temperature, weigh loss temperature and char yield of cured system, the curing rates and activation energy are important kinetic parameters in the curing reaction process. Therefore, study on the curing kinetics of modified epoxy resin have both practical and theoretical value (Horie *et al*., 1970; Acitelli *et al*., 1971; Zhao *et al*., 2006; Niu *et al*., 2008).

In this study, the curing kinetics of polyamide modified epoxy resin was studied by Differential Scanning Calorimetry (DSC) at different heating speeds and the characteristic temperatures of the curing process were analyzed when the heating speed is zero. The kinetics parameters of activation energy was calculated using Flynn-Wall-Ozawa equation and Kissinger equation respectively, then the kinetic model of curing reaction was built (Xia *et al*., 2010; Wang *et al*., 2011). The research results will provide theoretical basis for the choice of manufacturing process and the optimization of processing window.

METHODOLOGY

Reagents and instruments: Epoxy Resin E51, E20 (Hangzhou Wuhuigang Adhesive Co., Ltd., China), polysulfide rubber 121 (Tianjin Kailis Chemical Co., Ltd., China), organosilicone FJN-9802 (Changzhou Jianuo Organicsilicon Co., Ltd., China), DMP-30 (Sinopharm Chemical Reagent Co., Ltd., China), m-phenylenediamine (Sinopharm Chemical Reagent Co., Ltd., China), KH-560 (Shanghai Zhongyi Plastic Products Factory, China), polyamide 650 (Hangzhou Wuhuigang Adhesive Co., Ltd., China), accelerator of polyetherimide TKM-3908 (Qingdao Runbang Chemical Industry Co., Ltd., China); dibutyl phthalate (Sinopharm Chemical Reagent Co., Ltd., China), organotin (Sinopharm Chemical Reagent Co., Ltd., China), basic magnesium carbonate (Sinopharm Chemical Reagent Co., Ltd., China), mica powder (Sinopharm Chemical Reagent Co., Ltd., China), acetone and ethanol were of AR grade, obtained from Shanghai Chemical Reagent Co., Ltd. with purities of 0.995 in mass fractions.

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The shearing strength was measured according to national standard GB/T 7124-2008 method by using a WSM-100KN electronic tension instrument from Changchun intelligent equipment Co. Ltd; TGA was tested by Shimadzu Corporation DTA-TG thermal analyzer; DSC was tested by the Shimadzu Corporation DSC analyzer.

Preparation of the modified epoxy resin: Take out of the adhesive component epoxy resin E51 (100% Wt), E20 (10% Wt), a certain amount of organotin, DBP, KH560 and silicone resin (20% Wt), then mixed them together and stirred for 2 h at 140-160°C. And then the mixtures were cooled down to room temperature. Subsequently and polysulfide rubber was added in and then heated to 120°C for 1 h. After that, modified adhesive component is prepared.

Preparation of curing agent: The curing component were prepared by adding m-phenylenediamine, dicyandiamide, DMP30, KH560 etc., to polyamide and stirred for 30 min at room temperature and maintained at this temperature until used and then curing component is obtained.

Experimental method: Take out of the adhesive component (100% Wt), the curing component (60% Wt) and mixed them together, then dried them in vacuum at 65°C for 30 min to remove little water. Take out 5 mg samples accurately in a crucible and the kinetics was studied by non-isothermal DSC analysis with the DTA-TG thermal analyzer at the different heating rates of 5, 10, 15 and 20°C/min, respectively. The input rate of nitrogen with high purity is 20 mL/min.

RESULTS AND DISCUSSION

Analysis of the kinetic DSC curves: The DSC curves of polyamide as curing agents at different heating rates was shown in Fig. 1. We can see from Fig. 1 and that the initiative curing temperature T_i, the peak top temperature T_p and the finish curing reaction temperature T_f increase with the increase of the heating rate. The main reason is that the samples have enough time for the cured reaction at a relative low temperature when the heating rate is small. If the heating rate raises instead, the heat production per unit time increases, the greater temperature difference will yield in a short time and the exothermic peak of reaction shift forward to high temperature range.

Characteristic temperature of the curing process: The characteristic temperatures of the curing process can be found from Fig. 1 and they are listed in Table 1.

