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Curing kinetics of 4,4'-Methylenebis epoxy and m-Xylylenediamine

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Abstract. In this paper, the curing kinetics of 4,4'-Methylenebis epoxy resin(TGDDM) and m-Xylylenediamine(m-XDA) was investigated by non-isothermal differential scanning calorimetry(DSC) at various heating rates. Selected non-isothermal methods for analyzing curing kinetics were compared. The activation energy(E) and the correlation coefficient(R) were obtained by different isoconversional methods. The reaction order(n) was obtained by the activation energy in different isoconversional methods for the by Crane equation. The results show that the apparent activation energy are 65.23kJ/mol, 52.20 kJ/mol and 66.10 kJ/mol by using the method of Kissinger, Friedman and F-W-O, the reaction order are 0.911, 0.729 and 0.923 by using the method of Kissinger, Friedman and F-W-O.

1. Introduction

Epoxy are widely used in aviation materials, composite materials and other fields, because it performs very well on the aspects of thermal stability, chemical stability and so on [1,2]. The epoxy resin of 4,4'-Methylenebis perform well in high heat resistance, high strength and high modulus, so it became a hot research [3]. However, the resin usually needs high temperature curing to ensure its performance [4]. High temperature can affect the performance of the resin solidification, consume energy [5].

The performance of material after curing can be affected by kinetic parameters [6]. Therefore, the solidification kinetics of epoxy resins were studied to determine the suitable curing conditions. Although there have been many studies of the curing reaction of epoxy resin at home and abroad, the results are not the same. Therefore, it is necessary to study the curing of specific epoxy resin, curing process for composites forming and optimizing performance.

In this paper, the DSC curves of epoxy resin were measured based on the non- isothermal method, and the reaction kinetic parameters of the epoxy resin system were calculated by Kissinger method, Friedman method and F-W-O method.

2. Experiment

2.1. Raw material.

4,4'-Methylenebis(AG-80), Shanghai Huayi Resin Co., Ltd, Epoxy value is 0.85; m-Xylylenediamine(m-XDA), Shanghai Macklin Biochemical Co., Ltd.

2.2. Preparation of the sample.

The thermal curing reaction of the AG-80 epoxy resin and m-XDA under flowing N_2 gas was investigated using a DSC analyzer (Netzsch 204 F1). The DSC conditions were as follows: sample mass, 5.000 -8.000 mg; heating rates, 2.5, 5, 10, 15, and 20 K/min; atmosphere, N_2 gas at a flow rate of 20 mL/min; and temperature 30 ℃–180 ℃.

3. The results and discussion

3.1. DSC curves of Samples.

Figure 1. shows the DSC curves at different heating rate. Table 1. shows the thermal enthalpy ΔH, the initial temperature T_i, the peak temperature T_p and the final temperature T_f.

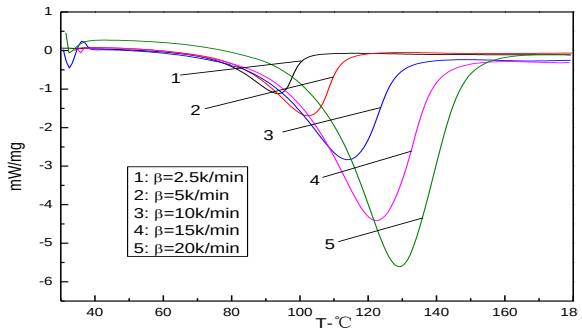

Figure 1. DSC curves of system different heating rates.

Table 1. The respective values of ΔH, T_i, T_p and T_f at different heating rates.

