Curing characteristics of bismaleimide/furan blends

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Abstract. The curing kinetics of the bismaleimide/furan blending system is studied by differential scanning calorimetry (DSC) under dynamic conditions. When the content of bismaleimide is 25wt%, the curing process parameters of the blending system are obtained by the extrapolation method of temperature-heat rate (T-β), that is, the gelation temperature, curing temperature and post-treatment temperature, thus providing a theoretical basis for the curing process of the system. The kinetic parameters of the system are calculated by using Kissinger equation and Crane equation, that is, apparent activation energy (Eѧ), apparent frequency factor (A) and reaction order (n), and then the curing kinetic model of the system is established according to the calculated kinetic parameters. The kinetic model is used to predict the curing reaction characteristics of the system under the same temperature and dynamic conditions.

1. Introduction

At present, the methods of studying the kinetic equation of resin matrix are Fourier transform infrared spectroscopy (FTIR), NMR method, dynamic rheology, dynamic mechanical analysis, differential scanning calorimetry (DSC) and so on[1-4]. Differential scanning calorimetry is the most commonly used method to study the dynamic equation of resin matrix.

Furan resin, because it comes from biomass energy[5,6], has the advantages of corrosion resistance and better compatibility with other resins[7-10], so it is one of the commonly used thermostetting resin matrix. However, due to its low heat resistance and carbon residue rate, furan resins are often modified to expand their application areas.

As a kind of high temperature resistant resin, bismaleimide resin has the advantages of stable aromatic ring, low water absorption rate and good dielectric properties, and is widely used in electronics and information departments, microelectronics packaging and aerospace[11-16]. However, the bismaleimide has the disadvantage of high processing temperature, and the blends of furan resin and bismaleimide resin can synthesize the advantages of the two, so as to obtain a better resin matrix with comprehensive performance.

At present, there are few studies on curing kinetics of modified furan resin by bismaleimide resin, so in this paper, DSC curves are obtained by heating the resin matrix at different rates, and curing kinetic parameters are obtained by using Kissinger and Crane equations, and a kinetic model is established to determine the curing process of the resin matrix.
2. Experiments

2.1 Materials
Resin: bismaleimide is produced by Wuhan Lanabai Pharmaceutical Co., Ltd., with an average molecular weight of 358.35; furan resin is produced by Shanxi Xingan Chemical Co., Ltd.; curing agent: p-toluene sulfonic acid (PTSA) is produced by Tianjin Kaitong Chemical Reagent Co., Ltd., The mass ratio of bismaleimide resin, furan resin and curing agent is 25:100:3 (denoted as 25%-BMI/FR system).

2.2 Experimental methods
Dsc-1 differential scanning calorimeter produced by mettler company in the United States is adopted to conduct heating scanning for the blend system of bismaleimide/furan resin. DSC test conditions: the scanning heating rate is 5, 10, 15, 20°C/min, the atmosphere is nitrogen, the amount of sample is 5-10mg, and the instrument is used indium for temperature and energy correction.

3. Results and Discussion

3.1 Determination of curing process parameters
The DSC curve of the 25%-BMI/FR system at different heating rates is shown in Figure 1, which is available from Figure 1, with the increase of heating rate, the beginning temperature (T_i), peak temperature (T_p), peak tail temperature (T_f) of the two exothermic peak increased, and the peak shape move to the high temperature area, this is because, on the one hand, heating rate increases, the dH/dt increased, the heating effect of the unit time increases, the greater the temperature difference, so the exothermic peak of the curing reaction is correspondingly move to high temperature area; On the other hand, the

![Figure 1 Dynamic DSC of 25%-BMI/FR system.](image-url)
increase of the heating rate makes the time taken by the system during curing decrease, which leads to the exothermic lag of the reaction and eventually causes the exothermic peak of the curing reaction of the system to shift to the right.

