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Study on Curing Kinetics of Fatty Amine/Epoxy Resin Using Non-Isothermal DSC Method

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Abstract. The curing processing of fatty amine/epoxy resin was studied by non-isothermal differential scanning calorimetry (DSC) at different heating rates. The curing kinetics mechanism function and the kinetic parameters were determined using n order reaction and autocatalytic reaction and the model-free method. The curing processing was determined by extrapolation method. The results indicated that n order reaction model does not accord with the basic reaction characteristics of curing system. While the DSC curves from the autocatalytic model can well agree with that of experiment. The whole curing reaction process accords with the autocatalytic reaction model. The results by using FWO and FR method can also confirm that the curing reaction of resin system belongs to the autocatalytic model.

1. Introduction

The process of curing reaction based on thermosetting resin is rather complicated, the curing reaction process can be studied by the exothermic curve measured by differential scanning calorimetry (DSC). The curing reaction mechanism can be inferred and the kinetic parameters of the curing reaction can be obtained by using the regular pattern that the reaction heat is proportional to the amount of epoxide group consumed during curing process [1].

Kinetic model is one of the methods to study the crosslinking mechanism of thermosetting resin. There are two main approaches used for cure kinetics can be distinguished: (i) phenomenological and (ii) mechanistic modeling [2]. The basic assumption of isoconversional method (model-free method) is that when the curing degree is the same, the curing rate is only related to temperature, and its core problem is to convert differential and integral signals into curing degree [3]. Vyazokin proposed nonlinear Vyazokin (NLV) method,which greatly promoted the development of isoconversional methods [4-5]. In this paper, the curing kinetics of fatty amine/epoxy resin was studied by using *n* order reaction model and autocatalytic reaction and the model-free method, and the curing reaction parameters and kinetic equations were obtained. It provides a theoretical basis for the application of epoxy resin.

2. Experimental part

2.1. Experimental principle
Analysis of curing reaction of thermosetting resin by DSC based on the following three basic assumptions [6]:
(1)The curing reaction rate is proportional to the heat flux rate.

$$\frac{d\alpha}{dt} = \left(\frac{dH/dt}{\Delta H}\right) = \frac{\Phi}{\Delta H}$$

(1)

In the formula: α is degree of cure, t is the time, $d\alpha/dt$ is the curing rate, Φ is the heat flow rate, ΔH and is the total exothermic of reaction.
(2)The basic rate equation satisfying the kinetic analysis.

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

(2)

In the formula: T is absolute temperature, $k(T)$ is the reaction rate constant. $f(\alpha)$ Is a function of curing degree and is related to the kinetic model. The reaction rate constant is a function of temperature and follows the Arrhenius parameters.

$$k(T) = A exp(-\frac{E_a}{RT})$$

(3)

In the formula: A is the pre-exponential factor, E_a is the apparent activation energy, and R is the ideal gas constant.
(3)The exothermic of curing reaction is proportional to degree of cure.

2.2. Raw material
Epoxy resin is bisphenol A type E-51 (WSR618) epoxy resin, epoxy value 0.51~0.54, viscosity 10000-16000 mPa·s (25°C), ethylene diamine, analytically pure.

2.3. DSC test program
Weigh 15 mg sample into the alumina crucible using the ultra-microelectronic balance, and test the isothermal temperature at 35-300 ℃ at 5, 10, 15, 20 K/min. High purity Ar protection was used during the test and the Ar flow rate was 20 mL/min. The ratio of the curing agent ethylenediamine to the epoxy resin E51 was m (E-51) = 9:100.

3. Results and discussion
According to the DSC curve at different heating rates (Fig.1), it can be seen that as the heating rate increases, the initial temperature, peak top temperature and reaction end temperature of the exothermic peak of the curing reaction increase, and the exothermic curve moves toward the high temperature. The curing temperature is widened, the curing time is shortened, and the exothermic enthalpy of the system is gradually increased. The reason is as follows: as the heating rate increases, dH/d*t* becomes larger, that is, the thermal effect per unit time becomes larger, the thermal inertia becomes larger, and the generated temperature difference increases, thus, the exothermic peak of curing reaction moves to high temperature and becomes higher [7]. The increase of the heating rate increases the curing reaction temperature, and the curing reaction rate increases, which leads to the shortening of the curing time [8]; due to the existence of many epoxy groups, the heating rate increases and more and more complicated. The curing reaction, so the exothermic enthalpy increases.
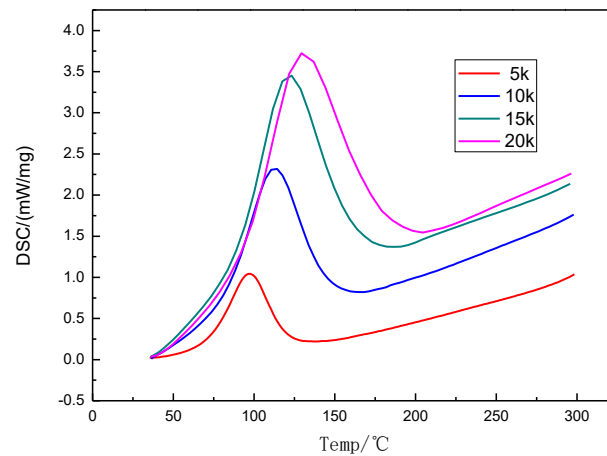
Figure 1. DSC curves at different heating rates

