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A self-crosslinking thermosetting monomer with both epoxy and anhydride groups derived from tung oil fatty acids: Synthesis and properties ☆

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ABSTRACT

A self-crosslinking compound with epoxy groups and anhydride groups (GEMA) was successfully synthesized from tung oil fatty acid by reacting with maleic anhydride via the Diels–Alder reaction. GEMA has very good storage stability and could be cured with trace amounts of tertiary amine. This advantage avoided the nonuniformity, bubbles and insolubility during the mixing procedure of the epoxy resins and curing agents. Compared to commercial Bisphenol A epoxy resins, GEMA has relatively lower mechanical properties and thermal properties. However, in view of its renewable properties, GEMA is still a very promising bio-based epoxy which may replace bisphenol A epoxy resins in some applications.

1. Introduction

Epoxy resin is one of the most important thermosetting resins. The cured epoxy resins are of high crosslinked network that often exhibit high tensile strength and modulus [1], excellent chemical and corrosion resistance [2], and good thermal stability [3]. However, the ordinary epoxy resin cannot crosslink alone without curing agents or accelerant. In order to convert the resins to practical materials, it is necessary to add a curing agent. Most of the epoxy curing agents in common use are polyfunctional amines [4,5], tertiary amines [6,7], anhydrides [8] and other latent curing agents [9,10]. During the mixing procedure of the resins and curing agents, nonuniformity, bubbles and insolubility are unavoidable. Some epoxy resins or

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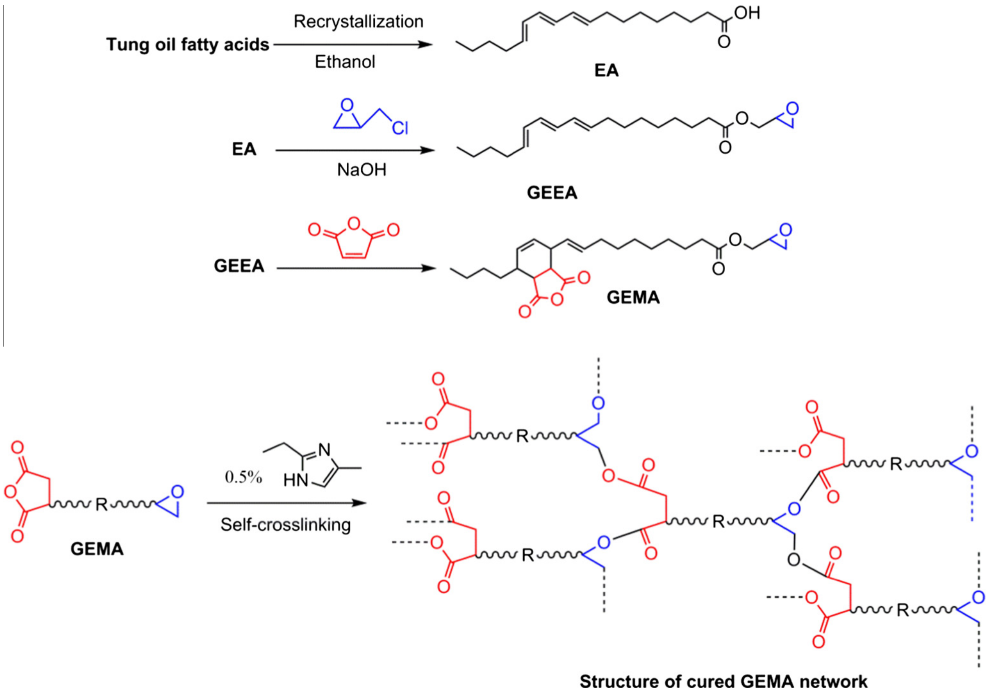


Scheme 1. The synthesis route of GEMA and the structure of cured GEMA network.

curing agents are too viscous to blend, so organic solvents must be added to lower their viscosity. The organic solvents then evaporate into the air, causing some environmental or health problems.

