Study on the curing behavior of polythiol/phenolic/epoxy resin and the mechanical and thermal properties of the composites

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Keywords: thermal performance, phenolic resin, epoxy resin, uniform experiment, curing kinetics, mechanical properties

Abstract
Phenolic/epoxy resin (EP-PF) composites were prepared, in which phenolic resin and epoxy resin was used as matrix, polythiol and triethanolamine as curing accelerators. The uniform experimental design method was used to obtain the scheme, in which the resin system had minimum curing temperature. The curing kinetics and the apparent activation energy of the resin system were studied and calculated by the differential scanning calorimetry., and the mechanical and thermal properties of the composite was analyzed. The results show that when the content of polythiol was 12% and the content of triethanolamine was 11%, the peak curing temperature of the resin system was 118 °C, which was lower than the phenolic resin or phenolic/epoxy resin. Tg dropped from 212 °C of EPF to 157 °C of EPF and then to 147 °C of EPF-B. The thermal decomposition temperature and residual carbon rate also showed a slight downward trend, but the mechanical properties were greatly improved. The strength and flexural modulus of EPF-B have increased from 291.4 MPa and 11.2 GPa of EPF to 440 MPa and 12.3 GPa, an increase of 49% and 27%. This research provides a theoretical basis for broadening the application range of phenolic resin and epoxy resin blending system.

1. Introduction
In recent years, polymer matrix composites have made many breakthroughs in mechanical properties, heat resistance, and electrical properties [1, 2]. The choice of resin matrix is particularly important. Phenolic resin itself has good flame retardant properties, lower smoke rate, and less harmful gases [3–5]. However, the curing of traditional phenolic resin requires a higher temperature and a slower rate. The use of strong acid/alkali catalysts can cause corrosion of the device, and it is easy to release small molecules such as amines during curing, which will cause the internal or surface of the product [6–8]. Nowadays, the requirements for various indicators of phenolic resin are getting higher and higher. In order to expand its application range and meet the needs of civilian and military industries, it is necessary to modify phenolic resin [9]. Epoxy resin is an excellent polymer matrix with excellent processing and mechanical properties [10, 11]. Therefore, the blending system of phenolic resin and epoxy resin not only has the heat-resistant and flame-retardant properties of phenolic resin, but also retains the excellent mechanical properties of epoxy resin [12, 13]. Moreover, the problem of easy foaming of phenolic resin is also improved in the process [14–16]. However, a single phenolic resin and epoxy resin blending modification method still cannot meet the requirements of practical applications [13]. The phenolic-epoxy blend system still has the problems of high curing temperature and slow curing rate. Most of the reports focus on the modification of toughening and flame retardant properties of the phenolic-epoxy resin system. Deng P used a new type of phosphorus-containing phenolic resin to cure epoxy resin, and studied the curing process and the corresponding crosslinking structure and mechanical properties through differential scanning calorimeter and dynamic mechanical thermal analysis [17]. S Yue and J.-C. Munoz and others studied epoxy resin modified phenolic resin [18, 19]. Reducing the curing temperature will bring great convenience in process...
production and also save energy [20]. Therefore, how to reduce the curing temperature of the blend system is an inevitable problem in the rapid prototyping process research process [21]. The research work of S Han showed that in the same epoxy phenolic curing system, when different curing accelerators are used, the curing process presents different curing reaction mechanisms [22]. S Han studied the effect of the amount of curing accelerator on the curing of epoxy-phenolic resin system [23]. As a common epoxy resin curing agent at room temperature, Polythiol is not only low in price, but also can effectively reduce the activation energy required for epoxy resin ring opening, thereby reducing the curing temperature, and the introduction of a large number of flexible segments can also achieve the effect of toughening the resin system [24–26]. Modification of the phenolic-epoxy blend resin system is a necessary means to improve the process and the comprehensive performance of composite materials.

