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Study of green epoxy resins derived from renewable cinnamic acid and dipentene: Synthesis, curing and properties

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Abstract

An epoxy based on cinnamic acid (Cin-epoxy) and an anhydride curing agent based on dipentene were prepared. Both products are liquid of low viscosity at room temperature. For the synthesis of the epoxy, cinnamic acid was first converted to a diacid by reacting with maleic anhydride via Friedel-Crafts reaction, followed by allylation of the carboxylic groups and subsequent epoxidation of the allyl double bonds. The curing agent was the Diels-Alder adduct of dipentene and maleic anhydride (DPMA). The chemical structures of Cin-epoxy and DPMA were confirmed by ¹H NMR, ¹³C NMR, FT-IR and ESI-MS. Non-isothermal curing of Cin-epoxy was studied using differential scanning calorimetry (DSC). In addition to DPMA, two commercial anhydrides were also used to cure Cin-epoxy and the curing reactivity and properties of cured resins were compared. Thermal mechanical properties and thermal stability of the cured epoxy resins were studied using dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA), respectively. Results showed that Cin-epoxy was slightly more reactive than the bisphenol A type epoxy DER 332 and displayed good dynamic mechanical properties and thermal stability.

Keywords: Cinnamic acid, dipentene, biobased epoxy, Friedel-Crafts reaction

Introduction

Epoxy resins are extensively used for coatings, composites, electronic materials and adhesives. Mechanical, physical and chemical properties of epoxies can be greatly manipulated through selection of the epoxy and curing agent pair. Bisphenol A (BPA) is by far the most widely used intermediate chemical in epoxy synthesis. The rigid aromatic ring structure of BPA imparts high mechanical properties and thermal resistance to epoxy resins. Because BPA is a chemical estrogen,^{1, 2} the residual BPA in epoxy products, especially in food contact packaging, may pose a potential risk to human immune and reproductive systems.^{3, 4} In recent years, there is a growing interest in developing epoxy resins from the less toxic and renewable feedstocks. Various natural chemicals have been attempted for the syntheses of epoxies and curing agents.

Vegetable oils are probably the most studied renewable feedstock for various polymers.⁵⁻⁷ Use of epoxidized vegetable oils, such as soybean oil, linseed oil and castor oil, etc., for epoxy applications have been attempted in many studies.⁸⁻¹³ However, the internal epoxy groups of the epoxidized vegetable oils exhibited low curing reactivity and the presence of long aliphatic chains often resulted in unsatisfactory thermal and mechanical properties for the crosslinked materials. On the other hand, glycidyl carboxylate esters built on fatty acid-derived diacids or triaicd exhibited sufficiently high curing reactivity and the stiffness of cured resins could be greatly manipulated.^{14, 15} Glycerol, sorbitol and isosorbide were also attempted as feedstocks for epoxies in the literature, but the resulting epoxies alone did not demonstrate the properties suitable for structural and engineering polymer applications.¹⁶⁻¹⁸ The properties of epoxy resins are highly dependent on their molecular architectures. If the chemical structure of an epoxy resin contains aliphatic or other flexible chains, its thermal resistance would be inferior to that of those containing aromatic or cycloaliphatic rings. Therefore, rigid molecular structures are desirable

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for high performance epoxy resins. Lignin is a naturally occurring aromatic polymer and is abundantly available in many lignocellulosic biomass. Because lignin has some hydroxyl groups, use of lignin as a reactive component in epoxy resins have received a lot of study.¹⁹⁻²⁴ IBM reported the incorporation of Kraft lignin into epoxies for the fabrication of printed wiring boards in microelectronics industry.²⁵⁻²⁷ However, such lignin filled epoxy resins exhibited slow curing and unsatisfactory properties due to the poor compatibility of lignin with other ingredients in the resins.^{20, 21} Rosin acids are a family of isomeric natural chemicals and present in pines and conifers. The characteristic rigid hydrogenated phenanthrene ring structure imparts rosin-based epoxy resins excellent thermal and mechanical properties.^{14, 28-33} However, rosin-based epoxies and curing agents are usually solids of high melting points.