3.1. N order model method

Most of the kinetic studies of resin curing reactions use the n order kinetic model in the phenomenological model:

$$\frac{d\alpha}{dt} = k(T)(1-\alpha)^n \tag{4}$$

α is the degree of cure; n is the number of reaction stages; K(T) is the reaction rate constant, independent of temperature in the formula (4).

Curing kinetic parameters such as apparent activation energy and reaction order have an important role in understanding the curing reaction. Generally, the DSC data obtained by different heating rates can be processed by Kissinger [9] and Crane [10] equations, and the reaction kinetic parameters such as E$_a$, n, and A can be obtained, and then the n order kinetic model equation of the curing reaction is determined.

Kissinger equation:

$$ln \frac{\beta}{T_p^2} = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_P} \tag{5}$$

β is the heating rate; Tp is the peak temperature; Ea is the apparent activation energy in the formula (5).

Crane equation:

$$\frac{d(ln\beta)}{d(1/T_P)} = -\left(\frac{E_a}{nR} + 2T_P\right) \tag{6}$$

When $\frac{E_a}{nR} \geq 2T_P$, $\frac{d(ln\beta)}{d(1/T_P)} = -\frac{E_a}{nR}$ is obtained. At different heating rates, in (β/T_P^2) and 1/T_P can be linearly fitted and exhibit a linear relationship.

Table 1. Reaction characteristic temperature of epoxy resin at different heating rates.

heating rates β	5K/min	10K/min	15K/min	20K/min
initiation temperature T_i	71.2	81.1	86.7	98.3
peak temperature T_p	97.2	112.9	121.5	130.5
finish temperature T_f	121.8	149.0	164.4	182.6

The DSC curves at different heating rates in Figure 1 were analyzed to obtain the curing reaction initiation temperature, peak top temperature and finish temperature of the resin at different heating rates. The specific values are shown in Table.1.

The apparent activation energy of the reaction system can be determined by dynamic DSC data and Kissinger equation, in (β/T_P^2) is linear with $1/T_P$. The activation energy and frequency factor of the curing reaction of bisphenol A epoxy resin can be obtained from the slope and cut of the line.. The DSC data of the epoxy resin curing system at different non-isothermal heating rates are shown in Table. 2.

Table 2. DSC data of epoxy resin curing system at different heating rates.

β(K/min)	T_p (K)	Lnβ	Ln (β/T_p^2)	$1/T_p$
5	370.35	1.609438	-10.2195	0.0027
10	386.05	2.302585	-9.60935	0.00259
15	394.65	2.70805	-9.24795	0.002534
20	403.65	2.995732	-9.00536	0.002477

According to the data in Table.2, the in (β/T_P^2) and $1/T_P$ curves are plotted and linearly fitted. As shown in Fig.2, the linear equation is obtained as follows:
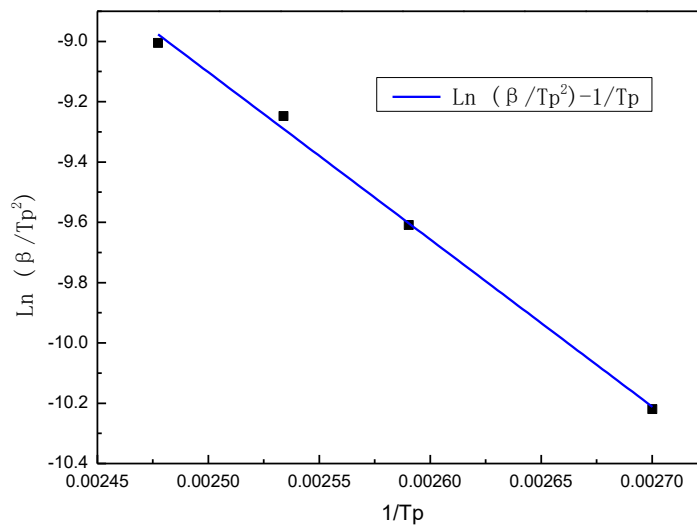
$$\ln(\beta/T_P^2)=4.7581-\frac{5544.1}{T_p} \tag{7}$$

Figure 2. ln ($\beta/TP2$) and $1/TP$ curve

Where intercept: S=4.7581; slope I = -5544.1. Substituting it into the Kissinger equation:
$\ln\frac{A\times R}{E_a}=4.7581$ $\frac{E_a}{R}=5544.1$

The activation energy is solved: E_a=46.09kJ/mol. Frequency factor: A=6.46$\times10^5$S^{-1}.