Heating rates (k/min)	ΔH(J/g)	T_i(℃)	T_p(℃)	T_f(℃)
2.5	465.1	76.9	93.7	100.8
5	435.6	82.7	102.4	112.5
10	453.7	89.2	113.9	128.7
15	509.7	96.8	122.4	139.3
20	503.2	104.6	129.1	147.4

3.2. Curing kinetic parameters of method of Kissinger.

Curing kinetic parameters such as apparent activation energy are important to understand the solidification. In general, the Kissinger equations [7,8] can be used to process the DSC data which is at different heating rates. The kinetic parameters can be obtained.

$$\ln(\frac{\beta}{T_P^2}) = \ln(\frac{AR}{E_a}) - \frac{E_a}{RT_p} \quad (1)$$

In equation (1), β is the heating rate; T_p is the peak temperature; E_a is the apparent activation energy. E_a and A can be obtained by the relationship between $\ln \beta/T_P^2$ and $1/T_p$. The calculating results show that E_a=65.23kJ/mol, A=3.07×$10^8 s^{-1}$ and the correlation coefficient R is 0.994.

3.3. Curing kinetic parameters of method of Friedman.

The Friedman method is also used to analyze apparent activation energy. The Friedman equation is shown below.

$$\ln[\frac{\beta d\alpha}{dT}] = \ln Af(\alpha) - \frac{E}{RT} \quad (2)$$

In equation (2), the physical meanings of β, E, T and A are the same as those of equation (1). The differential form of the reaction mechanism function is $f(\alpha)$.

At the different heating rates β, the same conversion rate α is selected, then $f(\alpha)$ is a constant value. So $\ln[\beta d\alpha/dT]$ and 1/T are linear relationship in shown Figure 2, the E and A of can be obtained by the slope and intercept. Using the slope and the intercept of the linear regression line at each conversion rate, the values of E and A of were obtained as shown in Table 2.

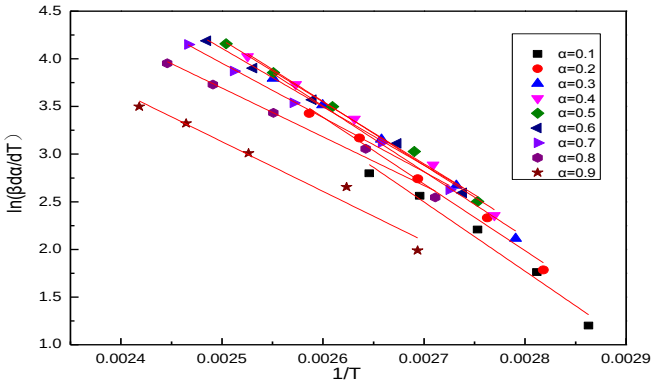

Figure 2. Relationship between $\ln[\beta d\alpha/dT]$ and (1/T).

Table 2. The values of E and A with the method of the Freidman.

α	Intercept	Slope	R	E(kJ/mol)
0.1	22.10	7260.67	0.985	60.37
0.2	21.57	6992.50	0.993	58.14
0.3	21.40	6882.40	0.994	57.22
0.4	20.98	6700.78	0.997	55.71
0.5	20.44	6496.80	0.997	54.01
0.6	19.45	6134.44	0.999	51.00
0.7	18.21	5702.82	0.997	47.41
0.8	16.49	5119.15	0.993	42.56
0.9	16.16	5213.57	0.977	43.35

The E obtained by the Friedman method in the Table 2. were averaged to the obtain the apparent activation energy that E_a=52.20kJ/mol.

3.4. Curing kinetic parameters of method of F-W-O.

The F-W-O [9] method allows to obtain apparent activation energy from a plot of $\lg\beta$ versus 1/T. The Friedman equation is shown below.

$$\lg\beta = \log\left[\frac{AE}{RG(\alpha)}\right] - 2.315 - 0.4567\frac{E}{RT} \quad (3)$$

In equation (3), the physical meanings of β, E, T and A are the same as those of equation (1).

$G(\alpha)$ is the integral form of the reaction mechanism function. Since the same conversion rate is chosen, $G(\alpha)$ is a constant value, so that $\lg\beta$ is linearly related to 1/T.

As with Friedman method, the values of E and A can be determined by the slope and intercept. For each α, a set of E and A value was obtained. Using the slope and the intercept of the linear regression line at each conversion rate in Figure 3, E and A were obtained as shown in the Table 3.