In this paper, phenolic resin and epoxy resin (EP-PF) are used as the resin matrix, Polythiol and Triethanolamine are used as curing accelerators to prepare EP-PF composite materials. The curing kinetics of the composite was studied by the differential scanning calorimetry (DSC), and the apparent activation energy was calculated by the Kissinger method and the Ozawa method. Furthermore, the thermal and mechanical properties of the composites under different proportions of curing accelerators were studied [27, 28]. Studying the effect of curing accelerator on the curing process of epoxy-phenolic resin system and the effect of cured product performance has important guiding significance for optimizing the process characteristics and material properties of epoxy-phenolic resin system [29–31].

2. Experimental

2.1. Materials

Bisphenol A epoxy resin (E-51), epoxy value (e.g./100 g) is 0.48 ~ 0.51, Baling Branch of China Petroleum & Chemical Corporation; Paracetamol resin, Hubei Aerospace Sanjiang Hongyang Electromechanical Co., Ltd; Polythiol, Shenzhen Huite Chemical Co., Ltd; Triethanolamine, analytical grade, Sinopharm Group Chemical Reagent Co., Ltd

2.2. Uniform test plan design

The three factors set in this experiment are the mass ratio of phenolic resin to epoxy resin, the mass ratio of polythiol to epoxy resin, and the mass ratio of triethanolamine to epoxy resin. The peak temperature $T_p$ measured by DSC is used as the evaluation. Select the appropriate level range to design a three-factor seven-level uniform test plan, and choose $U_7(7^4)$ uniform design table as shown in table 1 [32–34].

2.3. Preparation of fast-curing phenolic epoxy resin composite

Blend phenolic resin, epoxy resin, polythiol and triethanolamine according to the proportions in table 2 and mix them to form a low-viscosity resin mixture. Brush them evenly on the cut glass fiber cloth, so that it will be saturated. After the glass fiber cloths were placed at room temperature for 3–4 days, they were stacked and placed

| Group | PF | E-51 | Polythiol | Triethanolamine |
|-------|----|------|-----------|-----------------|
| PF    | 1  | 0    | 0         | 0               |
| EPF   | 1  | 1    | 0         | 0               |
| EPF-B | 1  | 1    | 0.12      | 0.11            |

Table 1. $U_7(7^4)$ Uniform design table.

| Test number | 1 | 2 | 3 | 4 |
|-------------|---|---|---|---|
| 1           | 1 | 2 | 3 | 6 |
| 2           | 2 | 4 | 6 | 5 |
| 3           | 3 | 6 | 2 | 4 |
| 4           | 4 | 1 | 5 | 3 |
| 5           | 5 | 3 | 1 | 2 |
| 6           | 6 | 5 | 4 | 1 |
| 7           | 7 | 7 | 7 | 7 |
in a hot press for compression molding. Curing process were PF: 80 °C, 150 °C/2 h; EPF: 80 °C h⁻¹, 150 °C/4 h; EPF-B: 80 °C h⁻¹, 130 °C/4 h.

### 2.4. Characterization

**Differential Scanning Calorimetry (DSC):** The curing reaction peak temperature $T_p$ and curing reaction kinetics of the blend system are carried out by a DSC4000 differential scanning calorimeter. Test conditions: the temperature range is 30 °C–250 °C; the heating rates are 5 °C min⁻¹, 10 °C min⁻¹, 15 °C min⁻¹, 20 °C min⁻¹; nitrogen atmosphere.

**Thermogravimetric analysis (TGA):** The test instrument is the STA449F3 synchronous thermal analyzer from NETZSCH from Germany. Test conditions: temperature range is 30 °C–800 °C; heating rate is 10 °C min⁻¹; nitrogen atmosphere.

**Dynamic thermomechanical analysis (DMA):** The glass transition temperature $T_g$ of the sample is analyzed by the Pyris Diamond DMA dynamic thermomechanical analyzer. Test conditions: the temperature range is 30 °C–300 °C; the heating rate is 5 °C min⁻¹; and the fixed frequency is 1 Hz. The sample size is: 60 mm × 10 mm × 3 mm.