When E_a/nR is much larger than $2T_p$, $2T_p$ in the Crane equation is negligible, and the reaction order n can be obtained by the slope of the line. According to the Crane equation, the lnβ and $1/T_P$ curves are plotted and linearly fitted, as shown in Fig.3, to obtain a straight line fitting equation:
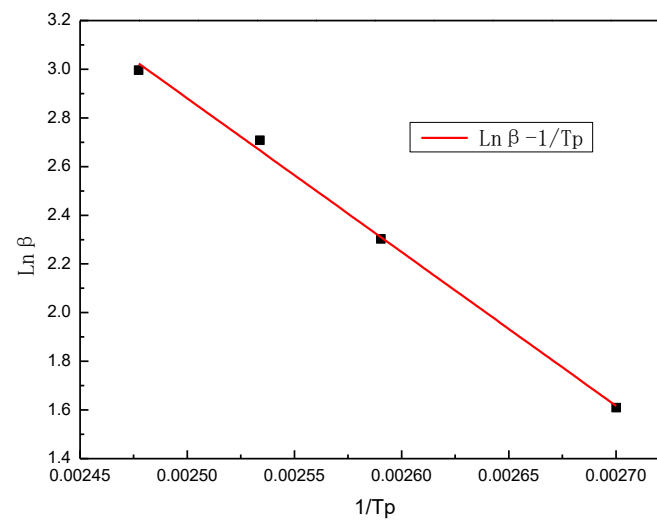
$$ln\beta = 18.67 - \frac{6316}{T_p} \tag{8}$$

Figure 3. In β and 1/TP curves

Where $E_a/nR=6316$, solution: n=0.8778. The epoxy resin curing reaction kinetic model is obtained as follows:

$$\frac{d\alpha}{dt} = 3.70 \times 10^5 \times \exp(-5.34/T)(1 - \alpha)^{0.8778} \tag{9}$$

The curing reaction formula and the experimental value curve obtained by the n-stage model were analyzed and compared by Thermo kinetics dynamic software, and the analysis results are shown in Fig.4.

The figure shows the curve of the relationship between dα/d*t-T* calculated by the n order kinetic model and the experimental value. It can be seen from Fig.4 that the n order kinetic model curve has a large deviation from the experimental curve, indicating that in order curing kinetics model does not describe well with the curing process of the epoxy resin system.
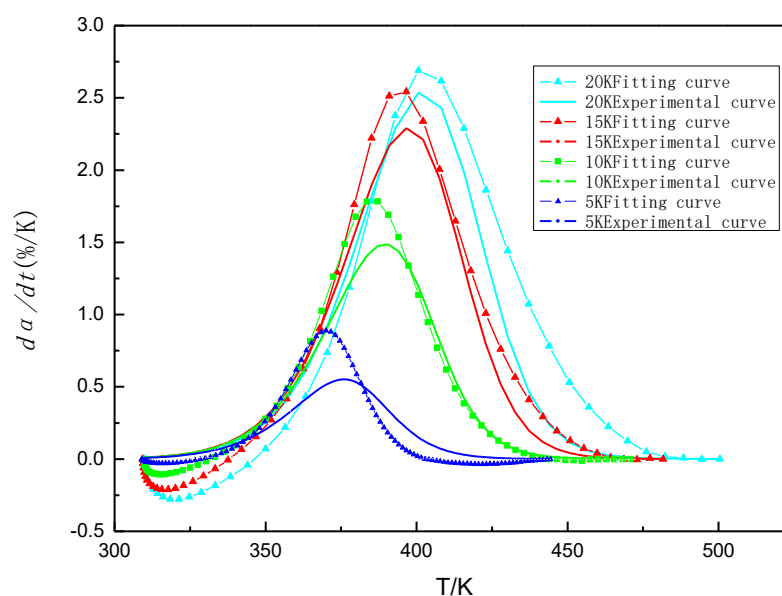

Figure 4. Comparison of experimental values with an order model calculated values

3.2. Autocatalytic reaction model

When the product of a chemical reaction can further catalyze the rate of this reaction, the rate of the reaction is increased at an extremely rapid rate. This reaction is called autocatalytic reaction.