To overcome these problems, Mikroyannidis synthesisized a series of self-curing epoxides bearing azomethine linkages [11]. These glycidyl ethers and esters contain free carboxyl, amino, or phenolic hydroxyl groups in their molecules, and they can be thermally crosslinked without adding a curing agent. Nevertheless, these self-curing epoxides containing an epoxy group and the other active group (carboxyl, amino, or phenolic hydroxyl), can only be converted into linear polymers rather than network polymers. These linear polymers no longer maintained the thermosetting properties of epoxy resins.

Generally, cyclic anhydrides could be one of the most important epoxy curing agents for high temperature curing. The mechanism of the curing reaction for epoxy resin with anhydride in the presence of tertiary amine catalysts has been investigated by several authors [12,13]. Tertiary amine attacks the carboxylic group in the anhydride structure, which leads to the opening of the anhydride ring. After that, a carboxyl anion is formed on the other end of the opened ring. The reaction propagates by attacks of the anion on the epoxide group to form an ester-alkoxide anion that can, in turn, react with anhydride to form an ester linkage and another carboxyl anion to propagate the reaction. Therefore, one epoxy group and one cyclic anhydride group could be enough to form tridimensional network structures.

In this work, a self-crosslinking monomer was synthesized from tung oil fatty acids, and the synthesis route and the crosslinked network were shown in Scheme 1. This compound has one epoxy group and one cyclic anhydride group, which can crosslink alone by epoxy/anhydride ring-opening reaction with catalyst. The curing behavior of the monomer, dynamic mechanical and tensile properties of the cured material were also investigated in this study.

2. Experimental

2.1. Materials

Tung oil was obtained from the Institute of Chemical Industry of Forestry Products (Nanjing, China). Epichlorohydrin (99%), sodium hydroxide (97+%), maleic anhydride (99%), benzyltriethylammonium chloride (97%), acetone (99%) and 2-ethyl-4-methylimidazole (99+%) were obtained from Sigma–Aldrich (St. louis, MO, USA) and used as received.

2.2. Synthesis

2.2.1. Preparation of EA

EA was prepared and purified in accordance with Refs. [14,15]. Tung oil (200 g) was stirred by refluxing with 60 g potassium hydroxide, 50 ml water, and 500 ml of 95% ethanol at 90 °C for 0.5 h. After cooling, the soap was acidified in a separatory funnel with 725 ml of 2 N hydrochloric acid. The liberated fatty acids were separated from the aqueous phase and dissolved without further treatment in 1000 ml of 95% ethanol. This solution was kept for 24 h at −20 °C to promote the formation of acid crystals. The very light-colored crystals were filtered and washed with about 75 ml of cold 95% ethanol, followed by vacuum drying. Both dark and light colored crystals were isolated for a total mass of about 142 g. Acid value was 201.3 mg/g (theory: 201.8 mg/g). ESI-MS: 277.2 $[M-H^+]$.

2.2.2. Synthesis of GEEA

GEEA was prepared and purified in accordance with Ref. [14]. To a 50 ml flask, equipped with reflux condenser, magnetic stirrer and thermometer were charged 55.60 g (0.20 mmol) EA, 185.00 g (2.00 mol) epichlorohydrin and 0.24 g (0.001 mol) benzyltriethyl ammonium chloride. The reaction temperature was increased to 117 °C and the reaction continued at that temperature for 2 h. After the mixture was cooled to 60 °C, 8.00 g (0.20 mol) sodium hydroxide was charged. The mixture was stirred at 60 °C for 3 h and then filtered. The filtrate was distilled under vacuum to recycle the excess epichlorohydrin, 62.60 g yellowish liquid was obtained with an epoxide equivalent weight 380 g/mol (theory: 334 g/mol). The product was purified using a silica gel column (ethyl acetate: hexane = 1: 10 v/v) to receive 59.00 g of a pure colorless liquid for analysis (yield: 88% relative to EA). Electrospray ionization mass spectrometry (ESI-MS) shows: 335.25735 $[M+H^+]$, 357.23917 $[M+Na^+]$, 373.23373 $[M+O+Na^+]$, 389.22845 $[M+2O+Na^+]$, 405.22351 $[M+3O+Na^+]$. The theoretical value are 335.25873 $[M+H^+]$, 357.24056 $[M+Na^+]$, 373.23996 $[M+O+Na^+]$, 389.23396 $[M+2O+Na^+]$, 405.23336 $[M+3O+Na^+]$.