**Mechanical performance test:** The flexural modulus and strength of samples were tested by CSS-44300 electronic testing machine according to the standard of GB/T 2567–2008. The tensile strength and elastic

### Table 3. Uniform test plan and results.

| Test number | Phenolic Resin | Polythiol | Triethanolamine | $T_p$ |
|-------------|----------------|-----------|-----------------|-------|
| 1           | 1 (10)         | 2 (0.2, 2%) | 3 (0.4, 4%)     | 122.97|
| 2           | 2 (20)         | 4 (0.6, 6%) | 6 (1.0, 10%)    | 121.13|
| 3           | 3 (30)         | 6 (1.0, 10%) | 2 (0.2, 2%)     | 124.94|
| 4           | 4 (40)         | 1 (0.0, 0%) | 5 (0.8, 8%)     | 134.20|
| 5           | 5 (50)         | 3 (0.4, 4%) | 1 (0.0, 0%)     | 141.53|
| 6           | 6 (60)         | 5 (0.8, 8%) | 4 (0.6, 6%)     | 130.48|
| 7           | 7 (70)         | 7 (1.5, 15%) | 7 (1.5, 15%)    | 127.74|

### Table 4. Model summary.

| Model | R    | $R^2$ | Adjusted $R^2$ | Standard skewness error | $R^2$ change | F value change | $d_1$ | $d_2$ | Significant F value change |
|-------|------|-------|----------------|-------------------------|--------------|---------------|--------|--------|----------------------------|
| 1     | 0.723| 0.523 | 0.489          | 6.68654                 | 0.523        | 15.346        | 1      | 14     | 0.002                      |
| 2     | 0.798| 0.637 | 0.581          | 6.21505                 | 0.114        | 4.099         | 1      | 13     | 0.064                      |
| 3     | 0.911| 0.830 | 0.788          | 4.42460                 | 0.193        | 13.650        | 1      | 12     | 0.003                      |
| 4     | 0.958| 0.919 | 0.889          | 3.20000                 | 0.088        | 11.942        | 1      | 11     | 0.005                      |

### Table 5. Partial regression coefficient and its significance test.

| Model | B        | Standard error | Standardization factor | T      | Significance |
|-------|----------|----------------|------------------------|--------|--------------|
| 1     | (Constant) | 139.994 | 2.343 | -0.723 | 59.743 | 0.000 |
|       | $x_1$    | -15.142 | 3.865 | -3.917 | 0.002 |
| 2     | (Constant) | 142.844 | 2.545 | -0.715 | 56.125 | 0.000 |
|       | $x_2$    | -14.968 | 3.499 | -4.278 | 0.001 |
|       | $x_2$    | -7.083 | 3.499 | -2.025 | 0.064 |
| 3     | (Constant) | 145.779 | 1.978 | -1.241 | 73.686 | 0.000 |
|       | $x_3$    | -25.976 | 3.883 | -6.689 | 0.000 |
|       | $x_2$    | -13.354 | 3.014 | -4.431 | 0.001 |
|       | $x_1x_3$ | 0.326  | 0.088 | 3.695  | 0.003 |
| 4     | (Constant) | 147.630 | 1.528 | -2.248 | 96.631 | 0.000 |
|       | $x_3$    | -47.065 | 6.718 | -7.006 | 0.000 |
|       | $x_2$    | -14.126 | 2.191 | -6.447 | 0.000 |
|       | $x_1x_3$ | 0.306  | 0.064 | 4.787  | 0.001 |
|       | $x_3x_3$ | 20.179 | 5.839 | 3.456  | 0.005 |
Figure 1. DSC curves at different heating rates.

Figure 2. Characteristic temperature linear fitting result.

Figure 3. Characteristic temperature linear fitting result.
modulus of samples were tested by CMT6104 mechanical performance testing machine according to the standard of GB/T 1446–2005.

