Zhenjiang Song*, Jianliang Xie, Peiheng Zhou, Jianing Peng, Xin Wang and Longjiang Deng

Thermal degradation of epoxy resin grafted with polyurethane

Abstract: Epoxy resin grafted with polyurethane was synthesized and characterized through a series of tests. The grafting reactive process between the pendant secondary hydroxyl groups on the side chains of epoxy resin and the isocyanate groups of pre-polyurethane were investigated by Fourier transform infrared spectroscopy. Thermal behavior of the grafted epoxy resin was investigated by thermogravimetric analysis within 40–500°C. The degradation of grafted epoxy resin involved two stages. Microstructures of the polyurethane section and grafted epoxy resin were observed by field emission scanning electron microscopy. Model fitting method was employed to calculate the thermal degradation model of grafted epoxy resin. In this paper, 15 typical kinetic mechanisms were introduced into the model fitting method, such as Coats-Redfern method and Achar-Brindley-Sharp-Wendworth method, to obtain the kinetic function of thermal degradation for grafted epoxy resin.

Keywords: grafted epoxy resin; kinetic function; polyurethane, thermal degradation.

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1 Introduction

Epoxy resin has excellent performance properties like size stability, creep and corrosion resistance, electrical insulation and high strength, which are considered to be useful in various fields of protective coatings, adhesives, electrical laminates and other engineering applications [1]. Among various epoxy resins, the diglycidyl ether of bisphenol A (DGEBA, shown in Scheme 1) is one of the most important. Generally, curing agents (also known as hardeners) are necessary for epoxy resin application. However, cured epoxy resin will form three-dimensional insoluble networks. On the one hand, these high-cross-linking structures endow their excellent properties; on the other hand, the cured epoxy resin will suffer from problems of rigidity and brittleness [2]. These epoxy materials have fracture energies some two orders of magnitude lower than those of common engineering thermoplastics [3]. Therefore, in order to alleviate these problems, tremendous work has been undertaken to enhance their toughness [4–8].

Among the methods of toughening, toughening of epoxy resin using polyurethane, like interpenetrating polymer network (IPN) structures, attracted intensive interest in both academia and industry because they facilitate processing and impart toughness [9, 10]. Baidak et al. used epoxy resin and acrylic resin to prepare IPN structures, and metastable phase diagrams were drawn for explaining phase separation [11]. Harani et al. have synthesized grafted epoxy resin with high impact strength at 22 J m⁻¹ [12]. Hsieh et al. have prepared a series of graft IPNs with excellent mechanical properties [13–17]. In this work, we synthesized polyurethane prepolymer first. Then isocyanate-terminated polyurethane was introduced into epoxy resin to form the grafted polymer structure. Generally, thermogravimetric analysis (TGA) was performed to estimate the initial degradation temperature and the apparent activation energies of degradation [18–21], especially the degradation kinetics. Abate et al. studied the degradation kinetic parameters of polymers containing ether, ketone and sulfone groups systematically by isothermal degradation experiments [22, 23]. There have been some research studies on thermal degradation of polyurethane, polyurethane nanohybrid elastomer [24, 25]. In this study, we investigated the thermal stability of the grafted epoxy resin and used a model fitting method to determine the kinetic function for thermal degradation.

2 Experimental

2.1 Grafted epoxy resin synthesis

First, the prepolymer was prepared with toluene diisocyanate (TDI) (purchased from Reagent No. 1 Factory,
Shanghai, China) and polyester (molecular weight: 1000, Pudong Gaonan Chemical Factory, Shanghai, China) according to a detailed previously described method [26]. Second, high-molecular-weight solid DGEBA (E03, with an epoxy equivalent weight of 2000–5000 g, obtained from Bluestar New Chemical Materials Co., Ltd, China) was dissolved into a mixture of butanone and cyclohexanone (purchased from the Kelong Reagent Factory, Chengdu, China). Then the prepared prepolymer was mixed with E03 based on stoichiometric ratio. This solution was stirred vigorously for about 10 min and then poured into a mold, which was put into a vacuum drying oven for the evaporation of solvent under room temperature. After 24 h of evaporation, the grafted epoxy resin was obtained.

2.2 Test methods

Fourier transform infrared (FTIR) spectra were observed with a Bruker Tensor 27 instrument (Bruker Optics, Inc., Germany) at transmission mode in the spectral range from 4000 to 400 cm⁻¹. The KBr powder was compressed into a disk pellet with a diameter of 13 mm. After the liquid mixture was stirred completely, a drop was placed directly on the pellet.