2.2.3. Synthesis of GEMA

To a 100 ml flask, equipped with reflux condenser, magnetic stirrer and thermometer were charged 33.4 g (0.1 mol) GEEA and 9.8 g (0.1 mol) maleic anhydride. The reaction temperature was increased to 90 °C and the reaction continued at that temperature for 2 h. 43.2 g liquid was obtained. The viscosity of GEMA at 25 °C is 1331 mPa s. The crude product was purified using a silica gel column (ethyl acetate : hexane = 1: 10 v/v) producing a pure colorless liquid for ^1H and ^{13}C NMR analysis and ESI-MS. ESI-MS: 455.24202 $[M+Na^+]$. The theoretical value is 455.24096 $[M+Na^+]$.

2.3. Preparation of test specimens

The GEMA used was a crude product which was not purified by silica gel column. 2-ethyl-4-methylimidazole was used as the catalyst and was added at 0.5 wt% on the basis of total weight of GEMA. The resin was preheated at 90 °C, and then the resin was charged in a steel mold preheated at 120 °C. The mold for tensile test is based on ASTM D 638 Type V. The dimensions of the mold for dynamic mechanical analysis (DMA) was 65 × 13 × 3 mm. Curing was performed at 120 °C for 2 h and then at 160 °C for 4 h. The cured specimens were carefully removed from the mold and examined for tensile test and DMA.

2.4. Characterizations

^1H NMR and ^{13}C NMR spectra of the compounds in deuterated chloroform ($CDCl_3$) were recorded with a Bruker 400 MHz spectrometer (Bruker, Rheinstetten, Germany) at room temperature. FT-IR spectra were recorded using a Thermo Nicolet Nexus 470 spectrometer (Madison, WI, USA). Mass spectra were recorded with an LTQ Orbitrap Discovery electrospray ionization mass spectrometry (ESI-MS) instrument (Madison, WI, USA). Viscosity was tested by TA ARES-G2 rheometer. The sample was loaded in a 25 mm steel parallel plate with a gap of 500 μm and swept from a shear rate of 100 to 0.1 s^{-1} at 25 °C.

Curing behavior was studied by differential scanning calorimetry (DSC) using a DSC 2910 (TA) instrument (New Castle, DE, USA). Approximately 5–10 mg of each sample was weighed and sealed in 40 μL aluminum crucible and the curing on DSC was performed immediately. DSC analysis for each sample was repeated twice.

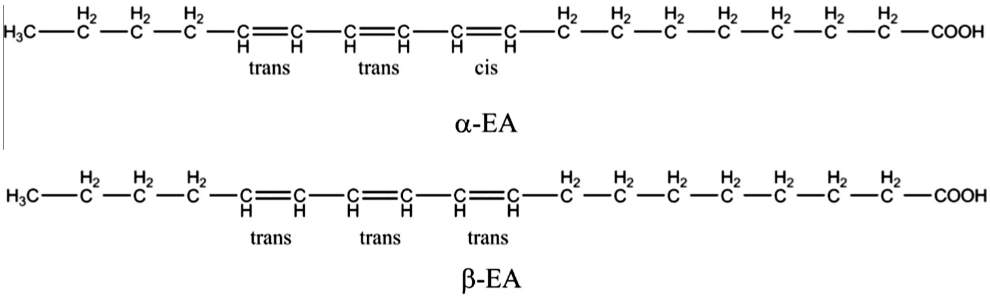
Dynamic mechanical analysis (DMA) was conducted by using a DMA Q800 (TA) instruments (New Castle, DE, USA) in a dual cantilever mode with an oscillating frequency of 1 Hz. The temperature was swept from 25 to 165 °C at 3 °C/min. For each sample, duplicated tests were performed in order to ensure the reproducibility of data.