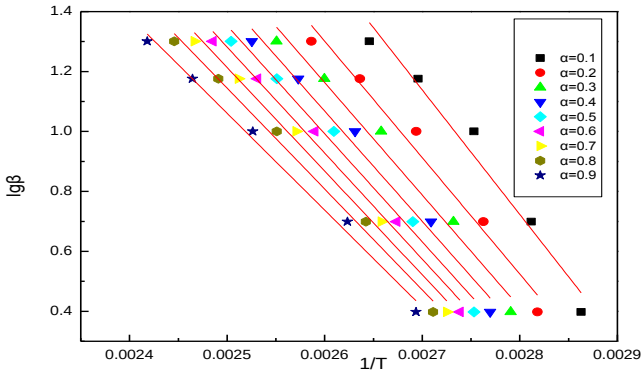

Figure 3. Relationship between $\lg\beta$ and $(1/T)$

Table 3. The values of E and A with the method of the F-W-O.

α	Intercept	Slope	R	E(kJ/mol)
0.1	12.35	4155.63	0.980	75.65
0.2	11.40	3884.86	0.986	70.72
0.3	10.92	3753.21	0.989	68.33
0.4	10.63	3677.23	0.991	66.94
0.5	10.37	3607.14	0.993	65.67
0.6	10.13	3539.35	0.994	64.43
0.7	9.86	3459.17	0.995	62.97
0.8	9.56	3367.33	0.995	61.30
0.9	9.14	3232.98	0.995	58.85

The E obtained by the F-W-O method were averaged to obtain that E_a=66.10kJ/mol.
The Table 4. shows the apparent activation energy in different methods.

Table 4. The values of E with the different methods.

Method	Kissinger	Friedman	F-W-O
E(kJ/mol)	65.23	52.20	66.10

3.5. Determination of curing reaction order.

The reaction order of the curing system can be obtained by the Crane equation.

$$\frac{d(\ln\beta)}{d\left(\frac{1}{T_p}\right)} = -\frac{E}{nR} \tag{4}$$

In equation (4), the physical meanings of β, E, T_p and R are the same as those of equation (1). Reaction order is n. Integrate the equation (4).

$$\ln\beta = -\frac{E}{nR} \times \frac{1}{T_p} + C \tag{5}$$

In equation (5), $\ln\beta$ is linearly related to $1/T_P$. The order of the reaction process is obtained from the slope of the line in Figure 4. According to the equation of Crane, the reaction order of the curing system is obtained by the three methods. The reaction order is shown below.
The calculated reaction order is not an integer, indicating that the curing reaction is a complex reaction [10].

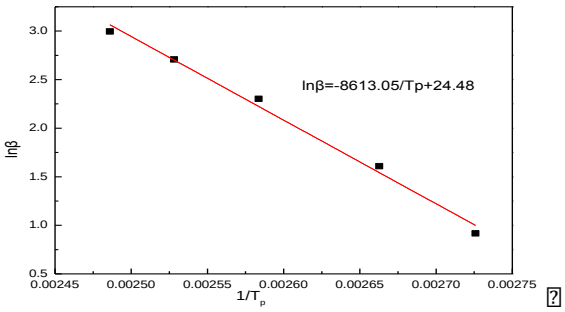

Figure 4. Relationship between $\ln \beta$ and $1/T_P$

Table 5. The values of n with the different methods.

Method	Kissinger	Friedman	F-W-O
n	0.911	0.729	0.923

4. Conclusion

The results show that with the increase of the heating rate, the exothermic peak gradually becomes steep, and the curing time is shortened. The initial temperature, peak temperature and termination temperature of the system are shifted to high temperature.

The curing kinetics of the system was studied by three kinds of analytical methods, and the kinetic apparent activation energy E and the reaction order n were obtained. The results show that the apparent activation energy E of the three methods is different, but it indicates that the system is a complex reaction.

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