3. Results and discussion

3.1. Uniform test

3.1.1. Test plan design and result analysis

According to the U7(7^4) uniform design table, the fixed epoxy resin is 10 g, and the test plan shown in table 3 can be obtained. After the resin is prepared, the DSC test is performed, and the test result T_p is recorded in the last column of the following table.

Regression analysis was performed based on the results of the above-mentioned test scheme [35], and the results obtained are shown in tables 4–6.

Four regression equation models can be obtained through stepwise regression analysis. The closer the model R^2 is to 1, the higher the credibility of the model. From table 4, it can be seen that the R^2 of Model 4 is the closest to 1. Therefore, model 4 is selected as the fitting reference model, and the regression equation of model 4 is as follows:

\[ y = 147.630 - 47.065x_3 - 14.126x_2 + 0.306x_1x_3 + 20.179x_1^2 \]

It can be seen from the regression equation that within the test range, when x_2 takes the maximum value and x_1 takes the minimum value, y has the minimum value. That is x_1 = 10 and x_2 = 1.2. The partial derivative of the regression equation can be obtained when x_3 = 1.09, and the optimal conditions are x_1 = 10, x_2 = 1.2, x_3 = 1.1. The optimized formula is: Phenolic resin 10 g, polythiol 1.2 g, and triethanolamine 1.1 g. According to the residual statistics in table 6, the minimum predicted value of the regression equation is 118.3942, which is less than the T_p value of either the uniform test or the single factor test.

3.1.2. Optimal scheme test verification

According to the preferred solution (10 g Phenolic resin, 10 g Epoxy resin, 1.2 g Polythiol, 1.1 g Triethanolamine), after preparing the resin, perform non-isothermal DSC test with heating rate of 5 °C min^{-1}, 10 °C min^{-1}, 15 °C min^{-1}, 20 °C min^{-1} respectively. The test result is shown in figure 1.
Figure 5. Linear fitting results of $\ln(\beta) \sim T^{-1}$.

Figure 6. Fitting results of Crane equation.

Table 7. Characteristic temperature at different heating rates. By linear fitting of each characteristic temperature in Table 7 to the heating rate, the relationship curve between each characteristic temperature and the heating rate can be obtained, as shown in Figure 2. The temperature when the heating rate is $\beta = 0$ is extrapolated to the characteristic temperature of curing. It can be seen that the peak characteristic temperature $T_p = 118.24 \, ^\circ C$, which is close to the minimum value predicted by the regression equation of 118.3942, indicating that the regression equation has a high degree of fit and good predictability for different heating rates.

| $\beta$ (°C min$^{-1}$) | $T_i$ (°C) | $T_p$ (°C) | $T_f$ (°C) |
|--------------------------|-----------|-----------|-----------|
| 5                        | 97.41     | 126.09    | 145.27    |
| 10                       | 112.16    | 139.25    | 158.82    |
| 15                       | 117.99    | 145.37    | 163.26    |
| 20                       | 128.37    | 154.95    | 173.37    |
Figure 7. Isothermal DSC curves at different temperatures and the relationship between curing reaction rate and time.

Figure 8. The relationship between curing reaction rate and curing degree.

Table 8. Kinetic models and equations of calculation parameters

| Model/Equation               | Formula                                                                 | Kinetic parameters |
|------------------------------|-------------------------------------------------------------------------|--------------------|
| n-order model                | $F(n) = \frac{d\alpha}{dt} = A_0(1 - \alpha)^n \exp \left( \frac{-E_a}{RT} \right)$ | $A_0, E_a, n$      |
| Kamal model                  | $F(k) = \frac{d\alpha}{dt} = (k_1 + k_2\alpha^n)(1 - \alpha)^n$         | $k_1, k_2, m, n$   |
| Kissinger equation           | $\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left( \frac{\beta}{T_p^2} \right) - \frac{E_a}{R}$ | $A_0, E_a$         |
| Flynn-Wall-Ozawa equation    | $\ln \beta = \ln \frac{A_0}{G_0}\frac{E_a}{R} - 2.315 - 0.456\frac{E_a}{R}$ | $E_a$              |
| Crane equation               | $\frac{dn}{\Delta T_p^2} = \left( \frac{k}{\Delta T_p^2} \right)$ $2T_p^2$ | $n$                |