The curve of heating rate β and the characteristic temperature of T_i, T_p and T_f was drawn and shown in Fig. 2.

In the polyamide system, the linear regression equation which describe the relations of β with T_i, T_p and T_f is y = 0.9334x + 47.625, y = 1.7488x + 86.19 and y = 1.7766x + 120.03 and their linear correlation coefficients are R_i = 0.952, R_p = 0.996 and R_f = 0.953, respectively. When the heating rate β is zero, the curing characteristic temperatures can be obtained by extrapolation and they are T_{i0} = 57.58°C, T_{p0} = 94.43°C and T_{f0} = 126.96°C, respectively.

Table 1: The characteristic temperatures of polyamide at different heating rates

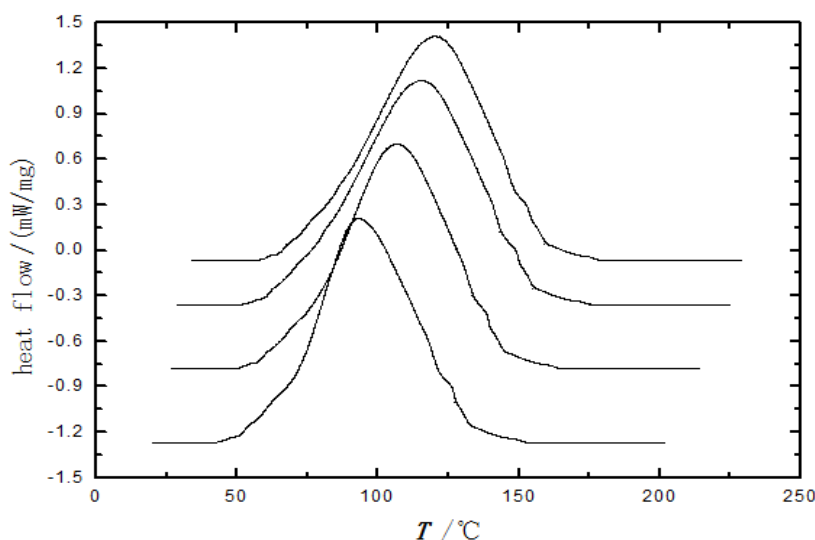| β /(°C/min)	T_i/°C	T_p/°C	T_f/°C
5	51.21	93.12	126.85
10	58.91	105.45	139.60
15	60.97	114.32	149.23
20	66.08	119.31	153.25

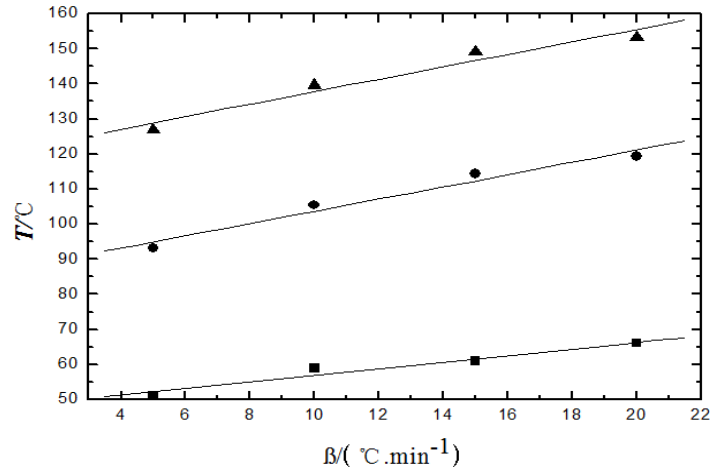Fig. 1: Kinetic DSC curves of polyamide

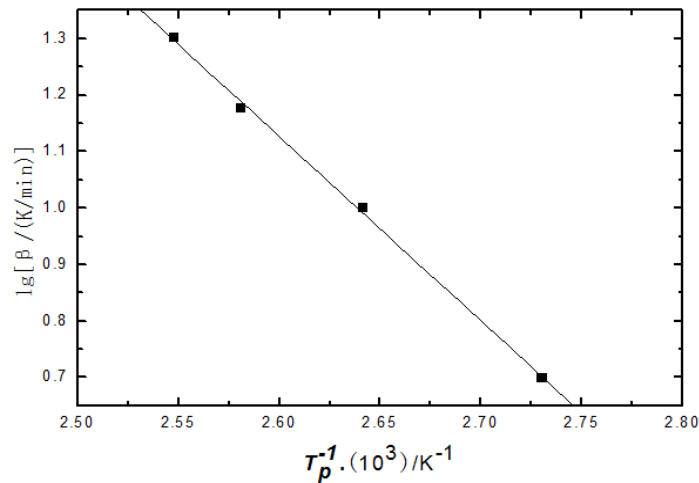Fig. 2: The curve of characteristic temperature T and heating rate β of polyamide ■: T_i; ●: T_p; ▲: T_f

