Synthesis and Degradation Mechanism of Self-Cured Hyperbranched Epoxy Resins from Natural Citric Acid

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ABSTRACT: Rapid and highly efficient degradation of cured thermoset epoxy resins is a major challenge to scientists. Here, degradable self-cured hyperbranched epoxy resins (DSHE-n, n = 1, 2, and 3) were synthesized by a reaction between 3-isocyanato-4-methyl-epoxy-methylphenylcarbamate and degradable epoxy-ended hyperbranched polyester (DEHP-n) prepared from maleic anhydride, citric acid, and epichlorohydrin. The chemical structure of DSHE-n was characterized by Fourier transform infrared and 1H NMR spectra. With an increase in DSHE-n molecular weight, the adhesion strength of self-cured DSHE-n films increases distinctly from class 1 to 4, and their pencil hardness remains about class B–2B. The study on the self-cured behavior and mechanism of DSHE-n shows that the carbamate group of the DSHE-n is decomposed into diamine group to react with epoxy group and form a cross-linked structure. The self-cured DSHE-n films were degraded completely in 2 h at 90 °C in the mixed solution of hydrogen peroxide (H2O2) and N,N-dimethylformamide under atmospheric pressure and produced the raw material citric acid, indicating good degradation performance and recyclable property of DSHE-n.

INTRODUCTION

Epoxy-ended hyperbranched polymers (EHPs)† as one of the important thermoset epoxy resins (EPs) have been widely used in coatings, adhesives,‡ paintings,§ and composites¶ due to their excellent mechanical and thermal performances. However, the three-dimensional cross-linked structures of thermoset epoxy resins,¶ including EHPs and the common diglycidyl ether bisphenol A (DGEBA), are insoluble and infusible,§ resulting in a large amount of cured EP wastes and great harm to the environment,‖ leading to severe difficulties in degradation and recycling.¶¶ Currently, several approaches have been used to decompose EP castoff,¶¶ including mechanical recycling,¶¶ pyrolysis process,¶¶ supercritical fluid process,¶¶ and biodegradation.¶¶ The later three degradation methods need high temperature and take a long time. However, ester,¶¶ ether bond,¶¶ disulfide bond,¶¶ and triazine ring structure,¶¶ and carbamate or carbonate¶¶ can promote degradation of the cross-linked structure of cured EPs, and they can be introduced into EP chains.¶¶ Shirui¶¶ synthesized a series of thermally degradable EPs carrying secondary or tertiary ester bonds. Among of them, the initial decomposition temperature of EPs containing tertiary ester is only 220 °C. Furthermore, if EPs contain an acetal, ketal, or unstable disulfide structure, it can be oxidized or reduced under the action of catalyst or degraded under acidic or alkaline conditions.¶¶

The cross-linking reaction of EPs needs a curing agent. Owing to the high reactivity of the epoxy group, both EPs and curing agents separate in storage.¶¶ Traditional curing agents, such as amines, carboxylic acids, carboxylic anhydrides, and phenols or thiols, can availably react with EPs to obtain different performances. However, the mixtures of both EPs and these curing agents show a short pot life, which limits their wide applications in advanced materials. Latent hardeners, such as dicyandiamide,¶¶ imidazole,¶¶ organic acid acylhydrazine, or ketamine, are inert to epoxy group under room temperature. Microcapsule latent curing agent, as a new type of latent hardener, can be broken up in the condition of heating or under pressure and release curing agents to react with the epoxy group.¶¶ The latent curing agents can mix with epoxy resin freely to form a single-component epoxy resin system. The single-component self-cured EPs not only reduce the cost of storage and packaging but also increase the processing window. Only if the external trigger or evaporating agent is added, it can be cross-linked with epoxy resin quickly. Therefore, single-component self-cured EPs can freely control the occurrence of a cross-linking reaction, which have been the focus of chemical engineers. A single-component EP
containing a carbamate group can be cured by diamine groups that are produced by the thermal initiation\(^{34,35}\) of the susceptibility cleavage of the functional carbamate group. Tang\(^{36}\) successfully synthesized a self-cured thermostet epoxy resin carrying an organic titanium chelate bond and confirmed that the initial self-curing temperature was about 172 °C.

