NON-ISOTHERMAL CURING KINETIC BENZOXAZINE/ HYDANTOIN EPOXY RESIN SYSTEM

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Abstract: Non-isothermal DSC was examined to follow the benzoxazin/ hydantoin epoxy resin curing reaction. A two-paramenter (m, n) autocatalytic model was found by Malke to describe the cure kinetic of the benzoxazin/ hydantoin epoxy resin. No-isothermal DSC curve obtained using the experimental data show agreement with calculated curve of autocatalytic model.

***Keywords*: reaction activation energy; benzoxazion; hydantion epoxy resin; curing kinetic**

1 Introduction

Epoxy resins with outstanding properties are one of the most widely used thermosetting polymers in automobile industries, shipbuilding, aerospace and laminates as adhesives, coatings and matrices of high performance composite materials. But fire risk is a major catastrophe of epoxy resins application. Conventional method is used halogenated compounds with epoxy resin to obtain flame-retardant materials. Nevertheless, flame-retardant epoxy resins containing halogen can produce corrosive and obscuring smoke and may send out super-toxic halogenated compounds with deleterious effects on the environment and human health[1]. Recently, in consideration of environmental problems, halogen-free retardant epoxy resins have become a subject of considerable attention, especially laminates, from scientists and engineers. Silicon, phosphorus and nitrogen, is regarded as an environmentally friendly flame retardant element because it can reduce the harmful impact on the environment more than the existing materials which halogen atoms (e.g. bromine or chlorine) can be used to form some of the most widely applied flame retardant materials[2]. We have synthesized hydantoin epoxy resin, benzoxazine resin was employed as a curing reagent, and called benzoxazine/hydantoin epoxy resins. The knowledge of the curing kinetics and find a mathematical expression for the cure kinetics are important, when modeling the cure kinetics, the curing rates at various cure temperatures and the activation energy of the reaction should be known to get a better control of the reactions and in consequence to optimize the physical properties of the final products. Cure kinetics of thermosetting resins can be studied by different techniques, in this work the DSC technique was used to investigate the kinetics of the benzoxazine/hydantoin epoxy resins cured under nonisothermal conditions.

2 Experimental

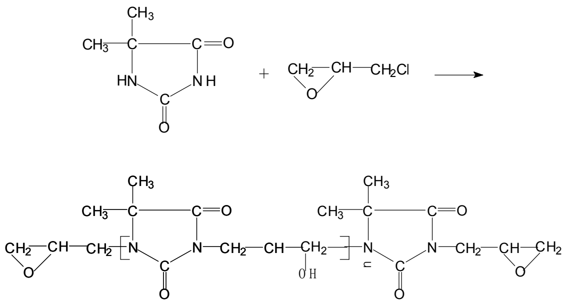
2.1 materials

Formaldehyde aqueous solution (37%), aniline, bisphenol A were purchased from beijing chemcial Co(China). The benzoxazine resin was synthesized according to the reported method [3]. 1-chloro-2, 3-epoxypropane, 5， 5'- dimethylhydantoin were purchased from beijing zhonglian chemcial Co(China).

2.2 Preparation of hydantoin epoxy resin

A three-necked flask equipped with a stirrer, reflux condenser and a thermometer were added 12.8g of 5，5'-dimethylhydantoin and 20g of 1-chloro-2, 3-epoxypropane, 19.1g of isopropyl alcohol was stirred. After that, the NaOH was added drop wise in to the mixture in 1h and further reacted at the reflux temperature for 5h. The organic phase was distillated isopropyl alcohol. IR(KBr, cm^{-1}): 3500 cm^{-1} (–OH of epxoypropyl), 1769 cm^{-1} and 1708 cm^{-1} (C==O), 2985 cm^{-1} 和 2938 cm^{-1} (—CH_3 of hydantoin), 849cm^{-1}(epxoypropyl).^1H-NMR($CDCl_3$,ppm):1.515ppm

(6H, CH_3 of hydantoin), 2.60-2.98ppm (2H, CH_2 of epxoypropyl), 3.12ppm (H, CH of epxoypropyl), 3.55-3.87ppm(2H, CH_2 of N atom of hydantoin).



2.2 Differential scanning calorimetry (DSC)

The polymerization behavior of benzoxazine/ hydantoin epoxy resins was examined using differential scanning calorimetry (DSC) Q100 from TA Instruments. The reaction mixture was cured in DSC under non-isothermal conditions at heating rates of 5, 10, and 20℃/ min which was heated from 30 up to 350℃ in a constant flow of nitrogen of 50 ml /min. The heat flow data, as a function of temperature and time, were obtained using the area under the peak of the exotherm. They were processed further to obtain a fractional conversion (α) and the rate of the reaction dα/dt.