Fig. 3: The linear fitting curve between lg β and $1/T_p$ in polyamide system

The activation energy of cured reaction: The activation energy of cured reaction can be obtained by Flynn-Wall-Ozawa equation and Kissinger equation. The Flynn-Wall-Ozawa equation is shown as follows:

$$\lg\beta = \lg\left(\frac{AE_\alpha}{RF(\alpha)}\right) - 2.315 - 0.4567\frac{E_\alpha}{RT} \qquad (1)$$

In the Eq. (1), "*A*" is frequency factor, "*β*" is heating rate of the cured reaction, $R = 8.314$ J/mol·K, is ideal gas constant and E_α, T and $F(\alpha)$ are activation energy, temperature and the integral form of kinetic mechanism function. The curve of $\lg\beta \sim 1/T_p$ was drawn according to the Eq. (1) and shown in Fig. 3.

The equations of the curing systems are obtained through linear regression, they are y = -3.2604x + 9.60282 and the correlation coefficients are R = 0.9987. According to its slope, we can get that $E_\alpha = 59.35$ kJ/mol.

The activation energy of cured reaction can also be obtained by Kissinger equation. The Kissinger equation can be expressed as follows:

$$\frac{d[\ln(\beta/T_p^2)]}{d(1/T_p)} = -\frac{E_\alpha}{R} \qquad (2)$$

The curve of ln $(\beta/T_p^2) \sim 1/T_p$ was drawn according to the Eq. (2) and shown in Fig. 4.

We can see through linear regression that, the equations of the curing systems are y = -6.7498x + 8.2369 and the correlation coefficients are $R = 0.9984$. According to its slope, we can get that $E_\alpha = 56.12$ kJ/mol.

The activation energies obtained by the above two kinds of different equations are approximate to each other and the activation energy should be obtained by averaging the above calculating values, therefore the activation energy of each curing system are $E_\alpha = 57.74$ kJ/mol.
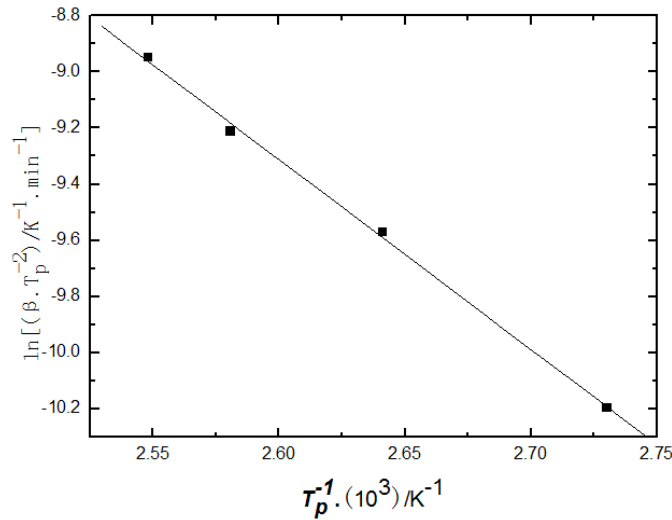
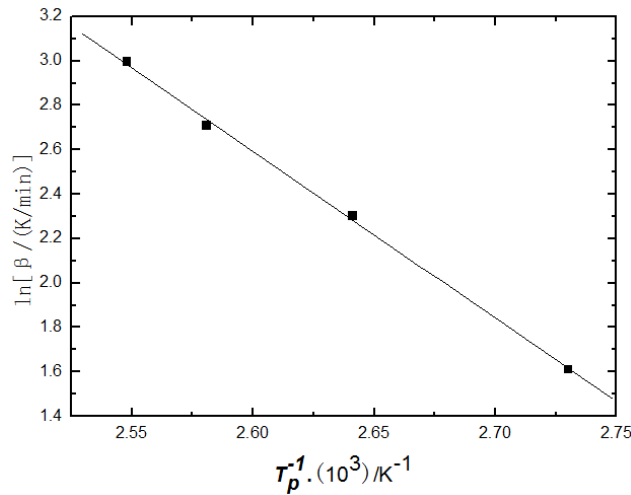Fig. 4: The curve of ln (β/T^2_p) with $1/T_p$ in polyamide system