The thermal degradation behavior was analyzed with Mettler Star SW software (Mettler Toledo, Inc., Greifensee, Switzerland). Samples of 10–15 mg were introduced into an aluminum crucible with a lid at 40°C–500°C with nitrogen as protection gas (22 ml min⁻¹). Under non-isothermal conditions, the relationship \( T = T_0 + \beta t \) holds. The heating rate \( \beta \) (K min⁻¹) is defined by the equation \( \beta = dT/dt \). The reaction rate can be rewritten as:

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

Combining Eq. (3) with Eq. (4) gives the following relation:

\[
\frac{d\alpha}{dT} = \frac{\alpha}{\beta} f(\alpha) \exp \left( -\frac{E_a}{RT} \right)
\]

Integration of Eq. (5) gives:

\[
\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{\alpha_0}^{\alpha} \exp \left( -\frac{E_a}{RT} \right) dT
\]

Generally, the rate of the reaction is low at the start [27], and the integral may be performed from 0 to \( T \). Combining Eqs. (1), (2) and (6), the following relationship can be obtained:

\[
G(\alpha) = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{\alpha_0}^{\alpha} \exp \left( -\frac{E_a}{RT} \right) dT
\]

2.4 Model fitting method

Treatment of thermal analysis data with the integral and differential methods together is considered as an effective method to yield the asymptotic mechanism of thermal degradation [28]. Among multitudinous
thermal reaction equations, the Coats-Redfern (CR) method and Achar-Brindley-Sharp-Wendworth (ABSW) method are commonly used to approximate the resolution of Eq. (7).

CR method:
\[
\ln \left( \frac{G(\alpha)}{T^2} \right) = \ln \frac{AR}{\beta E_a} - \frac{E_a}{RT} \tag{8}
\]

ABSW method:
\[
\ln \left( \frac{d\alpha}{f(\alpha)dT} \right) = \ln \frac{A}{\beta} - \frac{E_a}{RT} \tag{9}
\]

Eqs. (8) and (9) are based on 15 typical kinetic mechanisms of solid degradation listed in Table 1, which are utilized to consider these experimental data [29]. The plot of \( \ln[G(\alpha)/T] \) versus \( 1/T \) gives the slope \( -E_a/R \) by which the average activation energy \( E_a \) has been evaluated, whereas the pre-exponential factor \( A \) can be calculated directly from the intercept of the same fitting line. When the values of \( E_a \) and \( A \) obtained both from the differential and the integral method, respectively, are nearly the same or closest with a high correlation coefficient, this model can be applicable to the thermal degradation [30].

3 Results and discussion

The FTIR analysis of the chemical reaction between DGEBA and polyurethane is displayed in Figure 1. In the prime stages of the reaction, epoxy characteristic absorption peaks at 3318, 1225, 885 and 827 cm\(^{-1}\) [31] and the isocyanate -NCO absorption peak at 2270 cm\(^{-1}\) are evident. In the end stages of the reaction, the FTIR spectrum exhibits an intensive absorption peak of the urethane group at 1730 cm\(^{-1}\), with the intensity of the -NCO absorption peak at 2270 cm\(^{-1}\) reducing to a constant intensity [32]. However, the absorption peaks characteristic of epoxy are nearly unchanged in the prime stages except that the pendant secondary hydroxyl groups (-OH) on the side chains of epoxy resin absorption peak at 3389–3500 cm\(^{-1}\), which are shifted to a lower wave number. Thus, it is confirmed that chemical reaction occurred between NCO and OH and grafted epoxy resin is obtained. This reaction is displayed in Scheme 2. R stands for polyester Scheme 2.