Cinnamic acid (CA) or β-phenyl acrylic acid is one of the basic natural phenylpropanoids. It can be obtained from oxidation of cinnamic aldehyde which is the major component in cinnamon bark oil. Nowadays CA is primarily used in food additives, perfume and pharmaceutical applications. On the other hand, the characteristic structure of CA also makes it an attractive resource for renewable chemicals and monomers. CA derivatives were used as building blocks to improve the properties of some polyesters in the literature.³⁴⁻³⁷ Semi-flexible and rigid main-chain polyesters containing photoreactive mesogenic units derived from CA were synthesized by high-temperature polycondensation.³⁵ In addition, CA-derived amidoamines, polyamides or amine adducts were used to cure the epoxy binders in the literature.³⁸

In this work, CA was converted to a novel glycidyl ester type epoxy as shown in Scheme 1. The resulting epoxy was a liquid of low viscosity and easy to mix with curing agents. Since the resulting epoxy had a rigid aromatic ring and short aliphatic moieties, it was expected to demonstrate moderate mechanical and thermal properties. Additionally, the adduct of maleic

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anhydride and renewable dipentene (DPMA) was prepared and used as a curing agent in this study. Curing of Cin-epoxy with DPMA, hexahydrophthalic anhydride (HHPA) and methyl nadic anhydride (MNA) was studied and the properties of the cured resins were compared. The objective of this work is to develop a synthesis method of CA-derived epoxy and evaluate the properties of the cured resins. To the best of our knowledge, a diglycidyl ester epoxy derived from CA has not been reported elsewhere.



Scheme 1. Synthetic routes of cinnamic acid-derived epoxy (Cin-epoxy) and adduct of dipentene and maleic anhydride (DPMA).

Experimental

Materials

Cinnamic acid (98.0%), allyl bromide (99.0%) and *meta*-chloroperoxybenzoic acid (*m*CPBA, 70-75%) were purchased from ACROS. Maleic anhydride (95.0%), succinic anhydride (> 99.0%), hexahydrophthalic anhydride (HHPA, 97.0%), palladium on carbon (10% Pd/C, loading 10 wt%), ammonium formate (HCOONH₄, 97.0%) and tetrabutylammonium iodide (98.0%) were purchased from Sigma-Aldrich. Methyl nadic anhydride (MNA, 99%) was purchased from Electron Microscopy Sciences. Dipentene was a product of technical grade obtained from China. Sodium bicarbonate (NaHCO₃, \geq 95%), dimethylformamide (DMF, 99.8%), methylene chloride (CH₂Cl₂, 99.8%), methanol (MeOH, 99.8%) and zinc powder were obtained from J. T. Baker.

Synthesis of Cin-epoxy

Hydrogenation of cinnamic acid: To the solution of cinnamic acid (2 g, 13.5 mmol) in MeOH (50 mL) was added HCOONH₄ (1.106 g, 17.55 mmol) and 10% Pd/C (170 mg). The reaction mixture was refluxed for two days. The spectrum of ¹H NMR indicated the reaction was completed. After filtration, the filtrate was concentrated by removing methanol using a rotary evaporator. The residual solid was extracted with ethyl acetate (EA, 50 mL) and the organic phase was washed with 1N HCl solution (3 x 30 mL) and then with brine (3 x 30 mL). The organic layer was dried by MgSO₄ and concentrated to give a white solid hydrocinnamic acid **1** (1.8 g, yield 90%). ¹H NMR (CDCl₃, δ ppm) 7.34-7.20 (m, 5H), 3.00-2.95 (t, 2H), 2.72-2.67 (t, 2H). ESI-MS m/z 149, [M-H⁺].