We have prepared three degradable epoxy-ended hyperbranched polyesters (DEHP-\(n\)) by using the natural citric acid monomer. DEHP-\(n\) could not only distinctly improve the mechanical strength of the DGEBA but also promote the degradation ability of the cured DGEBA.\(^{26}\) However, the crosslinking reaction of DEHP-\(n\) needed additional curing agents due to the lack of self-curing function. In this paper, three kinds of degradable self-cured hyperbranched epoxy resins (DSHE-\(n\)) were synthesized by introducing a self-cured group (carbamate group) in DEHP-\(n\). The self-cured behavior of DSHE-\(n\) and the degradation mechanism of cured DSHE-\(n\) films have been discussed as well as their mechanical performance in detail.

## RESULTS AND DISCUSSION

The Fourier transform infrared (FT-IR) spectra of DSHE-1, DSHE-2, and DSHE-3 are shown in Figure 1a. It shows that the positions and shapes of the main absorption peaks are almost the same due to their similar chemical structures. The absorption peak at 3317 cm\(^{-1}\) belongs to the stretching vibration of \(-\text{OH}\). The absorption peak at 2925 cm\(^{-1}\) is attributed to the \(-\text{CH}_2\) group, and the absorption peak at 1729 cm\(^{-1}\) belongs to the \(\text{C}=\text{O}\) group. The stretching vibrations of \(\text{C}=\text{O}\) and \(\text{C}−\text{O}−\text{C}\) in the ester group are confirmed by the appearance of peaks at 1230 and 1063 cm\(^{-1}\). The absorption peak at 909 cm\(^{-1}\) is attributable to the characteristic absorption peak of the epoxy group. The disappearance of the absorption peak at 2273 cm\(^{-1}\) substantiates that the \(-\text{NCO}\) group has reacted with the \(-\text{OH}\) groups completely.

The \(^1\text{H}\) NMR spectra of DSHE-1, DSHE-2, and DSHE-3 are shown in Figure 1b. The peak at 1.70 ppm (i) belongs to hydrogen atom chemical shift in \(-\text{CH}_2−\) attached with the benzene ring. The peaks at 3.18 ppm (d) and 2.11−2.22 ppm (e) are attributable to hydrogen atom chemical shift of the epoxy group. The peaks at 2.64−2.88 ppm (b) are attributable to hydrogen atom chemical shift in \(-\text{CH}_2−\) attached with carbonyl. The peaks at 3.65 and 4.28 ppm (c) belong to hydrogen atom chemical shift in \(-\text{CH}_2−\) attached with the epoxy group. The peaks at 1.26 ppm (h) belong to hydrogen atom chemical shift in \(-\text{CH}_3\) attached with the carbamate. The peak at 3.94 ppm (f) is attributable to hydrogen atom chemical shift in \(-\text{CH}_2−\) attached with the ester group. The peak at 4.52 ppm (g) belongs to hydrogen atom chemical shift in \(-\text{CH}−\) attached with hydroxyl. The peaks at 6.57−7.82 ppm (j, k, m) belong to hydrogen atom chemical shift in benzene ring. The ratio of the peak area of the hydrogen atoms of the \(^1\text{H}\) NMR spectrum is close to the ratio of the number of hydrogen atoms in the chemical structure, indicating that the target products have been successfully synthesized.

Table 1 shows the properties of DSHE-1, DSHE-2, and DSHE-3. Compared to the experimental epoxy equivalent weights of DEHP-1, DEHP-2, and DEHP-3 of about 199.8, 216.9, and 220.3 g/mol, respectively, the experimental epoxy equivalent weights of DSHE-1, DSHE-2, and DSHE-3 are about 244.8, 251.2, and 255.4 g/mol, respectively, indicating an increase in epoxy equivalent weight and the successful synthesis of DSHE-\(n\).

### Table 1. Properties of Degradable Self-Cured DSHE-\(n\)

| DSHE-\(n\) | theoretical molecular weight (g/mol) | experimental epoxy equivalent weight (g/mol) | theoretical epoxy equivalent weight (g/mol) |
|-----------|-------------------------------------|---------------------------------------------|---------------------------------------------|
| DSHE-1    | 1332.8                              | 244.8                                       | 222.1                                       |
| DSHE-2    | 4111.4                              | 251.2                                       | 228.4                                       |
| DSHE-3    | 12459.5                             | 255.4                                       | 230.7                                       |

DeDSHE-1 was regarded as a typical example to study self-cured behavior due to the similar chemical structure of DSHE-\(n\).