<table>
<thead>
<tr>
<th>Number</th>
<th>Function</th>
<th>Reaction model</th>
<th>( f(\alpha) )</th>
<th>( G(\alpha) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mampel power law</td>
<td></td>
<td>( 4\alpha^{3/4} )</td>
<td>( \alpha^{1/4} )</td>
</tr>
<tr>
<td>2</td>
<td>Mampel power law</td>
<td></td>
<td>( 3\alpha^{2/3} )</td>
<td>( \alpha^{3/3} )</td>
</tr>
<tr>
<td>3</td>
<td>Mampel power law</td>
<td></td>
<td>( 2\alpha^{3/2} )</td>
<td>( \alpha^{3/2} )</td>
</tr>
<tr>
<td>4</td>
<td>Mampel power law</td>
<td></td>
<td>( 1 )</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>5</td>
<td>Parabola law</td>
<td>One-dimensional diffusion</td>
<td>( 1/2a )</td>
<td>( \alpha^2 )</td>
</tr>
<tr>
<td>6</td>
<td>Valensi</td>
<td>Two-dimensional diffusion</td>
<td>( -[\ln(1-a)]^{-1} )</td>
<td>( a+(1-a)\ln(1-a)^2 )</td>
</tr>
<tr>
<td>7</td>
<td>Ginstling-Broussstein</td>
<td>Three-dimensional diffusion</td>
<td>( 1.5[\ln(1-a)]^{1/2} )</td>
<td>( (1-2a)/3(1-a)^{2/3} )</td>
</tr>
<tr>
<td>8</td>
<td>Avrami-Erofeev</td>
<td>( n=2 )</td>
<td>( 2[\ln(1-a)]^{1/2} )</td>
<td>( -[\ln(1-a)]^{1/2} )</td>
</tr>
<tr>
<td>9</td>
<td>Avrami-Erofeev</td>
<td>( n=3 )</td>
<td>( 3[\ln(1-a)]^{2/3} )</td>
<td>( -[\ln(1-a)]^{1/3} )</td>
</tr>
<tr>
<td>10</td>
<td>Avrami-Erofeev</td>
<td>( n=4 )</td>
<td>( 4[\ln(1-a)]^{3/4} )</td>
<td>( -[\ln(1-a)]^{1/4} )</td>
</tr>
<tr>
<td>11</td>
<td>Phase boundary reaction</td>
<td>Contraction cylinder</td>
<td>( 2(1-a)^{1/2} )</td>
<td>( 1-(1-a)^{1/2} )</td>
</tr>
<tr>
<td>12</td>
<td>Phase boundary reaction</td>
<td>Contraction sphere</td>
<td>( 3(1-a)^{2/3} )</td>
<td>( 1-(1-a)^{2/3} )</td>
</tr>
<tr>
<td>13</td>
<td>Chemical reaction</td>
<td>( n=1 )</td>
<td>( 1-a )</td>
<td>( \ln(1-a) )</td>
</tr>
<tr>
<td>14</td>
<td>Chemical reaction</td>
<td>( n=1.5 )</td>
<td>( (1-a)^{3/2} )</td>
<td>( 2[(1-a)^{1/2}-1] )</td>
</tr>
<tr>
<td>15</td>
<td>Chemical reaction</td>
<td>( n=2 )</td>
<td>( (1-a)^2 )</td>
<td>( (1-a)^3-1 )</td>
</tr>
</tbody>
</table>

Figure 1 FTIR spectrum for the mixture of DGEBA and polyurethane: 1, prime phase; 2, end phase.
The mass loss (%) and derivative thermal gravimetric (DTG) plots are shown in Figure 2. Except for small volatilization amounts of residual solvent at the beginning, the degradation of grafted epoxy resin involves two stages: the first stage is dominated by the degradation of the urethane bonds and TDI [33], and the second stage correlates well with the dissociation of the polyester and epoxy resin [5]. Each peak of the DTG curves indicates the point of maximum rate of degradation change on the weight loss curve. The DTG traces are found to regularly shift toward a higher-temperature region with increasing thermal scanning rate, which can be explained by the lag of the relaxation time of molecular chain movement compared with the time of experimental recording [34]. The maximum rates of mass loss at the second step were labeled in DTG curves with 408.7°C, 417.8°C and 423.0°C for 10, 15 and 20 K min⁻¹, respectively. One may easily infer that the grafted epoxy resin remains stable before 230°C. However, the rate of mass loss increases sharply beyond 350°C, as shown clearly in Figure 2A. The initial degradation temperature (T₁, the starting point of deviation from the baseline), the temperature for maximum rate of mass loss (T_m) and the mass loss (%) of the first and the second stage mass loss step are summarized in Table 2.

Thermal degradation of the grafted epoxy resin at the first stage is attributed to the dissociation of urethane bonds. At this stage mass loss corresponds to about 15%, which is equal to the parts of TDI introduced into the pre-polymer. This result accords well with a previous investigation of grafted polymer based on castor oil carried out by Raymond and Bui [35]. The subsequent thermal degradation belongs to the degradation of polyester incorporated into polyurethane, DGEBA, and some broken chemical chains of degradation products generated from the first stage [36].

Table 2  Decomposition temperatures of the grafted epoxy resin.