Table 9. Apparent activation energy at different reaction levels.

| $\alpha$ | 10% | 20% | 30% | 40% | 50% | 60% | 70% | 80% | 90% |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $E_a$    | 46.27 | 50.80 | 53.76 | 55.27 | 59.66 | 61.05 | 63.57 | 65.48 | 67.02 |
| $\Delta T_p$ | 58.10 |       |       |       |       |       |       |       |     |
Figure 9. Under different constant temperature conditions, curing rate ($\frac{d\alpha}{dt}$)-curing degree ($\alpha$) curve nonlinear fitting.

Figure 10. Tan $\delta$ (a) and $E'$ (b) curves of the composites.

Table 10. Kamal equation fitting results under different constant temperature conditions.

| T/°C | Kamal equation | $R^2$ |
|------|----------------|-------|
| 100  | $F(k) = \frac{d\alpha}{dt} = (-0.00888 + 0.09883x^{0.18305})(1 - x)^{0.7914}$ | 0.99228 |
| 105  | $F(k) = \frac{d\alpha}{dt} = (0.01797 + 0.12197x^{0.3206})(1 - x)^{0.85482}$ | 0.99975 |
| 110  | $F(k) = \frac{d\alpha}{dt} = (0.01975 + 0.17251x^{0.27974})(1 - x)^{0.92919}$ | 0.99969 |
| 115  | $F(k) = \frac{d\alpha}{dt} = (-0.00727 + 0.30351x^{0.29739})(1 - x)^{0.92983}$ | 0.99921 |

$k_1 = 0.00539, k_2 = 0.17421, m = 0.25603, n = 0.88902$
According to table 2, the non-isothermal DSC test was performed at a heating rate of 10 degrees/min. And the results are shown in figure 3. We can see that the curing exothermic peak shifts to the left, which means that with the addition of epoxy resin and polythiol, the curing reaction temperature shows a downward trend. The curing reaction temperature of EPF-B is much lower than that of EPF and PF.

3.2. Curing kinetics of optimal scheme
It is a common analysis method to use DSC data to derive the curing kinetic parameters. Assuming that the curing process conforms to one dynamic model by using the model fitting method, then the kinetic parameters can be obtained. Different kinetic parameters are mainly based on the Kissinger equation to calculate the reaction activation energy and pre-exponential factor of the resin system, the Flynn-Wall-Ozawa equation to calculate the apparent activation energy of different reaction degrees, and the Crane equation to calculate the curing reaction order \( n \) \[36, 37\]. The main kinetic models and equations of calculation parameters are shown in table 8.

3.2.1. Kinetic analysis of non-isothermal curing
As is shown in figure 4, \( \ln(\beta/T_p^2) \sim 1/T_p \) is used to plot a linear fit. The result of the linear fitting is:
\[ y = 8.680 - 7.594x \]
\[ E_a = 63.14 \text{ KJ mol}^{-1}, A_0 = 4.468 \times 10^7/\text{s} \]
can be calculated by Kissinger equation. The addition of Polythiol and Triethanolamine reduces the activation energy of the epoxy resin. The simultaneous presence of thiol groups and tertiary amines makes it easier to open the epoxy ring, thereby reducing the overall activation energy of the resin system.

In the Flynn-Wall-Ozawa formula in table 9, since \( G(\alpha) \) is a function of the curing reaction degree \( \alpha \), even at different heating rates, when the curing reaction degree \( \alpha \) is the same, the corresponding \( G(\alpha) \) value is also equal \[38\]. Plot \( \ln(\beta) \) versus \( 1/T \), as is shown in figure 5. According to the Flynn-Wall-Ozawa equation, the slope of the fitted curve is the apparent activation energy

Comparing the activation energy obtained by the two methods, the apparent activation energy obtained by the Kissinger method is slightly higher than that of the Flynn-Wall-Ozawa method, but there is not much difference between the two values. It can be considered that the value is reliable. Calculate the average of the two as the final apparent activation energy, \( E_a = 60.62 \text{ KJ mol}^{-1} \).