Synthesis of diacid 2 (Friedel-Crafts reaction): To a solution of 1 (1.0 mmol) and maleic anhydride (0.99 mmol) in dichloromethane (DCM) under stirring was slowly added $AlCl_3$ (2.0 mmol). The reaction was continued at room temperature for 12 h. The reaction was followed using thin layer chromatography (TLC). After completion of the reaction, DCM was removed

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and the remaining mixture was added into ice-HCl, extracted by tetrahydrofuran (THF). The organic phase was washed with brine, dried with MgSO₄ and concentrated. The residue was washed by EA/hexane (1/3 v/v) and filtered to give a yellow solid diacid **2**. ¹H NMR of diacid **2** (DMSO-*d6*, δ ppm) 7.96-7.93 (d, 2H), 7.89-7.84 (d, 1H), 7.43-7.41 (d, 2H), 6.67-6.62(d, 1H), 2.92-2.87 (t, 2H), 2.60-2.55 (t, 2H). ¹³C NMR of diacid **2** (DMSO-*d6*, δ ppm) 194.32, 178.96, 171.78, 153.21, 141.64, 139.63, 138.14, 134.40, 39.93, 35.74. ESI-MS m/z 247, [M-H⁺].

Synthesis of diacid 3: Zinc dust (6.028 g, 93.2 mmol) was added to a mixture of 2 (20 g, 81 mmol), AcOH (168 mL) and H₂O (48 mL) at room temperature. The reaction was continued for 3 h. TLC shows the reaction was completed. The mixture was added THF (200 mL) and then filtered to remove the white solid. The obtained filtrate was concentrated to give a white solid 3 (14.5 g, yield 72%). ¹H NMR (DMSO-*d6*, δ ppm) 7.88-7.85 (d, 2H), 7.38-7.35 (d, 2H), 3.20-3.16 (t, 2H), 2.89-2.84 (t, 2H), 2.49-2.48 (t, 4H). ¹³C NMR (DMSO-*d6*, δ ppm) 198.81, 175.22, 147.59, 135.17, 129.27, 128.63, 35.74, 33.88, 31.27, 28.79. ESI-MS m/z 249, [M-H⁺].

Synthesis of allyl 4-(4-(3-(allyloxy)-3-oxopropyl)phenyl)-4-oxobutanoate (compound 4): K_2CO_3 (12.16 g, 88.1 mmol), tetrabutylammonium iodide (2.952 g, 8 mmol) and allyl bromide (38.72 g, 320 mmol) were added to the solution of **3** (10 g, 40 mmol) in DMF (120 mL). The reaction mixture was stirred at 50 °C for 24 h and then was poured into ice-H₂O. The aqueous phase was extracted with DCM and the combined organic phase was washed with H₂O and brine, dried over MgSO₄, and the solvent was evaporated. The residue was purified via flash column chromatography (0%-10% EtOAc/hexanes) to yield a light yellow oil **4** (10.3 g, 78%). ¹H NMR (CDCl₃, δ ppm) 7.93-7.90 (d, 2H), 7.31-7.28 (d, 2H), 5.98-5.81 (m, 2H), 5.36-5.20 (m, 4H), 4.62-4.55 (m, 4H), 3.32-3.28 (t, 2H), 3.04-2.99 (t, 2H), 2.81-2.76 (t, 2H), 2.71-2.66 (t, 2H). ¹³C

NMR (CDCl₃, δ ppm) 197.60, 172.65, 172.13, 146.44, 134.97, 132.39, 132.26, 128.76, 128.51, 118.42, 118.22, 65.39, 65.34, 35.31, 33.40, 30.93, 28.29. ESI-MS m/z 353, [M+Na].

Epoxidation of compound 4 with meta-chloroperoxybenzoic (*mCPBA*): To a solution of the compound 4 (10.3 g, 31.2 mmol) in DCM (310 mL) was slowly added *mCPBA* (22.9 g, 99.86 mmol). After stirred at room temperature for 48 h, the reaction mixture was filtered to remove the white solid produced during the reaction. The filtrate was washed by 0.1N Na₂S₂O₃ solution, saturated aqueous NaHCO₃ and brine successively. The organic layer was dried over MgSO₄, filtered and concentrated to receive Cin-epoxy as a light a yellowish oil (10.117 g, 96.5%). ¹H NMR (CDCl₃, δ ppm) 7.93-7.90 (d, 2H), 7.32-7.29 (d, 2H), 4.46-4.40 (m, 2H), 4.01-3.86 (m, 2H), 3.33-3.29 (t, 2H), 3.24-3.16 (m, 2H), 3.05-3.00 (t, 2H), 2.87-2.60 (m, 8H). ¹³C NMR (CDCl₃, δ ppm) 197.68, 172.87, 172.35, 146.38, 135.00, 129.52, 128.84, 128.61, 121.70, 65.38, 65.32, 49.56, 49.48, 44.92, 44.84, 35.26, 33.44, 30.95, 28.25. ESI-MS m/z 363,[M+H⁺]. The viscosity of Cin-epoxy was 0.67 Pa·s.

