Biobased Epoxies Derived from Myrcene and Plant Oil: Design and Properties of Their Cured Products

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ABSTRACT: Two biobased epoxy resin monomers derived from myrcene and plant oil are synthesized without using petroleum-based bisphenol A. To obtain material with balanced strength and toughness, the two epoxy monomers are cured together in different weight proportions. Properties of cured epoxy resin are tested by different techniques. Tensile and impact tests indicate that when the content of myrcene-based epoxy is 50−75 wt %, the cured sample has a high strain of 32.30−161.47%, and a moderate tensile strength of 9.57−15.96 MPa. Dynamic mechanical analysis suggests that the glass transition temperature (T_g) of cured samples increases from 17 to 71 °C with the increasing content of myrcene-based epoxy. Morphology of fracture surface indicates that the cured sample containing plant oil-based epoxy resin shows obvious plastic deformation. The curing kinetics of the two epoxies resin is studied by differential scanning calorimetry. Also, the calculated activation energy is 70.49 kJ/mol for myrcene-based epoxy and 64.02 kJ/mol for poly-fatty acid-derived epoxy resin. The thermogravimetric analysis indicates that the main degradation temperature of all cured samples is above 300 °C. The sustainable biobased epoxy has some potential in preparing flexible epoxy materials and can be used to toughen conventional petroleum-based epoxy.

1. INTRODUCTION

Epoxy resin is one important thermosetting polymer that combines excellent mechanical properties, chemical resistance, and thermal properties. It is used in various applications, including surface coatings, adhesives, printed circuit board coatings, and polymer composites.1−3 The most common and important type of epoxy resin (about 90%) is synthesized from bisphenol A (BPA) and epichlorohydrin. Depending on the molar ratio of BPA to epichlorohydrin, the bisphenol A epoxy resin is usually a monomer or oligomer with different molecular weights.3,4 However, as one of the main starting material for bisphenol A epoxy resin, BPA is synthesized from acetone and petroleum-based phenol, which are highly toxic chemicals. BPA is also a potential endocrine disruptor, which mimics the action of estrogen hormone.5−7 It can migrate into food and beverages from BPA-containing food containers and will accumulate in the human body.8 As a result, the food packaging materials containing BPA have been banned in Europe, United States, and Canada.9 Furthermore, the concerns about environmental issues and pressures of using petroleum-based resources are significantly increased. Therefore, substantial efforts have been made to developing BPA-free epoxy resins from natural resources.

A variety of natural resources, such as vanillin, itaconic acid, vegetable oil, cardanol, isosorbide, rosin, and lignin, etc., have been used as the renewable feedstock to synthesize epoxy. For example, a series of epoxidized sucrose esters of fatty acids (ESEFAs) were prepared and cross-linked with cycloaliphatic anhydride, and they possess high modulus, excellent rigidity, and ductility owing to the high epoxide functionality.10 Two tung oil fatty acid-derived epoxies (DGEC21 and TGEC22) generally outperform ESO were reported, and especially TGEC22 has strength, modulus, and glass transition temperature comparable to those of a commercial bisphenol A epoxy resin (DER332).11 Kumar et al. synthesized a trifunctional epoxy resin (TEIA) from itaconic acid, the epoxy resin has a high epoxy value of 1.02, lower viscosity, higher mechanical, and higher curing reactivity compared with epoxidized soybean oil and comparable with BPA epoxy.12 Kanehashi et al. synthesized cardanol-based epoxy resin for coating at room temperature. Thermal analysis showed that the cardanol-based epoxy prepolymer coating was in a rubbery state at room temperature because of the flexible side chains of cardanol and showed good chemical stability.13 Some biobased raw materials containing aromatic or other ring compounds also have raised considerable interests in epoxy production. For instance, an...
2. EXPERIMENTAL SECTION

2.1. Material. Myrcene (79 wt %) was obtained from Jiangxi Global Natural Spice Co., Ltd. Epoxy fatty acid methyl ester (EFAME, epoxy value 0.34) was purchased from Shijiazhuang Yongguang Chemical Technology Co., Ltd. Maleic anhydride (stabilized, 99.5%), boron trifluoride diethyl etherate (BF$_3$·OEt$_2$) (98%), benzyliatriethylamine chloride (98.0%), epichlorohydrin (99.0%), ethanol (99%), dioxane (98%), calcium oxide, concentrated hydrochloric acid (37 wt %), and sodium hydroxide were purchased from The Group Chemical Reagent Co., Ltd. 2,4,6-Tris(dimethylaminomethyl)phenol (DMP-30) and methyl nadic anhydride (MNA) were obtained from Aladdin Industrial Corporation. Distilled water was prepared in our laboratory.