The reaction order can be calculated by the Crane equation, in which \( T_p \) is much smaller than \( E/nR \), so \( 2T_p \) is ignored in the analysis and fitting \[39\], and the curve shown in figure 6 is obtained by linear fitting \( \ln(\beta) \) to \( 1/T_p \). According to figure 6, the fitting equation is \( y = 22.74-8.43x \), and the reaction order \( n = 0.904 \) can be calculated by Crane equation.

| Sample | \( T_g/°C \) | \( E/30 °C/GPa \) |
|--------|-------------|-----------------|
| PF     | 212         | 34.7            |
| EPF    | 157         | 31.2            |
| EPF-B  | 145         | 12.2            |

According to table 2, the non-isothermal DSC test was performed at a heating rate of 10 degrees/min. And the results are shown in figure 3. We can see that the curing exothermic peak shifts to the left, which means that with the addition of epoxy resin and polythiol, the curing reaction temperature shows a downward trend. The curing reaction temperature of EPF-B is much lower than that of EPF and PF.
also played a role in toughening, making the storage modulus gradually decrease. By comparison, it can be found that toughening agent. Their addition makes a large number of flexible segments connected to increase the chain length, which increases the relative molecular weight between the cross-linking points to reduce the cross-link density. This lowers the glass transition temperature. The introduction of a large number of flexible segments also played a role in toughening, making the storage modulus gradually decrease. By comparison, it can be found that toughening agent. Their addition makes a large number of flexible segments connected to increase the chain length, which increases the relative molecular weight between the cross-linking points to reduce the cross-link density. This lowers the glass transition temperature. The introduction of a large number of flexible segments also played a role in toughening, making the storage modulus gradually decrease. By comparison, it can be found that toughening agent. Their addition makes a large number of flexible segments connected to increase the chain length, which increases the relative molecular weight between the cross-linking points to reduce the cross-link density. This lowers the glass transition temperature. The introduction of a large number of flexible segments also played a role in toughening, making the storage modulus gradually decrease. By comparison, it can be found that toughening agent. Their addition makes a large number of flexible segments connected to increase the chain length, which increases the relative molecular weight between the cross-linking points to reduce the cross-link density. This lowers the glass transition temperature. The introduction of a large number of flexible segments also played a role in toughening, making the storage modulus gradually decrease. By comparison, it can be found that toughening agent. Their addition makes a large number of flexible segments connected to increase the chain length, which increases the relative molecular weight between the cross-linking points to reduce the cross-link density. This lowers the glass transition temperature. The introduction of a large number of flexible segments also played a role in toughening, making the storage modulus gradually decrease. By comparison, it can be found that toughening agent. Their addition makes a large number of flexible segments connected to increase the chain length, which increases the relative molecular weight between the cross-linking points to reduce the cross-link density. This lowers the glass transition temperature. The introduction of a large number of flexible segments also played a role in toughening, making the storage modulus gradually decrease.
that the addition of a small amount of polythiol will slightly reduce the glass transition temperature, but it can greatly reduce the modulus to achieve a toughening effect.

3.4. Thermal stability

The following figure 11 shows the TG and DTG curves of the cured resin. When the weight loss rate is 5%, the temperature point is the initial thermal decomposition temperature (T5%). The peak temperature of the DTG curve is the temperature (Tmax) at the maximum weight loss rate, and the maximum weight loss rate (Rmax) is at 800 °C. The mass retention rate is regarded as the residual carbon rate (CY). All data are listed in table 12.