Fig. 5: The curve of lg β with $1/T_p$ in polyamide system

The reaction order and the kinetic equation of curing reaction: The reaction order of curing reaction can be obtained by Crane equation. The Crane equation can be expressed as follows:

$$\frac{d(\ln \beta)}{d(1/T_p)} = -\frac{E_\alpha}{nR} + 2T_p \qquad (3)$$

In Eq. (3), because of $E_\alpha/nR \gg 2T_p$, the Eq. (3) can also be expressed as follows:

$$\frac{d(\ln \beta)}{d(1/T_p)} = -\frac{E_\alpha}{nR} \qquad (4)$$

The curve of ln $\beta \sim 1/T_p$ was drawn according to the Eq. (4) and shown in Fig. 5.

We can see through linear regression that, the equation of the curing system is y = -7.5073x + 22.111

and the correlation coefficient is $R = 0.9987$. According to Eq. (4), we can see that the reaction order "n" is 0.93, so it is the first order reaction, which is consistent with the single peak in DSC curve.

The pre-exponential factor in Flynn-Wall-Ozawa equation can be obtained by Kissinger equation:

$$A = \frac{\beta E \exp(E/RT_p)}{RT_p^2} \qquad (5)$$

The different β and T_p was substituted in Eq. (5), "A" is solved by averaging the calculating values, we can obtain that $A = 4.38 \times 10^7$, substituted these kinetic parameters in the kinetic equation, the kinetic equations of curing reaction of polyamide can be expressed as follows:

$$\frac{d\alpha}{dt} = 4.38 \times 10^7 \exp(-57740/RT)(1-\alpha)^{0.93} \qquad (6)$$

CONCLUSION

The curing kinetics of polyamide/epoxy resin system was studied by the method of non-isothermal DSC. When the heating rate is zero, the curing characteristic temperatures of the cured products are T_{i0} = 47.63°C, T_{p0} = 86.19°C and T_{f0} = 120.03°C. The apparent activation energy of the curing reaction is that E_α = 57.74 kJ/mol, pre-exponential factor "A" = 4.38×10^7 and the reaction order is 0.93. Therefore, the kinetic equations of curing reaction can be expressed as follows:

$$\frac{d\alpha}{dt} = 4.38 \times 10^7 \exp(-57740/RT)(1-\alpha)^{0.93}$$

REFERENCES

Acitelli, M.A., R.B. Prime and E. Sacher, 1971. Kinetics of epoxy cure: (1) the system bisphenol-a diglycidyl ether/m-phenylene diamine. Polymer, 12(5): 335-343.

Horie, K., H. Hiura and M. Sawada, 1970. Calorimetric investigation of polymerization reactions. III. Curing reaction of epoxides with amines. J. Polym. Sci. A1, 8(6):1357-1372.

Niu, H.X., T. Zhou, A.M. Zhang, S. Liu and L.B. Ren, 2008. Study of curing kinetics mechanism of DGEBF/DDS. Thermosetting Resin, 23(Suppl): 4-8.

Wang, H.B., X.P. Wei and Y.X. He, 2011. Investigation of thermal decomposition kinetics of epoxy resin cured by polyamide. Chinese J. Colloid Polym., 29(2): 75-77.

Xia, X.N., X.L. Zeng and J. Liu, 2010. Study on curing kinetics and thermal properties of biphenyl novolac epoxy resins. Thermosetting Resin, 25(4): 5-8.

Zhao, W.J., Z.G. Zhang, Z.J. Sun and D. Zhang, 2006. Cure kinetics of TGDDM/DDS system studied by non-isothermal method. Acta Polym. Sin., 4: 564-568.