Synthesis of adduct of dipentene and maleic anhydride (DPMA)

Maleic anhydride (9.8 g, 0.1 mol) was charged into a flask equipped with a stirrer, dropping funnel, inert gas inlet, thermometer, and reflux condenser. The temperature was raised to 180 °C, and dipentene (13.62 g, 0.1 mol) containing iodine (12 mg, 0.047 mmol) was added slowly. The reaction continued for 3 h at 200 °C after all the dipentene and iodine were added. The crude product (23.42 g) was purified by silica column using a hexane/ethyl acetate (6/1 v/v) as solvent, resulting pure DPMA (yield: 18.03 g, 77%). ¹H-NMR (CDCl₃, δ ppm) 6.07-6.10 (d, 1H), 5.99-6.02 (d, 1H), 3.20-3.23 (d, 1H), 2.83-2.86 (d, 1H), 2.48-2.62 (m, 1H), 1.49 (s, 3H), 1.29-1.48 (m, 4H), 1.06-1.08 (d, 3H), 0.99-1.01 (d, 3H).

Curing of the epoxy resins: Cin-epoxy and curing agent (HHPA, DPMA or MNA) in a 1:0.9 molar ratio together with 2-ethyl-4-methylimidazole (1wt% on the basis of the total weight of curing agent and epoxy) were mixed well (when HHPA was used, the mixture was first heated up to 40 °C). The mixture was transferred into a mold of 5 cavities with dimensions of 50 mm x 18 mm x 5 mm. The curing was performed at 150 °C for 2 h and then at 180 °C for 2 h. The cured samples were carefully removed from the mold and used for dynamic mechanical analysis and thermal tests.



Characterizations

¹H NMR spectra of the chemicals in CDCl₃ or DMSO-*d6* were recorded using a Bruker 300 MHz spectrometer at room temperature. Fourier transform infrared (FTIR) spectra were recorded from 4000 cm⁻¹ to 400 cm⁻¹ using a NEXUS 670 FT-IR spectrometer (Nicolet). The FTIR samples were prepared by dissolving a small amount of compound in DCM, followed by smearing the solution onto a KBr crystal plate and evaporating the solvent completely. Mass spectra were recorded with a LCQ advantage mass spectrometer system (Thermo Finnigan).

Viscosity of the epoxy was measured using a Discovery HR-2 rheometer (TA Instruments). Tests were performed using a steel parallel-plate geometry (d = 25 mm) with a gap of 500 µm at 25 °C, and the shear rate was swept from 10 to 1.0 s⁻¹.

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Non-isothermal curing of the epoxy resins was performed by differential scanning calorimetry (DSC) on a 2920 MDSC instrument (TA Instruments) under a nitrogen atmosphere. Heat scans ranging from 30 to 280 °C were performed at heating rates of 2.5, 5, 10, 15, 20 °C min⁻¹, respectively. The formulations of the samples for DSC analysis were the same as those used for the test specimens for dynamic mechanical analysis (DMA). Approximately 6 mg of each sample was weighed and sealed in a 40 μ L aluminum crucible and the DSC curing was conducted immediately. DSC analysis for each sample was repeated twice.

DMA was carried out on a TA Q800 analyzer (TA instruments) in a single-cantilever mode with an oscillating frequency of 1 Hz. All samples were tested from 30 to 180 °C at a heating rate of 3 °C min⁻¹. Two repeats of DMA test were performed for each sample. Thermogravimetric analysis (TGA) was performed on a TA Q600 analyzer (TA Instruments). Each sample was scanned from 50 to 600 °C at a heating rate of 5 °C min⁻¹ under a nitrogen atmosphere.