Tensile properties were measured using an Instron 4201 equipped with a 1 kN electronic load cell according to ASTM D 638 Type V. The tests were conducted at a crosshead speed of 10 mm/min. All samples were conditioned at 50% humidity and 23 °C for 2 days prior to tensile testing. Five replicates were tested for each sample to obtain an average value.

3. Results and discussion

3.1. Synthesis

Eleostearic acid (EA) was purified from tung oil fatty acids based on the method reported by Hoffmann et al. [15]. The purified EA contains 98% α-EA and 2% β-EA, seen in Scheme 2. Hence, the primary α-EA was treated as a starting feedstock for synthesis and characterization in this work. According to our previous research, there are three conjugated double bonds in the molecule of α-EA, but only the conjugated diene with cisoid conformation could react with maleic anhydride through



Scheme 2. The structure of α-EA and β-EA.

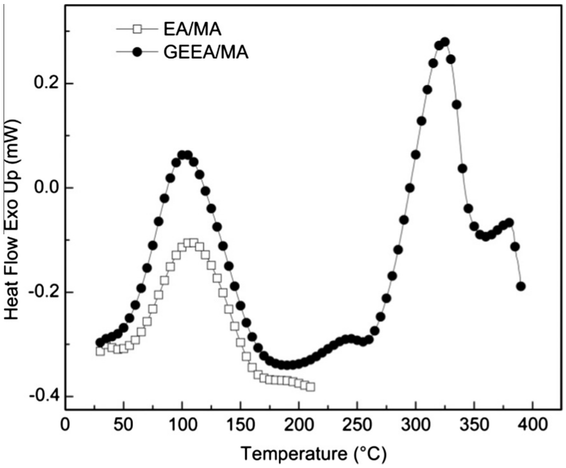


Fig. 1. The non-isothermal DSC scanning of the reaction between GEEA and MA at a heating rate of 10 °C/min.

Diels–Alder reaction [16]. In other words, the Diels–Alder reaction occurs between 11 and 14 carbons when GEEA is reacting with maleic anhydride to form GEMA.

GEMA was synthesized from the Diels–Alder reaction between GEEA and maleic anhydride. GEEA has a epoxy ring while maleic anhydride is an anhydride. It was reported that dynamic DSC tests performed on the mixture of bisphenol epoxy resin and anhydride without a catalyst did not show any reaction peak up to 250 °C [17]. In order to investigate whether the epoxy react with anhydride during the synthesis of GEMA, the non-isothermal DSC scanning of the reaction between GEEA and MA at a heating rate of 10 °C/min was demonstrated in Fig. 1. For a comparison, EA/MA was selected as a model system because EA would react with MA only by DA reaction. The scanning curve of EA/MA displayed a single exothermic peak around 105 °C. To avoid the evaporation of EA or MA, the scanning range was limited to no more than 220 °C. For GEEA/MA, there were two exothermic peaks, one was at a lower temperature (~105 °C) and the other was near the degradation temperature (~325 °C). The former peak should be caused by the Diels–Alder reaction of GEEA with MA, whereas the latter can probably be attributed to the reaction between epoxy and anhydride groups in the absence of catalyst. This result indicated that the epoxy/anhydride reaction hardly proceeded without any catalyst below 250 °C, but the Diels–Alder reaction tends to be much more active.

To gain further knowledge of the chemical groups involved during the synthesis of GEMA, the FT-IR spectra of GEEA/MA mixture and GEMA were illustrated in Fig. 2. Fig. 2(a) is the spectra of GEEA/MA mixture before reaction. The weak peak at 3114 cm^{-1} was due to the C—H stretching of MA. The strong peak observed at 1055 was assigned to the double bond C—H bending of MA. The strong band at 993 cm^{-1} should be attributed to the conjugated double bonds of GEEA. The typical anhydride C═O stretching of MA were found at 1849 and 1776 cm^{-1}. The characteristic peak of the epoxy group was observed at 908 and 761 cm^{-1}. Fig. 2(b) showed that all characteristic peaks from the double bond of MA, and the conjugated double bonds of GEEA had disappeared due to Diels–Alder reaction. However, there was no obvious change related to the peaks of both epoxy groups and the anhydride group under these conditions. This result suggested it is difficult for the mild synthesis conditions of GEMA to initiate the epoxy/anhydride reaction.