The initial and rapid decomposition temperatures of DSHE-1 appear at 114−252 and 252−400 °C, respectively, in Figure 2a. The weight loss at the initial stage (114−252 °C) should be attributed to the CO\(_2\) produced from the cleavage of carbamate groups in DSHE-1, confirmed by the appearance of an exothermic peak at 100−170 °C in the differential scanning calorimetry (DSC) curve (Figure 2b) of the DSHE-1. The initial self-cured temperature of the DSHE-1 is slightly lower than its initial decomposition temperature. The curing heat can further promote the fracture of the carbamate group to produce the curable diamine group because the cross-linking is an exothermic reaction.\(^{34}\) The weight loss at 252−400 °C is produced from the cleavage of chemical chains. Figure 2c compares the difference in absorption peaks of DSHE-1 and self-cured DSHE-1. With the increase of curing time of DSHE-
1, the content of the epoxy groups reduces and finally disappears at about 909 cm\(^{-1}\), suggesting that the epoxy group has been cross-linked completely.

The pyrolysis mechanism of the carbamate group is deduced according to the infrared spectra in Figure 2c and shown in Scheme 1. Both carbamate groups (marked with green and blue colors) should show a similar pyrolysis mechanism,\(^{39}\) but their degraded and produced alkenes contain various chemical structures, besides the same diamine and CO\(_2\).\(^{37,38}\) The blue carbamate group would be decomposed into amine and allyl ether monomers, and the green carbamate group would be degraded into 2-methyleneoxirane, amine monomers, and CO\(_2\). 2-Methyleneoxirane\(^{40}\) can copolymerize with the allyl ether under high temperature to form a new epoxy group (marked with green color) in Scheme 1. Both epoxy matrixes can be cured by the newly formed diamine to obtain a cross-linked structure.

Figure 2. (a) Thermogravimetric analysis (TGA), (b) DSC, and (c) FT-IR curves of DSHE-1.

Scheme 1. Degradation Mechanism of Carbamate Groups

Performance of Self-Cured DSHE-\(n\). The performance of self-cured DSHE-\(n\) films is shown in Table 2. With the increase of DSHE-\(n\) molecular weight, the adhesion strength increases distinctly from class 1 to 4, and their pencil hardness remains about class B–2B. The adhesion strength of epoxy resins is decided by the internal stress, polarity of functional groups, molecular weight, and so on. During the self-curing of epoxy resin, the fracture of the old bonds and the formation of new bonds result in the formation of internal stress. DSHE-1 with low epoxy equivalent weight (Table 1) should imply rapid curing speed, resulting in internal stress and low adhesion

| Table 2. Properties of Self-Cured DSHE-\(n\) Films |
|-----------------------------------------------|
| self-cured sample | DSHE-1 | DSHE-2 | DSHE-3 |
| pencil hardness   | B      | 2B     | 2B     |
| adhesion strength | 1      | 2      | 4      |
strength, compared to that of DSHE-3 with high epoxy equivalent weight. Additionally, the content of hydroxyl groups of DSHE-\( n \) increases with an increase in their molecular weights. The polar hydroxyl group content of DSHE-1 is also lower than that of DSHE-3, indicating the low adhesion strength of self-cured DSHE-1, being attributable to the fact that the hydroxyl group has hydrogen bonds that interact with the surface of metal materials to increase the adhesion strength.

TGA curings of the self-cured DSHE-\( n \) films are shown in Figure 3. Table 3 summarizes the typical thermal degradation temperatures for \( T_\text{s} \) (5% weight loss), \( T_{10} \) (10% weight loss), and \( T_{\text{max}} \) (maximum weight loss) and the char yield under 600 °C. The data show that the self-cured DSHE-\( n \) films are stable before 230 °C, and then their three-dimensional networks are gradually decomposed as the temperature rises. With an increase in molecular weight of DSHE-\( n \), the \( T_{\nu} \), \( T_{10} \) and \( T_{\text{max}} \) of the self-cured DSHE-\( n \) films decrease, substantiated by the higher content of ester bonds and lower cross-linked density of DSHE-1 than those of DSHE-3.

Degradation Mechanism of Self-Cured DSHE-\( n \).