The DTG curve of all resin cured products has only one peak, that is, there is only one weight loss stage. From the above table, we can see that with the addition of epoxy resin, polythiol and triethanolamine, the T5%, Tmax, Rmax and CY of the cured resin decreased slightly. But they basically maintained high ablation resistance and residual carbon rate. This phenomenon is due to the fact that the addition of epoxy resin and polythiol introduces a large number of flexible segments. Compared with the more benzene ring structure in phenolic resin, the thermal stability is poor, which makes T5% show a significant downward trend. The addition of amine curing accelerator will make the phenolic resin and epoxy resin crosslink more completely, so that the Tmax and Rmax of the cured product of EPF-B component are not much different from EPF. Phenolic resin will gradually be carbonized into residues at high temperatures. The higher the content of phenolic resin, the higher the residual carbon rate of the cured product. Therefore, with the addition of other components, the residual carbon rate will gradually decrease.

3.5. Mechanical properties of the composite

The flexural strength, flexural modulus, tensile strength and elastic modulus of composite materials are shown in table 13. Compared with PF, composite materials of EPF component has increased flexural strength, flexural modulus, tensile strength, and elastic modulus by 61%, 99%, 28% and 19% respectively. The addition of epoxy resin can appropriately increase the cross-linking density of the cross-linking system to make the internal connection of the cured product closer, thereby improving the mechanical properties of the composite materials. Compared with EPF, composite material of EPF-B component has increased flexural strength and flexural modulus by 49% and 27% respectively. And the tensile strength and elastic modulus are slightly reduced but still higher than composite material of PF component. Since the addition of polythiol will introduce a large amount of flexible chain structure, it is equivalent to adding a toughening agent. This will greatly increase the flexural strength and flexural modulus of the composite material. The addition of tougheners tends to decrease the tensile strength and elastic modulus.

4. Conclusions

Design a suitable uniform test plan to test, and perform stepwise regression analysis on the results to get the regression equation as:

\[ y = 147.630 - 47.065x_3 - 14.126x_2 + 0.306x_3x_3 + 20.179x_2x_3 \]

The optimal solution EPF-B can be obtained through the regression equation as x1 (phenolic resin) = 10 g, x2 (Polythiol) = 1.2 g, x3 (Triethanolamine) = 1.1 g. The minimum value of statistical prediction is 118.3924, and the test value of verification test 118.24 is close to the statistical forecast value. The apparent activation energy obtained by the Kissinger method and the Flynn-Wall-Ozawa method were 63.137 KJ mol⁻¹ and 58.10 KJ mol⁻¹, respectively. Take their average value as E_a. The pre-referential factor A_0 is 4.468 × 10⁷/s, and the reaction order n is 0.904. The curing kinetic equation is obtained as follows:

\[ \frac{d\alpha}{dt} = 4.468 \times 10^7 \left(1 - \alpha \right)^{0.904} \exp \left( \frac{-7.621 \times 10^3}{T} \right) \]

The Kamal autocatalytic model kinetic equation is obtained by calculating the average value of the model parameters at different temperatures, which is as follows:

\[ F(k) = \frac{d\alpha}{dt} = (0.00539 + 0.17421x^{0.25603})(1 - x)^{0.88902} \]

DMA research shows that T_g dropped from 212 °C of PF to 157 °C of EPF and then to 147 °C of EPF-B. The thermal decomposition temperature and residual carbon rate also showed a slight downward trend. The mechanical properties were greatly improved. The strength and flexural modulus of EPF-B have increased from 291.4 MPa and 11.2 GPa of EPF to 440 MPa and 12.3 GPa, an increase of 49% and 27%. The tensile strength and elastic modulus are also greatly improved compared to PF. The curing system obtained by uniform experimental
design solves the problem of high curing temperature and slow curing speed. At the same time, through this curing method, a cured product with excellent thermal and mechanical properties is obtained.

Acknowledgments

Financial supports from the National Natural Science Foundation of China (Grant Nos. 51672201 and 51373129) are gratefully acknowledged.

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