Results and Discussion

Synthesis of Cin-epoxy

Scheme 1 shows the synthetic route of Cin-epoxy. In order to synthesize the diacid **3** intermediate, two methods were investigated. First, the Friedel-Crafts reaction of succinic anhydride and hydrocinnamic acid was attempted to produce the diacid **3**. However, this method gave a very low yield of conversion ($\sim 20\%$). ¹H NMR analysis (spectrum not shown) revealed a lot of unreacted succinic acid remained in the product. It was difficult to purify the product because the diacid **3** and succinic acid had very similar properties. On the other hand, the Friedel-Crafts reaction of maleic anhydride and hydrocinnamic acid gave a good yield of diacid **2** (81%). Furthermore, the resulting diacid **2** could be easily purified by washing with EA/hexane

(v/v=1/3) to remove the small amount of unreacted CA (cinnamic acid). No maleic acid was noted in the ¹H NMR and ¹³C NMR (SI) spectra of the crude product. Because the conjugation of C=C and C=O in maleic acid helped to form much more stable carbocation than succinic acid,³⁹ this Friedel-Crafts reaction yielded a high conversion. The subsequent reduction of the double bond of maleate in diacid **2** using Zn powder in HAc/H₂O also gave a high yield (80%)⁴⁰ and the obtained diacid **3** could be used directly for the next step of reaction without further purification.

The synthesis of the glycidyl ester was first attempted by reacting diacid **3** with epichlorohydrin (ECH) and this process was a two-step reaction involving ring opening of the oxirane of ECH and dehydrochloration in the presence of NaOH. However, the first step produced more than three compounds including two mono- and one di-substituted compounds. Additionally, these intermediates continued to react with ECH. Therefore, the reaction of diacid **3** with ECH led to a non-controlled glycidylation. In order to receive a purer product, the epoxy was prepared by first forming allyl ester followed by epoxidation of the allyl double bonds. The allylation of diacid **3** by allyl bromide gave a decent yield (78%) of compound **4** after purification using column chromatography. The molecular structure of **4** was identified by ¹H NMR and ¹³C NMR (SI). The epoxidation was carried out using *m*CPBA. When the equivalent of *m*CPBA was higher than 1.6 times that of **4**, byproduct would be formed. A high yield of 96.5% was achieved at 1.6 eq *m*CPBA. The epoxy equivalent weight was found to be 200 g/mol by titration using the acetone hydrocloride method.

1H NMR confirmed the structure of Cin-epoxy. In the ¹H NMR spectrum of Cin-epoxy (Figure 1), the protons attributed to the allylic double bonds at 5.0-6.0 ppm disappeared completely, instead, the new peaks attributed to the protons of oxirane at 3.15-3.24 (c, d) and 2.60-2.87 (e, f) ppm presented. In addition, the chemical shift of allyl proton (-CH₂-) in compound **4** was shifted

from 4.50-4.66 ppm (SI-Figure S3) to 3.86-4.01 and 4.40-4.46 ppm (a, b) in the glycidyl groups. The chemical structure of Cin-epoxy was further verified using ¹³C NMR (Figure 2). After epoxidation, the peaks of the four carbons (c, d, e, f) in double carbon bond were at 49.43 - 49.56 and 44.84-44.92 ppm.



Figure 1. ¹HNMR spectrum of Cin-epoxy.



Figure 2. ¹³C NMR spectrum of Cin-epoxy.

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Synthesis of adduct of dipentene and maleic anhydride (DPMA)

The synthetic route of DPMA is illustrated in Scheme 1. The reaction first involved the isomerization of dipentene to terpinene in the presence of iodine, and then terpinene reacted with maleic anhydride via Diels-alder reaction.⁴¹ Nonetheless, these two reaction processes were carried out in a one-step reaction, and the reaction gave a yield of 77%. The obtained DPMA was a yellowish liquid and was able to mix with Cin-epoxy easily. Figure 3 shows the ¹H NMR spectrum of DPMA. The chemical shift of the protons i was higher than that of the protons because the shielding effect of the methyl group was weaker than that of the isopropyl group.