DSHE-1 was chosen as an example to investigate the degradation properties in detail due to its similar chemical structures as DSHE-2 and DSHE-3. Figure 4a shows that the degradation degree increases gradually with an increase in the content of catalyst H\( _2 \)O\( _2 \) solution. When the mass ratio of DSHE-1, N\( _x \)N-dimethylformamide (DMF), and H\( _2 \)O\( _2 \) is 1:15:15, the degradation degree of self-cured DSHE-1 is about 99.9%. With the increase of the mass of the H\( _2 \)O\( _2 \) content, free radicals produced increase, and the free radicals attack the chemical bonds of the self-cured DSHE-1 film to decompose, and then the degradation products can be dissolved completely in DMF solvent. Increasing the degradation reaction time approves the complete degradation of the self-cured DSHE-1 film, resulting in a high degradation degree in Figure 4b. During degradation, high temperature can increase the degradation rate and then shorten the reaction time. Therefore, the degradation degree of the self-cured DSHE-1 film increases from 46.4 to 99.9% apparently with the variation of reaction temperature from 50 to 90 °C in Figure 4c at the mass ratio (1:15:15) of DSHE-1/DMF/H\( _2 \)O\( _2 \) and degradation time of 2 h. Moreover, the degradation degrees of both self-cured DSHE-2 and DSHE-3 films in Figure 4d are about 99.9% in the same degradation condition as a self-cured DSHE-1 film, being attributable to their similar chemical structure.

The degradation solution of self-cured DSHE-1 films was extracted by the mixed solution of EtOAc and H\( _2 \)O for GC-MS analysis. In addition, the GC-MS spectrum of the resulting solution is shown in Figure 5. Thirteen main peaks (Figure 5) appear at the total ion chromatograph of the degraded products of the self-cured DSHE-1 film, indicating 13 degradation components. Table 4 shows their molecular weights of the fragments. The chemical structures and the degradation mechanism of the self-cured DSHE-1 film can be supposed and are shown in Scheme 2 according to molecular weights and retention time of the degradation products. H\( _2 \)O\( _2 \) as an oxidant is used to decompose the curing DSHE-1, and DMF as a solvent can dissolve the degraded products. The self-cured DSHE-1 is degraded by the fracture of C–O in the ester group, and the C–N of the curing agent. The formation of products (1) and (2) is attributed to the cleavage of the ester group on the main chain of the polyester. The formation of degraded product citric acid (2) indicates the fracture of the ester bond and the recyclable property of DSHE-1. Degradation products (3)–(13) are formed by the fracture of the C–N of other groups. At the same time, the acetone group in the substituent R\( _1 \) is obtained by hydroxyl oxidation, and the –NO\( _2 \) group in products (3), (4), and (12) is produced by amino oxidation due to the strong oxidation of H\( _2 \)O\( _2 \).

CONCLUSIONS

Degradable self-cured hyperbranched epoxy resins (DSHE-\( n \), \( n = 1, 2, \) and 3) have been synthesized by a simple method. The self-curing mechanism of DSHE-\( n \) was analyzed by TG, DSC, and FT-IR techniques. With the increase of DSHE-\( n \) molecular weight, the adhesion strength of self-cured DSHE-\( n \) films increases distinctly from class 1 to 4, and their pencil hardness remains about class B–2B. The effects of degradation time, temperature, content of H\( _2 \)O\( _2 \), and molecular weight of DSHE-\( n \) on the degradation degree of their self-cured films were researched in detail. Moreover, the self-cured DSHE-\( n \) film can be degraded completely in only about 2 h at 90 °C and produce citric acid, suggesting the good degradation and recyclable properties of DSHE-\( n \).

EXPERIMENTAL SECTION

Materials. Citric acid, maleic anhydride, toluene, 1,4-dioxane, \( p \)-toluenesulfonic acid, epichlorohydrin, ethyl acetate (EtOAc), NaOH, Na\( _2 \)SO\( _4 \), 2,4-toluene disiocyanate (TDI), glycidyl, chloroform, hydrogen peroxide (H\( _2 \)O\( _2 \)), and N,N-dimethylformamide (DMF) were commercially supplied by Shanghai Chemical Reagent Co., Ltd. All reagents were of analytical grade.

Synthesis of DSHE-\( n \). Three kinds of carboxyl terminated hyperbranched polyesters (DCHP-\( n \)) and degradable epoxy-ended hyperbranched polyesters (DEHP-\( n \)) with different
molecular weights were synthesized according to the literature (Scheme 3). The FT-IR of DCHP-1 (cm$^{-1}$): 3473 (O–H), 1729 (C=O), 1216 (C–O–C), 1631 (C=C). $^1$H NMR (400 MHz, D$_2$O, ppm): 6.27 (2H, s, CH=C), 2.69–2.93 (2H, s, CH$_2$).