3 Results and discussion

3.1 Non-isothermal kinetic analysis

The curing reaction of benzoxazine/yhdantoin epoxy resin can be studied by DSC at different heating rates. Fig.1 shows the DSC thermograms at 5, 10, and 20 ℃ /min. Fig.2 is the variation of the degree of conversion as a function of temperature at different heating rates.

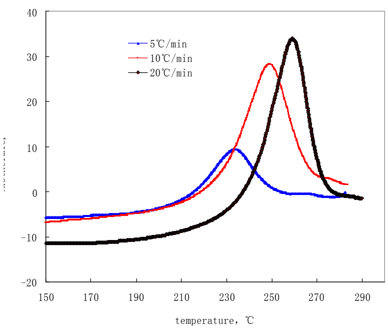


Fig.1 DSC curveof Benzoxazine/yhdantoin epoxy resin

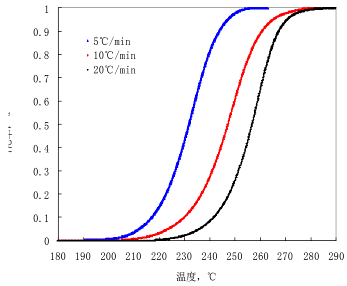


Fig. 2 Degree of conversion α vs temperature at different

From DSC thermograms obtained information about the curing reaction were get as follows: the initial curing temperature(T_i), the peak temperature (T_p), and the finishing temperature(T_f), Some data on the curing reaction are listed in table1. The curing process temperatures of the resin system is important such as gelation temperature (T_{gel})=145 ℃ , curing temperature (T_p)=227.8 ℃ and post-curing(T_{treat}) =260.6 ℃ were acquired by DSC extrapolation at various heating rates.

Tab.1 The datas for curing of benzoxazine / hydantoin epoxy resin from DSC thermograms at different rates

β，℃/min	T_i/℃	T_p/℃	T_f/℃
5	154.3	233.0	265.7
10	174.3	249.1	276.5
20	192.6	259.5	286.8

The reaction rate of the kinetic curing process for resin syetem can be described by Eq. (1)

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \qquad (1)$$

Where $K(T)$ is a temperature-dependent reaction rate constant, f(α) a dependent kinetic model function, and T is the absolute temperature. The rate constant is temperature dependent according to Arrhenius law shown in Eq. (2)

$$K(T) = A\exp(-\frac{E_a}{RT}) \qquad (2)$$

Where A is the pre-exponential factor and Ea is the apparent activation energy. In non-isothermal conditions, when the temperature is rise at a constant heating rate $\beta=dT/dt$, Eq. (2) can be modified as follows:

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = A\exp(-\frac{E_a}{RT})f(\alpha) \qquad (3)$$

The apparent activation energy of the curing process of resin system in non-isothermal conditions can be calculated by isoconversional method [4] which follows from logarithmic form of Eq. (2):

$$\ln(\frac{d\alpha}{dt}) = \ln[Af(\alpha)] - \frac{E_a}{RT} \qquad (4)$$

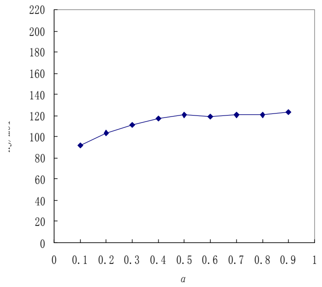


Fig.3 Variation of *Ea* versus conversion *α*

Fig.3 is variation of *Ea* versus conversion *α*, It show that has practically a few increasing in the conversion interval 0.2 <α< 0.8, mean value is 116.1 kJ/mol. However, mathematical expression of *f(α)* don't know.