The beginning temperature (Tᵢ) of four different scanning heating rate β curing reaction exothermic, peak temperature (Tₚ) and peak tail temperature (Tᵢ) to the heating rate β mapping, and linear fitting, as shown in Figures 2 (a) and 2 (b), through the straight lines in Figures 2 (a) and 2 (b) to the β=0 on the coordinates of the points, and the data is shown in Table 1. It can be approximate: the gelation temperature (T₆) at low temperature is 37 °C; the curing temperature (T₉) is 59 °C; the post-treatment temperature (T₈) is 89 °C; the gelation temperature (T₆) at high temperature is 172 °C; the curing temperature (T₉) is 194 °C; and the post-treatment temperature (T₈) is 225 °C.
3.2 Determination of kinetic parameters of curing reaction

3.2.1 Determination of activation energy \( E_a \) and frequency factor \( A \)

The DSC curve data obtained from Figure 1 is shown in Table 2 and Table 3.

### Table 2 Dynamic DSC data of peak-1 of 25%-BMI/FR system.

| \( \beta/(K\cdot min^{-1}) \) | \( T_p/K \) | \( \ln(\beta/T_p^2) \) | \( \ln\beta \) | \( 1/T_p/(\times 10^{-3}K^{-1}) \) |
|-----------------|-----------|----------------|---------|----------------|
| 5               | 337.25    | -14.13         | -2.48   | 2.97           |
| 10              | 344.35    | -13.47         | -1.79   | 2.90           |
| 15              | 350.05    | -13.10         | -1.39   | 2.86           |
| 20              | 355.25    | -12.84         | -1.10   | 2.81           |

### Table 3 Dynamic DSC data of peak-2 of 25%-BMI/FR system.

| \( \beta/(K\cdot min^{-1}) \) | \( T_p/K \) | \( \ln(\beta/T_p^2) \) | \( \ln\beta \) | \( 1/T_p/(\times 10^{-3}K^{-1}) \) |
|-----------------|-----------|----------------|---------|----------------|
| 5               | 476.85    | -14.82         | -2.48   | 2.10           |
| 10              | 486.45    | -14.17         | -1.79   | 2.06           |
| 15              | 495.45    | -13.80         | -1.39   | 2.02           |
| 20              | 505.45    | -13.55         | -1.10   | 1.98           |

In this paper, the equation of Kissinger is used to analyze the non-isothermal DSC curves with different heating rates, so as to calculate the activation energy \( E_a \) and frequency factor \( A \) of the curing reaction. The equation of Kissinger assumes that the maximum rate of the curing reaction occurs at the peak temperature of the exothermic peak of the curing reaction, and the reaction order remains unchanged during the curing reaction.

The equation of Kissinger\(^{[17]} \) is as follows:

\[
\ln \frac{\beta}{T_p^2} = \ln \left[ \frac{AR}{E_a} \right] - \frac{E_a}{R} \frac{1}{T_p} \tag{1}
\]

Among them: \( \beta \) is the heating rate; \( T_p \) is peak temperature; \( E_a \) is for reaction activation energy; \( A \) is the frequency factor; \( R \) is the gas constant.

In Kissinger equation, the \( 1/T_p \) is plotted with \( -\ln(\beta/T_p^2) \) and the linear fitting is carried out, as shown in Figure 3, the linear regression coefficient at low temperature is 0.992, straight slope is 8218.98, intercept is -10.33, by a type of the \( E_a/R = 8218.98 \); \( -\ln(AR/E_a) = -10.33 \), it is possible to calculate that apparent activation energy \( (E_a) \) is 68.33 kJ·mol\(^{-1} \), and apparent frequency factor \( (A) \) is 2.52 x 10\(^8 \) min\(^{-1} \); the linear regression coefficient at high temperature is 0.977, the slope of the line is 10450.00, and the intercept is -7.23. According to the formula, \( E_a/R=10450.00 \); \( -\ln(AR/E_a) = -7.23 \), the apparent activation energy \( (E_a) \) of blends at high temperature is 86.88 kJ·mol\(^{-1} \), and apparent frequency factor \( (A) \) is 1.44 x 10\(^7 \) min\(^{-1} \).
3.2.2 Determination of Reaction order n