The autocatalytic model considers two independent reaction orders: m and n, which can simultaneously calculate multiple parameters, and the curing kinetic equations are also:

$$\frac{d\alpha}{dt} = A exp(-\frac{E_a}{RT})f(\alpha) \tag{10}$$

Where $f(\alpha) = \alpha^m(1-\alpha)^n$, take the logarithm, then you can get:

$$ln\frac{d\alpha}{dt} = lnA + mln\alpha + n(1-\alpha) - \frac{E_a}{RT} \tag{11}$$

It can be seen that if the same α is obtained at different heating rates, then $ln\ d\alpha/dt$ is proportional to $1/T$ under this α, and value of E_a can be obtained, It is important that the value of E_a determines the appropriate kinetic model. To this end, two special equations y (α) and z (α) [11-12] need to be introduced:

$$Y(\alpha) = (\frac{d\alpha}{dt})e^x \tag{12}$$

$$Z(\alpha) = \pi(x)(\frac{d\alpha}{dt})\frac{T}{\beta} \tag{13}$$

Where x is $\frac{E_a}{RT}$; β is the heating rate, T is the absolute temperature; $\pi(x)$ is the expression of the temperature integral, and the following approximate expressions proposed by Senum and Yang are usually used:

$$\Pi(x) = \frac{x^3 + 19x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{14}$$

y(α) is proportional to f(α), y(α) represents the trend of kinetics, and the function values of y(α) and z(α) vary within the interval (0,1), according to the shape of the function. And the maximum value can be selected for its suitable curing kinetics model.

Using the obtained activation energy E_a value and the determined kinetic model, the pre-exponential factor A of the reaction can be obtained according to the following equation.

$$A = -\frac{\beta x_p}{T f'(\alpha_p)}expx_p \tag{15}$$

Where $f'(\alpha_p)$ the derivative is form of the kinetic equation; α_p is the degree of cure at the peak temperature of the DSC curve.

The relationship between the degree of cure of the epoxy resin and the temperature can be obtained by integrating the DSC curve at different heating rates in Fig. 1, as shown in Fig. 5.
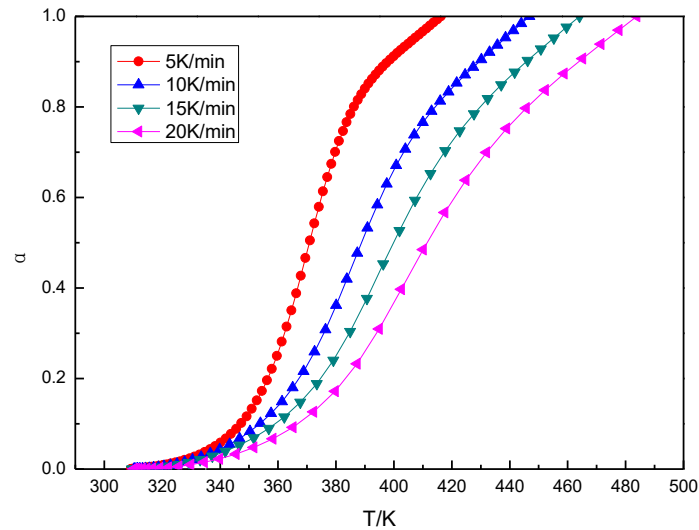
Figure 5. Relationship between curing conversion rate and curing temperature

From the relationship between the curing conversion rate and the curing temperature in Fig.5, the autocatalytic reaction equation can be used to obtain the linear relationship between the solidification conversion rate and the temperature reciprocal at different degrees of cure, ie, ln dα/dt and 1/*T*, as shown in Fig.6, the activation energy E_a of different degrees of cure can be obtained by the slope of the straight line, as shown in Fig.7.
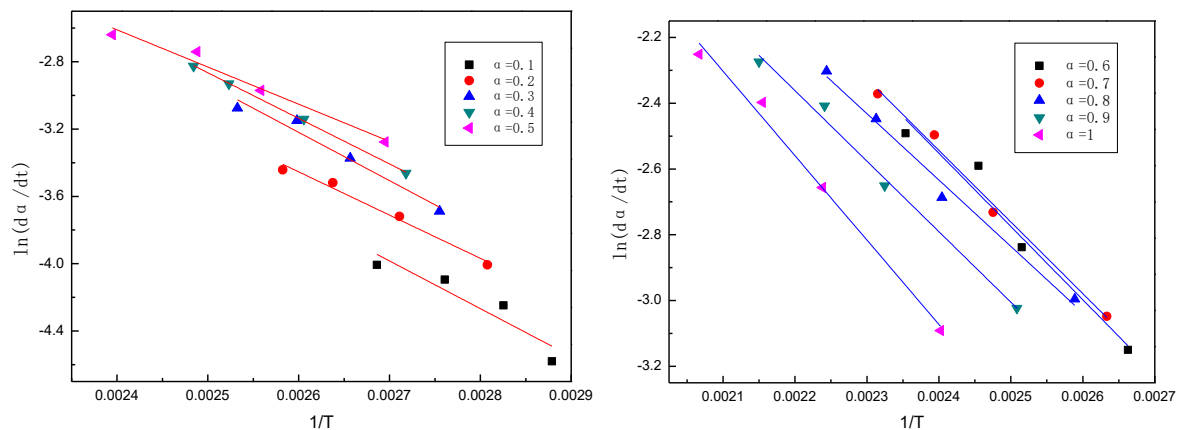