2.2. Synthesis. 2.2.1. Synthesis of Myrcene-Based Epoxy Resin. First, adduct of myrcene and maleic anhydride (MMY) was synthesized, and the synthesis method has been described in our previous work. The synthesis route is shown in Figure 2 (yield: 92.35%).

Then, 150.00 g of MMY, 13.40 g of water were added to a 1000 mL flask; the mixture was heated to 80 °C and hydrolyzed for 2 h. Next, 592.13 g of epichlorohydrin and 2.85 g of sodium hydroxide were added to the flask. Then, the reactants kept reacting at 117 °C for another 2 h. After this, the mixture was cooled to 60 °C and filtered. The filtrate was collected. Finally, the excess epichlorohydrin was removed via rotary vacuum evaporation, and myrcene-based epoxy (EMMY) was obtained (yield: 88.03%, epoxy value 0.46). The synthesis route is shown in Figure 2.

2.2.2. Synthesis of Poly-Fatty Acid-Derived Epoxy Resin (PFAME). First, 200.00 g of EFAME was dissolved into 240.00 g of PFAME (yield: 95.02%).

\[
\text{MY} + \text{EFAME} \xrightarrow{76 \degree C, 4 h} \text{EMMY}
\]

Then, the reactants kept reacting at 117 °C for another 2 h. After that, 1.8 mL of ethanol water solution (v/v was 1:1) was added to deactivate the catalyst. Finally, the dioxane, ethanol, and water were removed by vacuum distillation and poly-fatty acid methyl ester (PFAME) was obtained (yield: 95.02%).

Then, 12.80 g of NaOH was dissolved into a 125 mL of ethanol water solution (v/v was 1:1) in a 500 mL flask. After the solution was heated up to 70 °C, 100.00 g of PFAME was

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Myrcene

EFAME

Figure 1. Structures of myrcene and epoxy fatty acid methyl ester (EFAME).

Figure 2. Synthesis route of myrcene-based epoxy.
added dropwise. After reacted for 2 h, the PH value was adjusted to 2–3 by 5 mol/L HCl, and the mixture was continued to stir at 70 °C for 1 h. After the reaction, the mixture was stood for 30 min, and the supernatant organic layer (polyether multi-fatty acid, PFA) was taken out. The crude PFA was washed with distilled water several times until the solution was neutral. Finally, the residual water was removed with a rotary evaporator and a high viscous liquid (PFA) was obtained (yield: 87.69%, acid value of 172.51 mg/g, and theoretical value of 178.63 mg/g).

PFA (80 g), 240.56 g of epichlorohydrin, and 0.592 g of benzyltriethylamine chloride were added to a 500 mL flask. The temperature was heated to 117 °C and kept reacting for 2 h. Then, the mixture was cooled to 60 °C, and 14.56 g of CaO and 10.04 g of NaOH were added to the flask twice and kept reacting at 60 °C for 3 h. After cooled to room temperature, the mixture was filtered with celite powder, and the filtrate was

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**Figure 3.** Synthesis route of poly-fatty acid-derived epoxy resin (EPFA).

**Figure 4.** Chemical structures of DMP-30 and MNA and their curing mechanism with epoxy.
collected. Finally, the excess epichlorohydrin was removed using a rotary vacuum evaporator, and a dark red viscous liquid, poly-fatty acid-derived epoxy resin (EPFA) was obtained (epoxy value, 0.26). The synthesis route is shown in Figure 3.

2.3. Preparation of Epoxy Samples. EMMY and EPFA were mixed uniformly at weight ratios of 100:0, 75:25, 50:50, 25:75, 0:100%, respectively. MNA was used as a curing agent and DMP-30 was used as a catalyst (chemical structures of MNA and DMP-30 and the curing mechanisms are shown in Figure 4).