<table>
<thead>
<tr>
<th>B (K min⁻¹)</th>
<th>T₁ (°C)</th>
<th>First stage</th>
<th>Second stage</th>
<th>Char yield (% at 500°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass loss (%)</td>
<td>Tₘ₁ (°C)</td>
<td>Mass loss (%)</td>
<td>Tₘ₂ (°C)</td>
</tr>
<tr>
<td>-------------</td>
<td>-------------</td>
<td>-----------</td>
<td>-------------</td>
<td>-----------</td>
</tr>
<tr>
<td>10</td>
<td>235.2</td>
<td>15.0</td>
<td>325.3</td>
<td>67.8</td>
</tr>
<tr>
<td>15</td>
<td>232.0</td>
<td>16.1</td>
<td>348.0</td>
<td>72.70</td>
</tr>
<tr>
<td>20</td>
<td>251.5</td>
<td>14.4</td>
<td>356.0</td>
<td>72.9</td>
</tr>
</tbody>
</table>
The synthesized grafted epoxy resin exhibits better toughness than crude epoxy resin. The selected epoxy resin is a high-molecular-weight solid with good mechanical properties [37], which is grafted with softer polyurethane. The microstructures of grafted epoxy resin and polyurethane section observed by FE-SEM show the phase separation, indicating the thermodynamic immiscibility shown in Figure 3 [38]. This phase separation is generated from polyurethane constructions TDI (hard segment) and polyester (soft segment). Thus, the toughening for epoxy resin can be explained by this soft segment and phase separation [39]. The mechanism for alleviating rigidity and brittleness problems of epoxy resin is considered to be cavitations, which can relieve the triaxial tension from cracking [40–42]. We can obtain the toughening effect using the stress-strain curve shown in Figure 4. The grafted epoxy resin exhibits ductile deformation (70%), indicating an improved toughness compared with epoxy resin [15].

3.1 Model fitting method

The thermal degradation model is essential to analyze the process of the whole thermal reaction. Model fitting method is widely used to determine the model. Each single heating rate is introduced into integral and differential methods with model-free method in this paper. When average activation energy $E_a$ and pre-exponential factor $A$ from both differential and integral methods are nearly the same and closest with a high correlation coefficient $R$, this model can be applicable to the thermal degradation [30]. After calculation, the No. 5 reaction model is the appropriate model. These close values of $E_a$ and $A$ are summarized in Table 3. The curves for the No. 5 reaction model with integral and differential method are also displayed in Figure 5.

The No. 5 reaction model belongs to a one-dimensional diffusion reaction, depending on the mobility of constituents in the reaction system [43]. In our experiment, the resultants are produced along with thermal
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Table 3  Kinetic parameters based on No. 5 reaction model for grafted epoxy resin.

<table>
<thead>
<tr>
<th></th>
<th>Integral method</th>
<th>Differential method</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>$\ln A$ (min$^{-1}$)</td>
<td>$R$</td>
</tr>
<tr>
<td>10 K</td>
<td>139.5</td>
<td>22.1</td>
</tr>
<tr>
<td>15 K</td>
<td>140.0</td>
<td>22.4</td>
</tr>
<tr>
<td>20 K</td>
<td>150.6</td>
<td>24.3</td>
</tr>
</tbody>
</table>

degradation, whereas the samples are put in a small crucible ($\Phi$ 8.0 × 12.5 mm) with a lid so the room of the aluminum crucible is filled easily. However, the gas resultants are volatilized only through the aperture between the crucible and the lid, so that the resultants cannot be emitted timely. As mentioned before, the layers of resultant around the sample are diluted slowly, which will control the rate of the degradation reaction. The kinetic function for thermal degradation of grafted epoxy resin can be written as follows:

$$\frac{d\alpha}{dt} = \frac{A}{2\alpha} \exp \left( -\frac{E_a}{RT} \right)$$

(10)

The plots of experimental data and thermal degradation model based on Eq. (10) are illustrated in Figure 6. We can see that calculation results agreed well with experimental results to some extent, which indicates that this kinetic function is the appropriate thermal degradation model.

4 Conclusions

First, grafted epoxy resins were prepared based on DGEBA and polyurethane. The chemical reaction between DGEBA and polyurethane was investigated by FTIR. FE-SEM clearly showed phase separation of polyurethane and grafted epoxy resin, which can be used to alleviate the brittleness problem. The stress-strain curve showed an improved toughness of grafted epoxy resin. Second, TGA was introduced to reckon the thermal stability of the grafted epoxy resin at the heating rates of 10, 15 and 20 K min$^{-1}$. Third, model fitting method was used to calculate the kinetic parameters of degradation based on the CR method and the ABSW method. We compared different degrees of conversion from experimental and calculation results. It was notable that the calculation results of conversion $\alpha$ fit well with the experiment to some degree. Kinetic function for thermal degradation of grafted epoxy resin can be obtained.

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References