Figure 6. Relationship between ln dα/dt and 1/T (a) and (b)

It can be seen from Fig.7 that the autocatalytic effect is obvious in the early stage of the reaction, and the activation energy is gradually decreased. As the reaction steric hindrance increases, the energy required for the movement of the molecular segment increases, and the curing reaction is mainly converted from chemical reaction activity to diffusion, and thus the activation energy of the reaction increases.

The calculated values of the average activation energy Ea can be used to obtain the values of y(α) and z(α), which are normalized to the range of [0,1] for the relationship between y(α) and z(α) versus α. , as shown in Fig.8 and Fig.9.
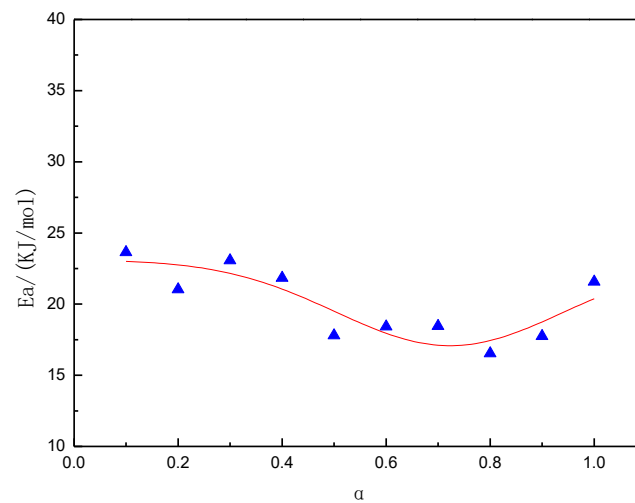
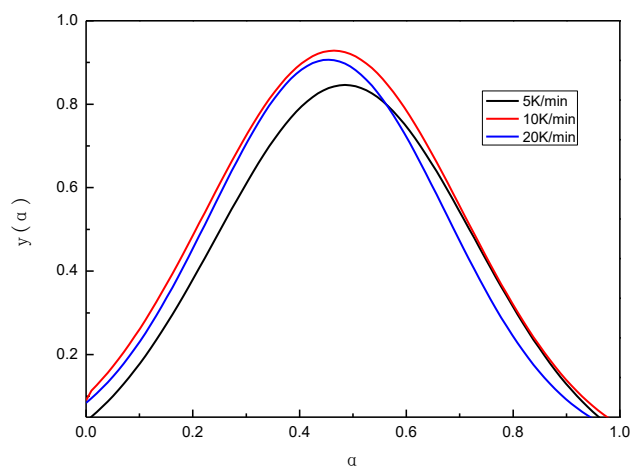**Figure 7.** Relationship between different degrees of cure α and activation energy Ea
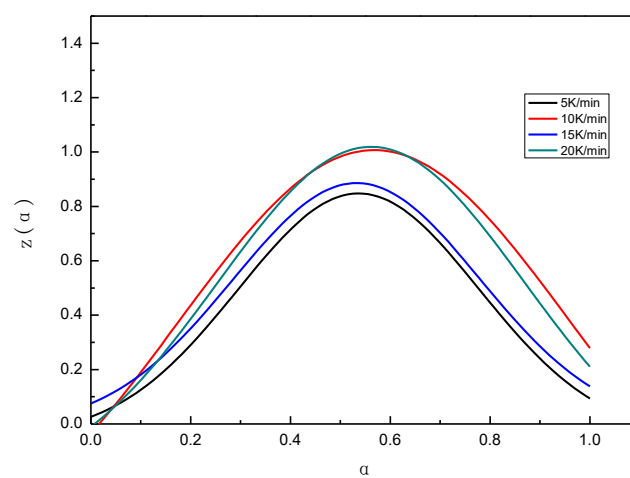

Figure 8. Relationship between y (α) and α

Figure 9. Relationship between z (α) and α

The degrees of cure corresponding to the maximum values of $y(\alpha)$ and $z(\alpha)$ are denoted as α_M and α_p^{∞}, respectively, and these two values can be used to judge the expression of the mechanism function. The values of α_M and α_p^{∞} at different heating rates are listed in Table.3 below, where AP is the degree of cure at T_p in the DSC curve.