The mole ratio of the epoxy group to the anhydride group was maintained in 1:1 in all formulations. DMP-30 was added at 1 wt % on the basis of total weight of epoxy resin and curing agent (the formulas are listed in Table 1). The mixtures were charged into mold with a cavity dimension of 80 × 10 × 4 mm² and 50 × 10 × 5 mm³. The samples were cured at 120 °C for 2 h and 160 °C for 3 h. Then, the specimens were carefully removed from the mold and used for tensile, impact, dynamic mechanical property, fracture morphology, and the thermal property tests.

2.4. Characterization. 2.4.1. Fourier Transform Infrared (FTIR) Analysis. FTIR was carried out with an IS10 spectrometer (Nicolet, America) by an attenuated total reflection method. Each sample was scanned from 4000 to 400 cm⁻¹.

2.4.2. Nuclear Magnetic Resonance Spectroscopy (NMR). 1H NMR and 13C NMR (300 MHz) spectra were recorded with an ARX300 spectrometer (Bruker, Germany). The chemical shifts relative to that of deuterated chloroform (d = 7.26 and d = 76.5 ppm, respectively) were recorded.

2.4.3. Gel Permeation Chromatograph (GPC). GPC measurements were performed on a GPC 1515/2414 (Waters, USA). The testing conditions are as follows: mobile phase is chromatographic grade THF, flow rate was 1 μL/min, chromatographic column temperature is 35 °C, and relative molecular weight is 580−19,600.

2.4.4. Tensile and Impact Test. Tensile property test was carried out with a CMT4303 universal test machine (SANS, China). The tensile speed is 3 mm/min and test method is in accordance with ASTM D638−03. Impact property was tested, following GB/T 1043.1 using a ZBC1400-C impact tester. To ensure the accuracy of the test result, five replicates were tested and the average values were obtained.

2.4.5. Scanning Electron Microscopy (SEM). The fracture surfaces of the cured epoxy resin were observed with an S-3400 N scanning electron microscopy (Hitachi, Japan). A thin gold layer, which is a few nanometers thick, was coated on the fracture surfaces to aid in feature resolution. Then, the SEM images of all samples were collected.

2.4.6. Dynamic Mechanical Analysis (DMA). DMA was carried out with a Q800 dynamic mechanical thermal analyzer (TA, America) in a double cantilever mode with a frequency of 1 Hz, and the dimension of the samples were 60 × 10 × 4 mm³. All the tests were swept from −70 to 150 °C at a heating rate of 3 °C/min.

2.4.7. Thermogravimetric Analysis (TGA). TGA was performed using a 409PC thermogravimetric analyzer (Netzsch, Germany). Each sample was tested from 25 to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.4.8. Differential Scanning Calorimetry (DSC). Non-isothermal curing kinetics was studied by differential scanning analysis (DSC) using a 2920 MDSC (TA instruments). Samples were scanned from 25 to 230 °C at heating rates of 5, 10, 15, 20 °C/min, respectively.

2.4.9. Gel Content. The gel content of cured sample was determined by Soxhlet extraction. Cured sample (1.5 g) was extracted for 24 h using 200 mL acetone as solvent.

3. RESULTS AND DISCUSSIONS

3.1. Fourier Transform Infrared (FTIR) Analysis. Figure 5 shows the spectra of myrcene, MMY, and EMMY. In the spectrum of MMY, the characteristic peaks of a conjugated double bond (1644 and 1594 cm⁻¹) that ever appeared in myrcene were disappeared. Absorption peaks of carbonyl in cyclic anhydride (1835 and 1770 cm⁻¹) and the absorption peak of C−H in the hexatomic ring (1311 cm⁻¹) were appeared. These evidences indicated that the Diels−Alder reaction between myrcene and maleic anhydride occurred. On the contrary, in the spectrum of EMMY, the absorption peaks of carbonyl in MMY and epichlorohydrin. Besides the characteristic peaks of C−O−C at 1439 and 1176 cm⁻¹, the epoxy group at 906 and 756 cm⁻¹ all appeared. The absorption peak at 3528 cm⁻¹ was attributed to the −OH in the oligomers of dimeric or trimeric of the epoxy. These changes verified the reaction between MMY and epichlorohydrin has occurred.