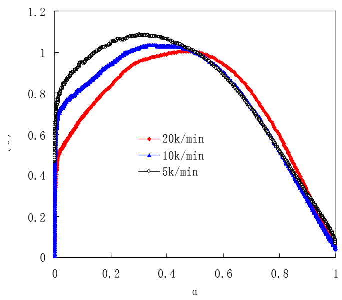


Fig4 Variation of y(*α*) function versus conversion *α*

Mathematical expression of *f(α)* is deduced effectively as defined by Malek. Two functions y(α) and z (α) are defined by Malek method. According to cures *y(α)~ α* and *z(α)~ α* to deduce, it is necessary to appeal to the special functions y(*α*) and *z*(*α*) shown as follows.

$$y(\alpha) = \frac{d\alpha}{dt}e^{\chi} \qquad (5)$$

$$Z(\alpha) = \pi(\chi)(\frac{d\alpha}{dt})\frac{T}{\beta} \qquad (6)$$

Where χ=E/RT, π（χ） is the expression of the temperature integral. As is pointed out[5], π（χ) can be well approximated using the 4th rational expression of Senum and Yang as in Eq.(7).

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

Fig.4 and Fig.5 represent the characteristics curves y(α) and z (α) at different curing degree, resperctively. Curing degree of peak value of y(α) and z(α) curve resperctively are α_M 和 α^{∞}_p ,which are used to estimate characteristic value of mechanism function. α_M and α^{∞}_p at different heating rate are listed in Table 3. As can be

Tab.3 The values of α_M 、 α^{∞}_p and α_p for benzoxazine/hydantoin epoxy resin system

β, ℃/min	α_M	α^{∞}_p	α_p
5	0.3007	0.5946	0.5706
10	0.3445	0.6069	0.5930
20	0.4693	0.6229	0.6109

seen from Tab.3 α^{∞}_p < 0.632. According to what mentioned above, curing reaction of benzoxazine/ hydantoin epoxy resin system can be described by the two-parameter autocatalytic kinetic model of Sestal-Berggren in Eq.(8).

$$f(\alpha) = \alpha^m(1-\alpha)^n \qquad (8)$$

Kinetics parameter of benzoxazine/ hydantoin

Tab.4 The kinetic parameters evaluated for the curing of benzoxazine / hydantoin epoxy resin system

β, ℃/min	*n*	*m*	*A*	*E* , Kj/mol
5	0.88	0.38	5.45×10^{11}	
10	0.91	0.48	4.87×10^{11}	
20	1.07	0.95	1.03×10^{12}	
mean	0.95	0.60	6.87×10^{11}	116.1

epoxy resin obtained from the data listed in Tab.3 is presented in Tab.4. According to the data presented in Tab.4, Mechanism function of benzoxazine/ hydantoin epoxy resin is given by: The data presented in Tab.4 show the relation of curing rate and curing degree of benzoxazine/ hydantoin epoxy resin system is expressed as in Eq.(9).

$$\frac{d\alpha}{dt} = 6.87\times10^{11}\alpha^{0.60}(1-\alpha)^{0.95}\exp(\frac{-116200}{RT}) \qquad (9)$$

Calculated result is compared with experimental data, which is used to test the reliability of the two-parameter autocatalytic kinetic model of Sestal-Berggren. Fig.6 shows that non-isothermal DSC curve obtained using the experimental data show good agreement with simulated data of autocatalytic model.

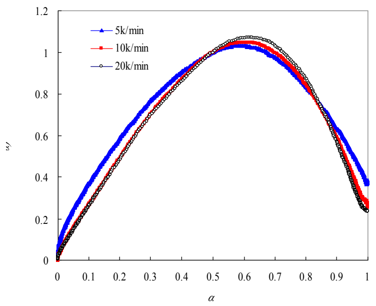


Fig.5 Variation of z(α) function versus α

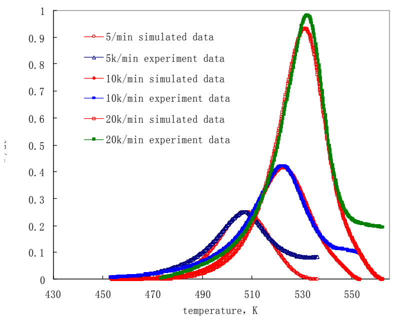


Fig.6 Comparison of experimental data and simulated(red) data for benzoxazine/ yhdation epoxy resin

4. Conclusion

The curing reaction processing of characteristic temperature benzoxazine/ hydantoin epoxy resin system is obtained by extrapolation, which according to dynamic DSC datas. The apparent activation energy (*Ea*) increased with increasing the curing degree of benzoxazine/ hydantoin epoxy resin, the mean value of curing degree ranged from 0.2 to 0.8 is 116.1 Kj/mol. The curing reaction processing rate equation of benzoxazine/hydantoin epoxy resin is found. Experimental DSC curve show a good agreement with calculated curve in this paper, which can describe the curing reaction processing of benzoxazine/ hydantoin epoxy resin system.

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