Table 3. α p, αM and αp∞ values obtained from DSC curve analysis

β(°C/min)	α_p	α_M	α_p^{∞}
5	0.50508	0.48485	0.53535
10	0.47722	0.46465	0.56566
15	0.45317	0.31313	0.53535
20	0.39697	0.45455	0.56566

It can be seen from Table.3 that α_M and α_p^{∞} in the system are independent of the heating rate; $\alpha_p^{\infty} \neq 0.632; \alpha_M \in (0, AP)$. According to the criteria of Malek, the solidification process of the system can be expressed by the Sestak-Berggren autocatalytic kinetic model:

$$f(\alpha) = \alpha^m (1 - \alpha)^n \tag{16}$$

From the autocatalytic equation:

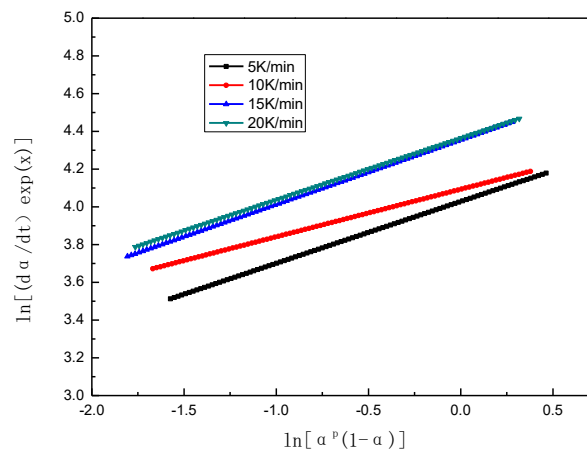$$\ln \frac{d\alpha}{dt} e^x = lnA + nln[\alpha^p (1 - \alpha)] \tag{17}$$

Figure 10. The relationship between $\ln \frac{d\alpha}{dt} e^x$ and $ln[\alpha^p(1 - \alpha)]$

As shown in Fig.10, the kinetic parameters n and A can be obtained by the relationship between $\ln \frac{d\alpha}{dt} e^x$ and $ln[\alpha^p(1 - \alpha)]$. Where p=m/n, and α_M=m (m+n), that is, p=α_M/ (1-α_M), after obtaining n, m can be obtained by m=pn. The kinetic parameters obtained are listed in Table.4.

Table 4. Autocatalytic model kinetic parameters

β(°C/min)	m	n	lnA	E_a/(J/mol)
5	0.081775	0.3274	4.0275	
10	0.06266	0.2519	4.0926	
15	0.073471	0.3416	4.3539	20011.80
20	0.080975	0.3266	4.364	
average	0.07472	0.311875	4.2095	

From the kinetic parameters of Table.4, the solidification kinetic model equation for the fatty amine/epoxy resin system is:

$$\frac{d\alpha}{dt} = A\exp(-20011.80/RT)\alpha^{0.07}(1-\alpha)^{0.31} \qquad (18)$$

The curing reaction formula and the experimental value curve obtained by the autocatalytic model were analyzed and compared by Thermo kinetics dynamic software, and the results are shown in Fig.10.
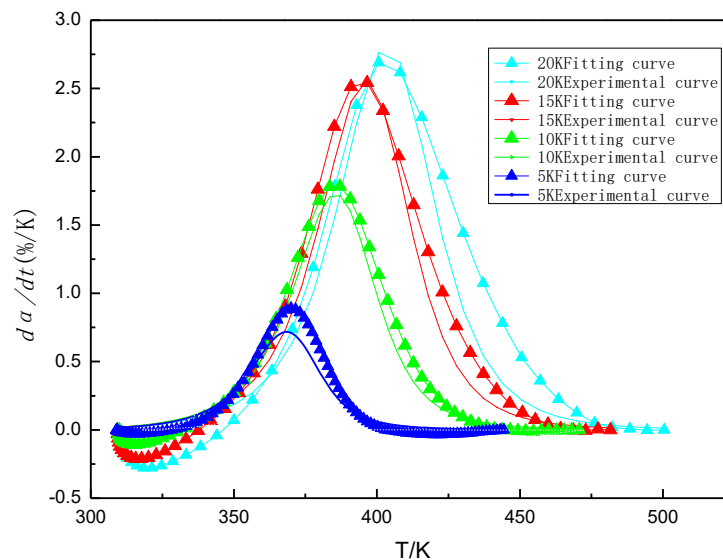

Figure 11. Comparison of experimental values with calculated values of autocatalytic models

As shown in the Fig.11, the model curves at different heating rates are basically consistent with the experimental curves, except that some deviations occur in the late stage of the curing reaction. The reason for the deviation may be that the curing reaction is converted from chemical reaction control to diffusion control as the temperature increases. The model can well describe the curing reaction of the epoxy resin system in the range of 5-20 K/min heating rate.