Table 1. Formulas of Epoxy Mixture for Curing

| sample   | EMMY/g | EPFA/g | MNA/g | DMP-30/g |
|----------|--------|--------|-------|----------|
| EMMY100  | 40.00  | 0.00   | 28.52 | 0.69     |
| EMMY75/EPFA25 | 30.00  | 10.00  | 26.04 | 0.66     |
| EMMY50/EPFA50 | 20.00  | 20.00  | 23.52 | 0.64     |
| EMMY25/EPFA75 | 10.00  | 30.00  | 21.04 | 0.61     |
| EPFA100 | 0.00   | 40.00  | 18.52 | 0.59     |

EMMY75/EPFA25 stands for the weight ratio of EMMY and EPFA is 75:25%.

Figure 5. FTIR spectra of myrcene, MMY, and EMMY.
Figure 6 shows FTIR spectra of EFAME, PFAME, PFA, and EPFA. In the spectrum of EFAME, 841 and 1740 cm\(^{-1}\) were attributed to the absorption peaks of epoxy group and carbonyl on ester group, respectively. In the spectrum of PFAME, the peak at 841 cm\(^{-1}\) was disappeared, and the absorption peak of C=O at around 1071 cm\(^{-1}\) was appeared. In addition, a small absorption peak of \(-\text{OH}\) at 3493 cm\(^{-1}\) was appeared. This indicated that the ring-opening polymerization of the epoxy group in EFAME has been happened. In the spectrum of PFA, the absorption peak at 1710 cm\(^{-1}\) was assigned to the stretching vibration of C=O in the carboxyl group. In addition, an overlapped absorption peak at around 2000 to 3750 cm\(^{-1}\) was corresponded to the O-H in the carboxyl group. Due to the association of hydroxyl, the absorption peak was very wide and overlapped with the absorption peak of C-H in \(-\text{CH}_{2}\) and \(-\text{CH}_{3}\). The absorption peak at 931 cm\(^{-1}\) was attributed to the non-plane swing vibration of associated O-H. In spectra of EPFA, the peak at 2000 to 3750 and 931 cm\(^{-1}\) were disappeared, and peaks at 906 and 850 cm\(^{-1}\) corresponding to the epoxy group were appeared. The absorption peak of C=O at 1710 cm\(^{-1}\) in carboxyl was disappeared, and the absorption peak of C=O at 1740 in the ester group was appeared. All these evidences indicated that the EPFA has been prepared successfully.

3.2. \(^1\text{H NMR and }^{13}\text{C NMR Analysis.} \)\(^1\text{H NMR and }^{13}\text{C NMR spectra of EMMY are shown in Figure 7. }^{1}\text{H NMR: (CDCl}_3\text{, }\delta \text{ ppm), 5.38 (s, 1H), 5.05 (t, 1H), 4.41 (m, 2H), 3.91 (m, 2H), 3.07 (m, 2H), 2.80 (t, 2H), 2.60 (t, 2H), 2.30–2.51 (m, 4H), 1.97–2.05 (m, 4H), 1.58–1.65 (d, 6H).}

The \(^1\text{H NMR spectrum of EPFA is shown in Figure 8. EPFA: (CDCl}_3\text{, }\delta \text{ ppm), 4.32 (d, 1H), 4.02 (d, 1H), 3.81 (m, 2H), 3.10 (m, 1H), 2.75 (d, 2H), 2.56 (t, 2H), 2.25 (m, 2H), 1.53 (m, 4H), 1.37 (m, 2H), 1.18 (m, 12H), 0.78 (t, 3H).}

GPC measurement was performed to test the molecular weight of EPFA. The GPC results indicated that the average molecular weight of EPFA was 1134 g/mol, which was very close to the theoretical molecular weight of the trimer. It is further demonstrated that the EPFA has been synthesized.

3.3. Curing Kinetics Analysis. The DSC thermograms of EMMY and EPFA are shown in Figure 9, detailed DSC data are summarized in Table 2. Clearly, as the heating rate increases, the initial temperature (\(T_i\)), peak exothermic temperature (\(T_p\)), and temperature at curing end (\(T_e\)) of EMMY and EPFA are all increased. Also, the exothermic peaks

![Figure 6. FTIR spectra of EFAME, PFAME, PFA, and EPFA.](image)

![Figure 7. \(^1\text{H NMR and }^{13}\text{C NMR spectra of EMMY.}](image)

![Figure 8. \(^1\text{H NMR spectrum of EPFA.}](image)
become sharper, which indicates a much more focused exothermic process.