Figure 3. ¹H NMR spectrum of DPMA.

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Curing behavior

Cin-epoxy appeared a colorless liquid with a viscosity of 0.67 Pa·s which was much lower than that of DER332 (3.31 Pa·s). Therefore, it was mixed easily with all curing agents selected. Figure 4 shows the DSC thermograms of non-isothermal curing of Cin-epoxy with HHPA, DPMA and MNA systems. Each sample displayed a main exothermic peak in its DSC curing thermogram which corresponded to the ring-opening reaction between epoxy and anhydride groups. With increasing heating rate, the peak exothermic temperature shifted to higher temperatures. This shift of peak curing temperature with heating rate was a typical methodological phenomenon for non-isothermal curing. The peak temperature of exothermic peak usually reflects the reactivity of the compound in curing reaction. HHPA seemed to be slightly more active than DPMA and MNA under the same heating rate (Figure 4a-4c). By comparing the curing results of Cin-epoxy and bisphenol A type epoxy resin (DER 332) with the same MNA that reported in our early study,¹⁵ it was noted that the peak curing temperature of Cin-epoxy (146.5 °C) was much lower than that of DER332 (152.9 °C) at heating rate 5 °C/min. This result indicates that the reactivity of Cin-epoxy was higher than that of DER 332.

The activation energy of the curing reaction was determined by the Kissinger's method. The activation energy could be obtained from the Kissinger's equation:

$$\frac{d[\ln(q/T_p^2)]}{d[1/T_p]} = -\frac{E_a}{R}$$
(1)

Here T_p is the peak exothermic temperature, q the constant heating rate, E_a the activation energy of the curing reaction, and R is the gas constant with the value of 8.314 J mol⁻¹·K⁻¹ (Figure 5). At the same time, the activation energy was also determined by the Ozawa method. Table 1 lists the

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activation energies of curing of Cin-epoxy with three different curing agents. As it can be seen, the two methods gave very similar E_a values. In curing with MNA, Cin-epoxy exhibited a lower activation energy than DER322 (63.3 KJ mol⁻¹ vs. 79.9 KJ mol⁻¹),¹⁵ which indicated Cin-epoxy was more reactive. Because Cin-epoxy has a more flexible molecular structure than DER 332, therefore, it is likely to exhibit high reactivity that DER 332 under the same reaction conditions.

Figure 4. DSC thermograms of non-isothermal curing of Cin-epoxy with HHPA (a), MNA (b)

and DPMA (c).

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Figure 5. Linear plot of $-\ln(q/T_p^2)$ versus $1/T_p$ based on Kissinger's equation.

Tabla 1	Curing	activation	anarow of	Cin anovy	y and thermal	nronartias	of the cured	raging
Table 1.	Curing	activation	energy of	Cm-epoxy	y and thermal	properties	of the curec	resms

	E_a /KJ mol ⁻¹		DMA			TGA ^a	
Sample	Ozawa	Kissinger	$T_g(^{\circ}\mathrm{C})$	E' at T_g +50	$v_e(x10^3)$	$T_{5\%}$	$T_{10\%}$
				°C(MPa)	$mol mm^{-3})$	$(^{\circ}C)$	$(^{\circ}C)$
Cin-epoxy/DPMA	77.6	74.7	85.4	9.69	0.95	301.1	325.3
Cin-epoxy/HHPA	75.7	72.9	90.4	13.99	1.36	331.5	352.3
Cin-epoxy/MNA	66.8	63.3	116.6	21.9	2.00	328.0	355.0

^a $T_{5\%}$ and $T_{10\%}$: temperature of 5% degradation and 10% degradation.

Dynamic mechanical analysis

Figure 6 shows the storage modulus (*E'*) and damping (tan δ) as functions of temperature for Cin-epoxy resins cured with different curing agents. The glass transition temperatures (*T*_gs) of the cured samples were determined from the peak temperatures of the tan δ . The *v*_e of the cured Published on 16 January 2014. Downloaded by Aston University on 21/01/2014 20:24:08.