The reaction order of curing reaction can be obtained from Crane equation\cite{18}, which is:

\[
\frac{d \ln \beta}{d \left(1/T_p\right)} = -\frac{E_a}{nR} + 2T_p
\]  

(2)

When $E_a/nR > > 2T_p$, the equation is reduced to

\[
\frac{d \ln \beta}{d \left(1/T_p\right)} = -\frac{E_a}{nR}
\]  

(3)

The $1/T_p$ is plotted with $-\ln \beta$ and the linear fitting is carried out, the linear regression coefficient at low temperature is 0.993, and the reaction order (n) is 0.93 which can be obtained by linear slope 8788.32, the linear regression coefficient at high temperature is 0.980, and the reaction order (n) is 0.92 which can be obtained by the linear slope of 11350.00, as shown in Figure 4.

Through the above calculation, the kinetic parameters of curing reaction at low temperature of the 25%-BMI/FR system are $A=2.52\times10^8\text{min}^{-1}$, $E_a=68.33\text{kJ}\cdot\text{mol}^{-1}$, $n=0.93$, respectively, and the kinetic parameters of curing reaction at high temperature are $A=1.44\times10^7\text{min}^{-1}$, $E_a=86.88\text{kJ}\cdot\text{mol}^{-1}$, $n=0.92$, respectively.

Figure 3 Curves of $-\ln \left(\beta/T_p^2\right)$ vs $1/T_p$ for peak-1 and peak-2 of 25%-BMI/FR system

Figure 4 Curves of $-\ln \beta$ vs $1/T_p$ for peak-1 and peak-2 of 25%-BMI/FR system at low temperature.

3.2.3 Determination of curing reaction kinetics

From the above calculation, it is found that the curing reaction order of the resin system is within the $0.9\leq n\leq1.1$ range, so it satisfies the 1-stage kinetic equation at low temperature and high temperature:

\[
d\alpha/dt = k(1-\alpha)
\]  

(4)

Among them, $\alpha$ is the reaction curing degree, while the Arrhenius equation is
The 1-stage kinetic equation is obtained by substituting (4) of the formula (5):

\[ \frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right)(1-\alpha) \]  

The kinetic equations of curing reaction of low temperature and high temperature of the resin system are obtained by substituting the kinetic parameters of curing reaction at low temperature and high temperature, respectively:

\[ \frac{d\alpha}{dt} = 2.52 \times 10^8 \exp(-6.83 \times 10^4/RT) \]  
\[ \frac{d\alpha}{dt} = 1.44 \times 10^7 \exp(-8.68 \times 10^4/RT) \]

### 3.3 Predicting the curing reaction characteristics of the blends by using the kinetic equation

The curing reaction characteristics of the resin system can be further predicted by curing kinetic equation, and when a given curing degree is to be reached, the time required for curing reaction is the following relationship with the reaction temperature:

\[ t = \frac{-\ln(1-\alpha)}{Ae^{x_p\left(-\frac{E_a}{RT}\right)}} \]  

**Figure.5 (a) Curves of time vs temperature for peak-1 of 25%-BMI/FR system.**

**Figure.5 (b) Curves of time vs temperature for peak-2 of 25%-BMI/FR system.**

The prediction diagram of the time-temperature of the blends under different curing degrees can be obtained by using different curing degrees, respectively, as shown in Figure 5. As can be seen from Figure 5 (a) and 5 (b) for resin curing reaction, there are two ways to achieve a certain curing degree: to prolong the reaction time at low temperature, and to increase the reaction temperature.