The influence of the curing rate on curing reaction can be eliminated by extrapolating the heating rate linearly to infinity slow, so that the curing temperature at zero heating rate is determined.29 The data at a zero heating rate is shown in Table 2. The temperature ranged from 98.19 to 147.48 °C for EMMY and 101.13 to 163.99 °C for EPFA. These data can provide references for studying the curing of EMMY and EPFA.

The activation energy (E_a) can be calculated using the Kissinger’s method, as follows30

\[
\ln\left(\frac{\beta}{T_p^2}\right) = \ln(AR/E_a) - \left(\frac{E_a}{RT_p}\right)
\]

where, \(\beta\) is the heating rate, \(T_p\) is peak temperatures on a DSC curve, \(A\) is the pre-exponential factor, and \(R\) is the gas constant (8.314 J/mol).

The plot of \(\ln(\beta/T_p^2)\) against \(1/T_p\) exhibits a good linear relationship, and their standard linear regression equations are determined by linear regression (Figure 10). The slope is equal to \(-E_a/R\) and the \(E_a\) is calculated to be 70.49 kJ/mol for EMMY and 64.02 kJ/mol for EPFA. The higher \(E_a\) of EMMY is likely attributed to the alicyclic structure in EMMY, which would enhance the steric hindrance when the curing reaction occurred.

To further verify whether the epoxy groups were completely cured, IR and DSC tests of cured samples are conducted. IR result indicates the absorption peaks of epoxy at around 907 and 850 cm\(^{-1}\) are completely disappeared (marked with box in Figure 11). Also, DSC result (Figure 12) indicates that there are no exothermic peaks appeared in the curing temperature range except for the \(T_g\) peak. These evidences indicate that the epoxy groups have completely cured.

### 3.4 Dynamic Mechanical Analysis (DMA)

The curves of storage modulus and loss factor (tan δ) against temperature are shown in Figure 13a,b. The results of glass transition temperature (\(T_g\)), which corresponds to the peak temperature of tan δ, storage modulus (\(E_s\)), loss modulus (\(E''\)), and curing gel content are listed in Table 3. The DMA test is performed under dynamic force with a certain frequency, the measured modulus value is generally higher than that of the tensile test. Clearly, the storage modulus of EMMY100 is higher than that of other samples. This is attributed to the alicyclic structure in EMMY and high cross-link density. With the increasing content of EPFA, the storage modulus decreases.

### Table 2. DSC Results of Non-Isothermal Curing Epoxies of EMMY and EPFA

| sample | \(\beta\) (°C/min) | \(T_i\) (°C) | \(T_p\) (°C) | \(T_e\) (°C) | \(\Delta H\) (J/g) | \(\Delta H'\) (kJ/mol) |
|--------|--------------------|--------------|--------------|--------------|----------------|------------------|
| EMMY   | 0                  | 98.19        | 131.75       | 147.48       |                |                  |
|        | 5                  | 106.22       | 138.52       | 155.35       | 163.52         | 35.55            |
|        | 10                 | 116.75       | 151.79       | 169.61       | 171.65         | 37.32            |
|        | 15                 | 126.12       | 159.62       | 178.61       | 159.87         | 34.75            |
|        | 20                 | 132.81       | 165.33       | 185.35       | 155.98         | 33.91            |
| EPFA   | 0                  | 101.13       | 139.17       | 163.99       |                |                  |
|        | 5                  | 110.28       | 147.32       | 172.52       | 123.65         | 47.56            |
|        | 10                 | 117.89       | 161.91       | 190.72       | 133.41         | 51.31            |
|        | 15                 | 129.69       | 170.69       | 199.37       | 168.09         | 64.65            |
|        | 20                 | 136.19       | 178.22       | 207.79       | 195.50         | 75.19            |

### Figure 9. DSC curves of non-isothermal curing of EMMY and EPFA.

### Figure 10. Linear plots of \(\ln(\beta/T_p^2)\) vs \(1/T_p\) based on the Kissinger equation.

![Figure 10](https://dx.doi.org/10.1021/acsomega.0c02166)
gradually, which is caused by the increase of flexible aliphatic chain, ester bond, and ether bond as discussed above. In addition, the gel content of EPFA was lower than that of other samples; this is due to the long aliphatic chains without epoxy groups in EPFA or oligomers in cured samples.