3.3. *Flynn-Wall-Ozawa method*

This paper studies two non-model methods: the Flynn-Wall-Ozawa method and the Friedman method. Both belong to the equal conversion rate method [13]. Their greatest advantage is that the kinetic parameters can be calculated without knowing the reaction model, thus fitting the curing reaction model.

The Flynn-Wall-Ozawa (FWO) method is an integration method. When the same degree of cure α is selected at different heating rates β, the integral form of the dynamic excitation function g (α) is a constant value. Taking lnβ and in (β/T^2) as the ordinate and 1/T as the abscissa, after linear fitting, the activation energy E_a is obtained by the slope. Its integral form is:

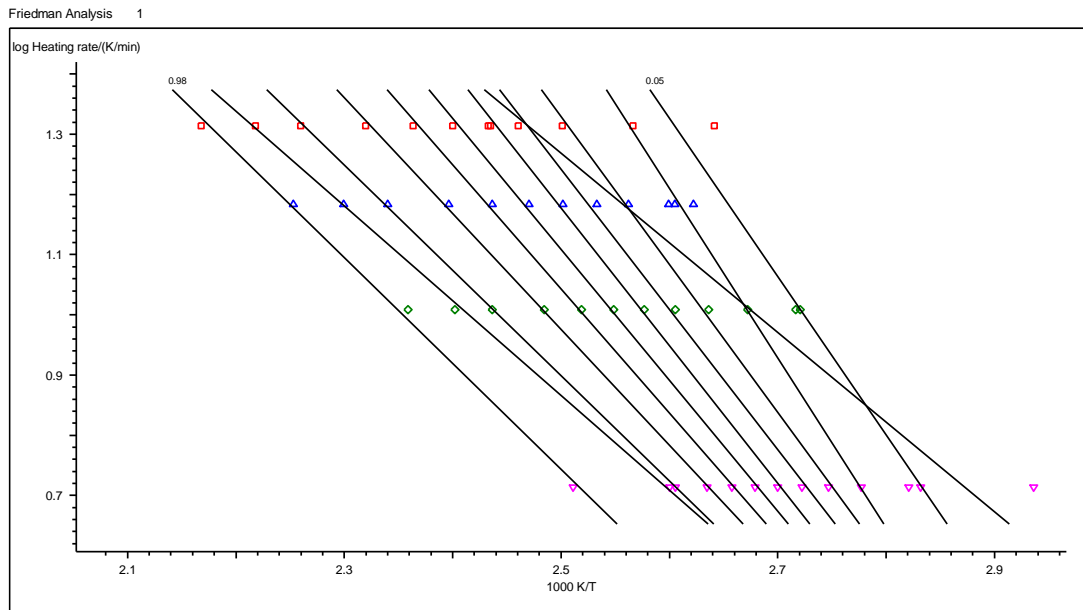$$\ln\beta = \ln A - \lg(\alpha) - 5.331 - \frac{1.502E_a}{RT} \qquad (19)$$

Figure 12. Lnβ-1000/T diagram of different degrees of cure by Flynn-Wall-Ozawa method

It can be seen from Fig.13 that the activation energy E_a of the fatty amine/epoxy curing reaction decreases with the increase of the degree of solidification, which is consistent with the characteristics of the autocatalytic model. The late activation energy increases, because the crosslinking density increases as the degree of solidification increases, and the reaction gradually changes from chemical reaction control to diffusion control.
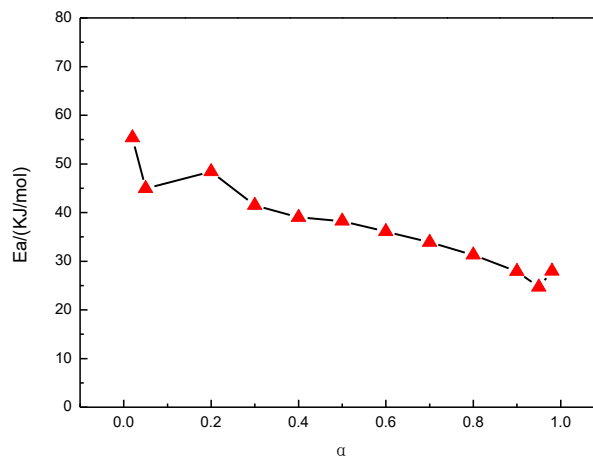