Also using the kinetic equation, the curing degree and curing reaction time can be deduced under different constant temperature conditions to meet the following formula:

\[ \alpha = 1 - \exp\left[-Ae^{x_p\left(-\frac{E_a}{RT}\right)}\right] \]  

At different constant temperature points, the relationship between curing degree and curing time is shown in Figure 6 (a) and 6 (b), it is obvious that the higher the constant temperature point, the shorter...
the curing time required to reach a certain curing degree.

![Figure 6a](image_url)

**Figure 6 (a)** Curves of $\alpha$ vs time for peak-1 of 25%-BMI/FR system.

![Figure 6b](image_url)

**Figure 6 (b)** Curves of $\alpha$ vs time for peak-2 of 25%-BMI/FR system.

Under the condition of non-constant temperature, the factors affecting the curing degree of resin curing reaction

![Figure 7a](image_url)

**Figure 7 (a)** Curves of $\alpha$ vs temperature for peak-1 of 25%-BMI/FR system.
are not only the reaction time and temperature, but also the rate of temperature rise.

After integrating the kinetic equation, the relationship between curing degree and curing temperature at different heating rates can be obtained:

\[ \alpha = 1 - \exp \left( - \frac{\frac{E_a}{R} \exp(\frac{-E_a}{RT})}{\beta} \right) \]  

(11)

According to equation (11), the curing degree-temperature relationship of the blends at different heating rates is drawn, as shown in Figure 7. As can be seen from Figure 7 (a) and 7 (b), when curing reaction occurs in the blends, the same degree of curing is achieved, and higher temperature is required for the resin that heats up faster than the resin that heats up slower.

Similarly, after integrating the kinetic equation, the relationship between curing degree and curing reaction time at different heating rates can be obtained:

\[ \alpha = 1 - \exp \left( -A_t \exp \left[ \frac{-E_a}{R(T_0 + \beta t)} \right] \right) \]  

(12)

According to Formula (12), the curing degree-time diagram at different heating rates is plotted, as shown in

Figure 8 (a) Curves of \( \alpha \) vs time for peak-1 of peak-1 of 25%-BMI/FR system.
Figure 8 (b) Curves of α vs time for peak-2 of 25%-BMI/FR system at high temperature.
Figure 8 (a) and 8 (b). The same curing degree can be achieved when the resin system is cured by Figure 8, and it takes longer to heat up faster than the heating rate.

4. Conclusions

(1) Differential scanning calorimetry is used to determine the dynamic DSC curve of the bismaleimide/furan blends. Three kinetic parameters of the resin of peak-1 and peak-2 are obtained by T-β figure extrapolation method: the gelation temperature (T_{gel}) at low temperature is 37 °C; cure temperature (T_{cure}) is 59 °C; post-treatment temperature (T_{treat}) is 89 °C; the gelation temperature (T_{gel}) at high temperature is 172 °C; cure temperature (T_{cure}) is 194 °C; post-treatment temperature (T_{treat}) is 225 °C.

(2) The kinetic parameters of the curing reaction of the blends are calculated by using the Kissinger equation and the Crane equation, and the apparent frequency factor (A) is 2.52×10^8 min^{-1}, the apparent activation energy (E_a) is 68.33kJ·mol^{-1}, and the reaction order (n) is 0.93 are obtained at low temperature, the kinetic parameters of curing reaction at high temperature are obtained, which apparent frequency factor (A) is 1.44×10^7 min^{-1}, apparent activation energy (E_a) is 86.88kJ·mol^{-1}, reaction order (n) is 0.92.

(3) The curing characteristics of the resin are predicted by using the established curing kinetics model \frac{d\alpha}{dt}=2.52×10^8 \exp(-6.83×10^4/RT)(1-\alpha) (low temperature) and \frac{d\alpha}{dt}=1.44×10^7 \exp(-8.68×10^4/RT)(1-\alpha) (high temperature), which providing a theoretical reference for optimizing process parameters.

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