Each tan δ curve shows one peak, indicating that each cured sample has only one Tg and is homogeneous. With the increasing content of EMMY, the Tg of the cured epoxies increased from 17 to 71 °C. Generally, high gel content corresponds to high cross-link density in the same curing system. Thus, the high cross-linking density of EMMY also contributes to the increase of Tg, which is consistent with the results of the tensile test.

E’ is closely related to the cross-linking density, which can be determined according to the rubber elasticity theory. Thus, the experimental crosslinking density (νe) of the cured resins can be calculated, as follows:

\[ E' = 3\nu e RT \]

where E’ is the storage modulus of the cross-linked polymer in the rubber state, R is the gas constant, and T is the absolute temperature. In this study, the E’ at Tg + 20 °C was used, which ensured that the cured epoxies were in the rubber state. The calculated results of cross-link density are listed in Table 3.

The cross-link density of cured EMMY100 is higher than that of other samples, and with the increasing content of EPFA, the cross-link density is decreased. This is because the epoxy value of EMMY is higher than that of EPFA, which can provide more curing reaction site.
3.5. Tensile Properties. The representative stress–strain curves of the cured epoxy with different weight ratios of EMMY/EPFA are shown in Figure 14, and the detailed tensile and impact data are shown in Table 4. Clearly, the cured epoxy with 100% of EMMY exhibited the characteristic of a brittle fracture without showing the yielding point. The tensile strength and elongation at break were 39.31 MPa and 4.24%. While the cured epoxy with 100% of EPFA showed a low value in terms of tensile strength and elongation at break, and the tensile strength was only 0.85 MPa. With the increasing content of EPFA, tensile strength was decreased gradually while the elongation at break showed a trend of first increased and then decreased. This was because there were large number of flexible long aliphatic chain, ester bond and ether bond in the structure of EPFA, which would improve the toughness of cured epoxies significantly. Thus, the impact strength increased gradually with the increasing content of EPFA. The tensile strength and modulus of the cured epoxies was affected by the chemical structure and the cross-linking density of the cured system. There were many rigid alicyclic hexatomic structures in EMMY, and the epoxy value of EMMY was higher than EPFA, thus, the crosslinking density of EMMY was higher. All these factors endowed cured EMMY with higher tensile strength and modulus. Therefore, the tensile strength and modulus of the cured epoxies increased with the increasing content of EMMY.

We can notice that both the strength and strain of the pure cured EPFA were low. This could be explained by the lower epoxy value, lower crosslink density, and lack of a rigid alicyclic structure in EPFA. The chemical structures and cross-linked states of the cured epoxies varied along with the weight ratio of EMMY/EPFA. When the weight ratio of EMMY/EPFA is about 75/25, the cured epoxy showed a moderate strength of 15.96 MPa and relatively high elongation at break of 32.30%. Though the tensile strength is lower than other epoxy, the elongation at break is higher than the reported biobased epoxy and that of BPA-based epoxy usually no more than 5%. The good toughness was due to the incorporation of EPFA whose \( T_g \) is lower than EMMY, the EMMY acted as the rigid joint point, endowing the cured epoxies with high strength and long aliphatic in EPFA endowed it good toughness. When the cured sample was stretched, long aliphatic chain in the structure of EPFA moved more freely to offset the external forces and achieved a balance so it could endow the cured sample with higher ability to extend and high strain. When the weight ratio of EMMY/EPFA is about 50/50, the stress is 9.57 MPa while the strain is as high as 161.47%, which is 5 times as the sample of EMMY75/EPFA25. In the application, we can adjust the proportion of EMMY/EPFA to an appropriate value to meet the needs and obtain cured epoxies with good comprehensive properties.

3.6. Morphology of Fracture Surface. To observe the internal structure of the cured epoxies, the fracture surfaces of cured products after tensile tests were investigated by SEM (Figure 15). Obviously, the morphologies of the tensile fracture surfaces with different EMMY/EPFA weight ratios are very different from each other. Especially, the fracture surface of EMMY100 is extremely rough, and the crack is irregular, showing plenty of fish scale-like fragmental structures with microcrack (Figure 15a), which was due to the stress concentration during the stretch process. The low movability of rigid alicyclic structure in EMMY prevents the timely stress diffusion and thus causes crack propagation along different directions. Therefore, the fracture surface of EMMY100 presents a characteristic of brittle failure, which is in accordance with the tensile tests.