Figure 13. Ea curve of different curing degrees by Flynn-Wall-Ozawa method

3.4. *Friedman method*

Friedman is a differential method, with in (βdα/dt) as the abscissa and $1/T$ as the ordinate. The data under each degree of cure is linearly fitted, and the activation energy E is obtained at some rates. FR is:

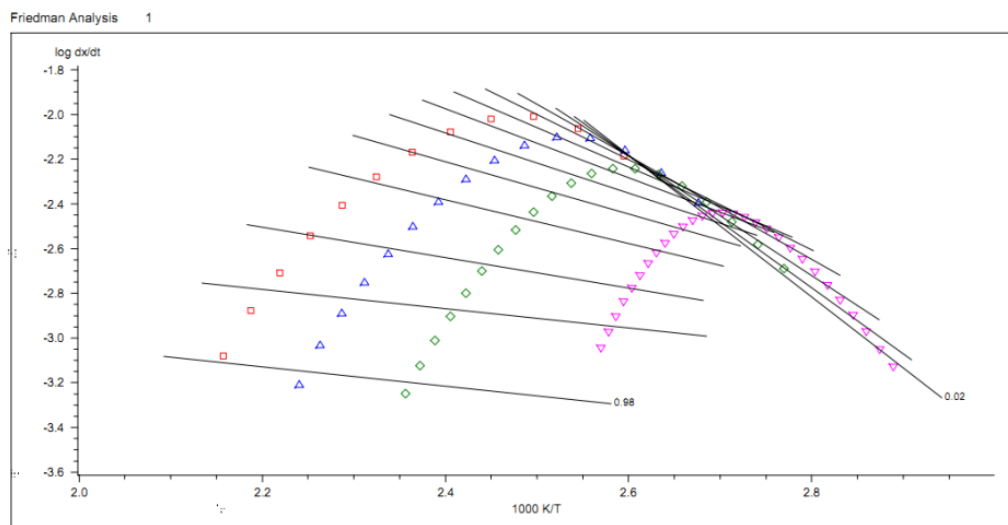$$ln \frac{d\alpha}{dt} = lnA + lnf(\alpha) - \frac{E_a}{RT} \tag{20}$$

Figure 14. The lndx/dt-1000/T curve at different degrees of cure by the Friedman method
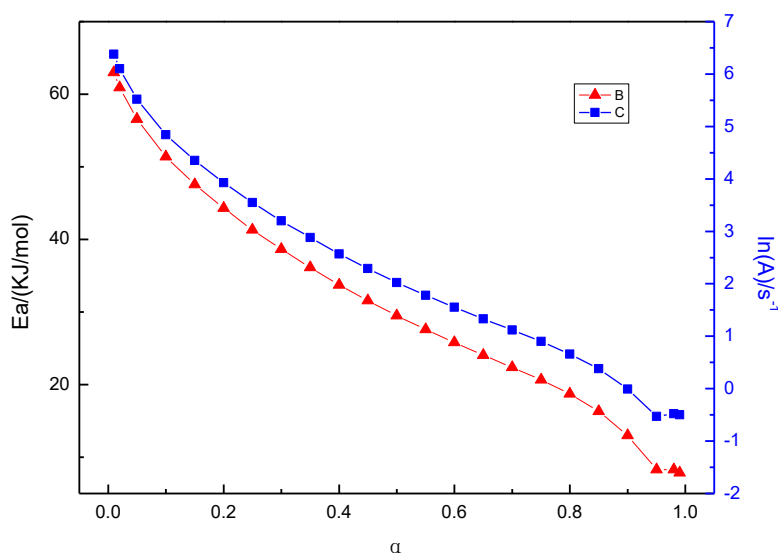

Figure 15. Ea curve at different degrees of cure by Friedman method

It can be seen from Fig.15 that the autocatalytic effect is obvious in the early stage of the reaction, and the activation energy is gradually decreased. As the reaction steric hindrance increases, the energy required for the movement of the molecular segment increases, and the activation energy of the reaction increases.

4. Conclusion

(1) The non-isothermal DSC method was used to study the curing kinetics of epoxy resin by n order model method. The results show that the n order reaction model does not meet the basic characteristics of the curing reaction.

(2) The whole curing reaction process conforms to the autocatalytic reaction model, and the kinetic model is $\frac{d\alpha}{dt} = Aexp(-20011.80/RT)\alpha^{0.07}(1-\alpha)^{0.31}$, the autocatalytic reaction model curve agrees well with the experimental values.

(3) According to the data analysis results of model-free method such as FWO method and FR, it can be concluded that the activation energy E_a of the curing reaction decreases with the increase of the degree of solidification, and the reaction gradually changes from chemical reaction control to diffusion control. The reaction is consistent with the characteristics of the autocatalytic model.

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