The FT-IR and $^1$H NMR of DCHP-2 and DCHP-3 are similar to that of DCHP-1.

The FT-IR of DEHP-1 (cm$^{-1}$): 1739 (C=O), 1240, 910, 844 (epoxy group). The $^1$H NMR of DEHP-1 (400 MHz, DMSO-$d_6$, ppm): 6.1 (2H, s, CH=C), 2.79 (2H, s, CH$_2$ attached with hydroxyl), 3.17 (H, m, CH of epoxy group), 2.5–2.63 (2H, s, CH$_2$ of epoxy group), 4.41 (H, m, CH), 3.81–4.21 (2H, s, CH$_2$ attached with the epoxy group). The FT-IR and $^1$H NMR of DEHP-2 and DEHP-3 are similar to that of DEHP-1.

DSHE-$n$ were prepared by an addition reaction between DEHP-$n$ and 3-isocyanato-4-methyl-epoxy-methylphenylcarbonate (EMPC) according to Scheme 3. The synthetic method of DSHE-1 was followed. First, TDI (1.74 g, 0.01 mol) and chloroform (20 mL) were added into a three-necked flask.
equipped with a mechanical stirrer. A constant pressure drop funnel was used to slowly drop glycidyl (0.74 g, 0.01 mol) to the flask, and the temperature was increased to 50 °C and the mixture was stirred for 3 h. The solvent was removed to obtain EMPC. Second, DEHP-1 (8.69 g, 0.01 mol), EMPC (9.84 g, 0.02 mol), and chloroform were added into a three-necked round-bottomed flask, and the reaction was warmed to 60 °C for 6 h. When the solvent was removed, a yellow brown liquid with a yield of 92% was obtained, which proved to be DSHE-1. DSHE-2 with a yield of 91% and DSHE-3 with a yield of 90% were synthesized by a similar method. The structure of DSHE-1 is shown in Scheme 4.

Preparation of the Self-Cured DSHE-\(n\) Films. DSHE-\(n\) was placed in a tin box and then warmed at 80 °C for 4 h, 160 °C for 4 h, 180 °C for 3 h, and 200 °C for 2 h. Next, the samples were cooled gradually to room temperature and stored for about 12 h. A similar curing condition was used to prepare standard DSHE-\(n\) films for measuring the pencil hardness and adhesion strength.

Degradation of the Self-Cured DSHE-1 Film. The cured samples (0.5 g) were cut into about 1 mm × 2 mm × 2 mm specimens and put into a 20 mL glass tube with H\(_2\)O\(_2\) and DMF. The glass tube was heated to appropriate temperature and maintained for appropriate hours and then cooled to room temperature. After this process, the remaining solid was filtered and washed with water several times and then dried in vacuum at 80 °C for 3 h.

Characterization. FT-IR studies were performed using a Nicolet Nexus 470 FT-IR spectrometer. \(^1\)H NMR measurements were conducted using a Bruker Avance III-400 NMR spectrometer with tetramethylsilane as an internal standard and CDCl\(_3\) as solvents.

Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (NETZSCH TG209) at a heating rate of 10 °C/min and a nitrogen flow of 20 mL/min performed in the temperature range of 40−600 °C. A DSC study was carried out using a NETZSCH DSC200F3 instrument in nitrogen atmosphere. The self-cured behavior of DSHE-\(n\) was studied from room temperature to 240 °C at a heating rate of 2 °C/min using a 5−10 mg sample in standard aluminum pans.

The mechanical properties of self-cured samples were tested by a paint film adhesion tester and a pencil hardness tester according to GB/T 6739-2006 and GB/T 1720-92 at room temperature, respectively.
The degradation degree \( (D_d) \) of the self-cured DSHE-\( n \) was calculated using eq 1

\[
D_d = \frac{W_0 - W}{W_0} \times 100\% \quad (1)
\]

where \( W_0 \) is the mass of DSHE-\( n \) before degradation and \( W \) is the mass of solid residues after degradation. Next, 50 mL of the degradation solution of the self-cured DSHE-\( n \) film was extracted three times by a mixed solution of 15 mL of EtOAc and 8 mL of \( \text{H}_2\text{O} \), and then the organic phase was analyzed by an Agilent Model 6890 gas chromatograph that was coupled with an Agilent Model 5973 quadrupole mass spectrometer.

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