Cin-epoxy resin was estimated using the following equation based on the theory of rubber elasticity:

$$v_e = \frac{E}{3RT} \tag{2}$$

where *E* is the elastic modulus of the thermoset in the rubbery state, R is the gas constant and T is the absolute temperature. Since measuring the elastic modulus of thermoset in rubbery state is a very tedious experiment, it is a convenient custom to use *E*' in the rubbery state, e.g., at T_g + 50 °C, to roughly substitute *E* in the calculation.

The DPMA and MNA cured Cin-epoxy resins had similar E's at room temperature, which were both higher than that of the HHPA cured resin. This was probably because DPMA and MNA had more bulky structures than HHPA and therefore resulted in more rigid glassy resins at room temperature. In Table 1, it is noted that the T_g s of the HHPA and DPMA cured resins were similar but both were lower than that of the MNA cured resin. It is understood that the T_g of an epoxy network is dependent on both crosslink density and the chemical structure of the chain segment. Higher crosslink density and more rigid chain segment both lead to a higher T_g . The former is determined by the curing reactivity, molecular structure and mobility of curing agent and epoxy. As suggested by the activation energy of curing, MNA had the highest reactivity among the three curing agents. In addition, MNA was already a liquid at room temperature and was probably still more accessible in the late stage of curing when the curing was controlled by diffusion. Therefore, the MNA cured Cin-epoxy exhibited the highest v_e and T_g in the three cases.

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Figure 6. Storage modulus (a) and tan δ (b) *versus* temperature for Cin-epoxy cured with DPMA, HHPA and MNA.

Thermogravimetric analysis (TGA)

TGA is a convenient method to evaluate the thermal stability and degradation behaviors of polymers. Figure 7 shows the TGA curves of the cured Cin-epoxy resins under nitrogen atmosphere. Table 1 gives the temperatures at which 5% weight loss ($T_{5\%}$) and 10% weight loss ($T_{10\%}$) were incurred. These three cured resins displayed very similar weight loss curves at the initial stage. Cin-epoxy/MNA exhibited a $T_{5\%}$ of ~328.0 °C which was about equal to that of DER332/MNA (327.1 °C).¹⁵ This result suggested that Cin-epoxy had a comparable thermal stability to that of BPA-based epoxy resins. The Cin-epoxy resins cured with HHPA and MNA exhibited almost the similar $T_{5\%}$ (331.5 °C, 328.0 °C) and $T_{10\%}$ (352.3 °C, 355.0 °C), which were higher than that (301.1 °C, 325.3 °C) of the Cin-epoxy cured with DPMA. In other words, the Cin-epoxy resins cured with HHPA and MNA were more thermally stable than the Cin-epoxy resins had higher crosslink densities than the latter one (Table 1).

Figure 7. TGA plots of the cured epoxy resin under nitrogen atmosphere.

Conclusions

A cinnamic acid-derived epoxy and a dipentene-derived anhydride curing agent were successfully synthesized. Unlike the traditional method for the synthesis of glycidyl ester which involves the reaction of carboxylic acid and epichlorhydrin, in the synthesis of Cin-epoxy a two-step method involving allylation of the carboxylic groups and subsequent epoxidation was employed. This two-step method resulted in a high yield and few byproducts. Cin-epoxy and DPMA were both liquid products and displayed comparable properties in curing compared to some petroleum-based commercial epoxies and curing agents. The T_g of the renewable DPMA cured Cin-epoxy was similar to that of the resin cured with HHPA but was lower than that of MNA cured one. In curing with MNA, Cin-epoxy exhibited slightly higher reactivity than DER

332. The Cin-epoxy resin cured with MNA exhibited a moderate T_g of 116 °C. In general, these

results suggest that Cin-epoxy is a potential alternative to some of the petroleum-based epoxies.

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An epoxy based on cinnamic acid and an anhydride curing agent based on dipentene were prepared.