It can be seen from Figure15b–d that the fracture surfaces present a regular gully structure, this was related to the plastic shear deformation occurred in the internal of the cured epoxies when they were stretched. The gully-like structure gradually decreased with the increase content of EPFA, which can be explained by the fact that with the increasing content of EPFA, the flexible structure (such as aliphatic chain, ester bond, and ether bond) are increased. Under the external tension, the freely moving segments began to arrange orderly along the direction of the tension. When the external tension increased to a certain extent, the cured epoxy began to fracture from the weak part. The gully-like rough surfaces are related to the high failure energy dissipation, which would increase the elongation at break.

It is noticeable that EPFA has different fracture surfaces (Figure 15 e,f) from others, it has some serrated structure. Except for the serrated structure, the other parts of the fracture surface are flat and mirror-like. This is because when the tension is up to a certain value, the cured epoxies begin to tear

Table 4. Tensile and Impact Properties Data of the Cured Epoxy Samples

| sample         | stress (MPa) | strain (%) | tensile modulus (MPa) | impact strength (kJ/m²) |
|----------------|--------------|------------|-----------------------|-------------------------|
| EMMY100        | 39.31 ± 0.68 | 4.24 ± 0.32| 1012.55 ± 12          | 1.99 ± 0.06             |
| EMMY75/EPFA25  | 15.96 ± 0.40 | 32.30 ± 0.89| 825.47 ± 8.50         | 4.86 ± 0.16             |
| EMMY50/EPFA50  | 9.57 ± 0.21  | 161.47 ± 1.56 | 130.31 ± 2.25       | 8.86 ± 0.32             |
| EMMY25/EPFA75  | 2.91 ± 0.18  | 148.17 ± 1.23 | 88.80 ± 1.31         | 12.28 ± 0.33            |
| EPFA100        | 0.85 ± 0.06  | 40.49 ± 0.65 | 28.50 ± 1.22         | unbroken                |

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along the weak part of the material, thus showing a serrated tear section just like the fracture surface of rubber.

### 3.7. Thermal Stability Analysis

The curves of weight ratio against temperature are shown in Figure 16. Clearly, the TG curves of EMMY/EPFA with different weight ratios are similar trend, showing two-stage degradation. The first stage of weight loss is caused by the volatilization of some small molecules and the breaking of the unstable chemical bond. The second stage of weight is attributed to the breakdown of the main molecular chain, which shows a significant weight loss in the TG curves. As can be seen from the TG curves, the carbon residue of EMMY100 is significantly higher than that of other cured samples. This is due to that the heat resistance of the alicyclic structure in EMMY is better than aliphatic structure in EPFA. Generally, carbon residue of cured resin is inversely proportional to the hydrogen content of the resin. As EPFA contains more methyl and methylene than EMMY does, which

![Figure 15. SEM images of cured epoxy with different EMMY/EPFA weight ratios (a) EMMY100 (500×), (b) EMMY75/EPFA25 (500×), (c) EMMY50/EPFA50 (500×), (d) EMMY25/EPFA75 (500×), (e) EPFA100 (500×), and (f) EPFA100 (250×).]
will also reduce the carbon residue of the cured sample that contained EPFA.

4. CONCLUSIONS
Two novel biobased epoxy resin monomer derived from myrcene and epoxy fatty acid methyl ester were successfully synthesized. The pure cured EMMY was proved to be a rigid and brittle material with high tensile strength, hardness, and modulus. However, the toughness of pure cured EMMY was poor. Thus, EPFA which contained more flexible chain was used to copolymerize with EMMY to obtain materials with excellent comprehensive performance.

Tensile test showed that the stress and strain of cured EMMY100 were 39.31 MPa and 4.24%, respectively. When the weight ratio of EPFA was about 25 to 50 wt %, the toughness of cured EMMY/EPFA could reach as high as 161.47 MPa. The strain can significantly improved. The strain can increase from 17 to 71 °C with the increasing content of EMMY. The activation energy of curing reaction was 70.49 kJ/mol for EMMY and 64.02 kJ/mol for EPFA. The main degradation temperature was above 300 °C. Using renewable resources to synthesize epoxy resin monomers can reduce the reliance on a petroleum-based resource. Moreover, copolymerization of EMMY and EPFA made the cured epoxy with balanced toughness and strength. Thus, the biobased epoxy resin can be applied in preparation of flexible epoxy materials and can be used to toughen BPA epoxy resin.

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