3.2. Characterization

GEMA was characterized by ^{1}H NMR, ^{13}C NMR and Distortionless Enhancement of ^{13}C NMR signals by Polarization Transfer (DEPT ^{13}C NMR). The proton chemical shifts of GEMA were labeled in Fig. 3. The chemical shifts at 2.64 (1H), 2.84 (1H), 3.21 (1H), 3.90 (1H) and 4.41 (1H) ppm showed the typical peaks of five protons in the glycidyl ester group, which

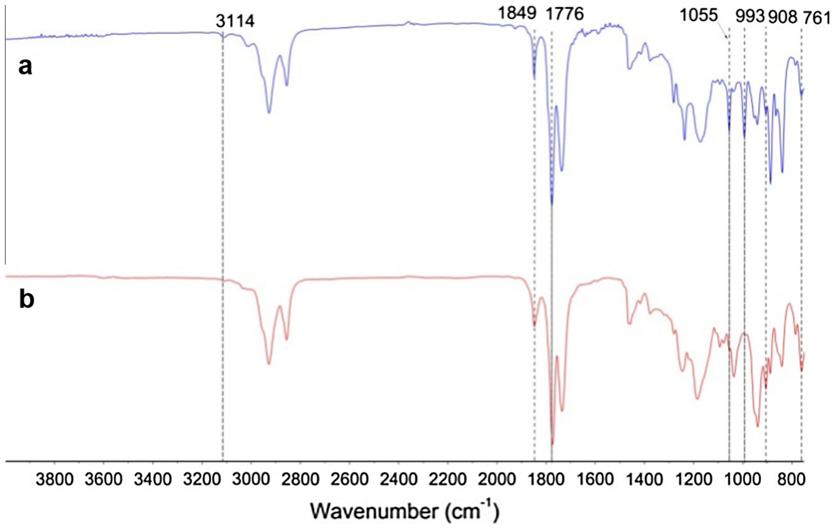


Fig. 2. The FT-IR spectra of GEEA/MA mixture (a) and GEMA (b).

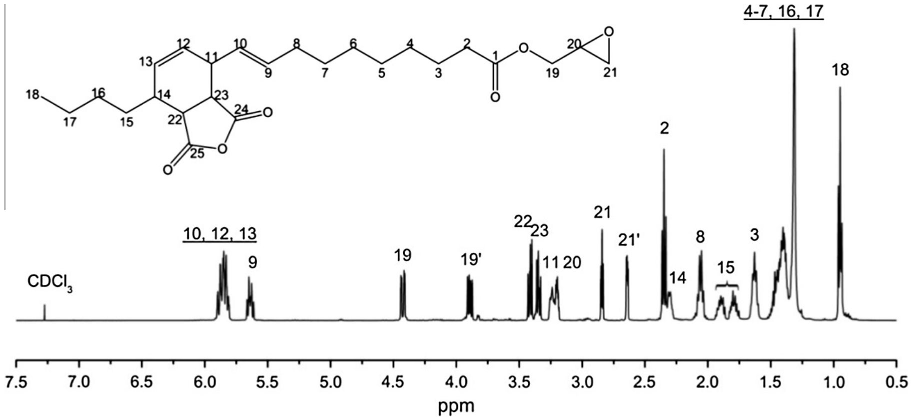


Fig. 3. The ^{1}H NMR of GEMA.

indicated the existence of an epoxy group. The peaks at 2.30, 3.24, 3.35 and 3.42 ppm are the chemical shifts of protons in the cyclohexenyl formed by the Diels–Alder reaction between GEEA and MA. The peaks around 5.63 (1H) and 5.85 (3H) ppm are the chemical shifts of double bond protons which proved that the three conjugated double bonds of GEEA had been converted into two double bonds. Fig. 4 is the ^{13}C NMR of GEMA. The chemical shifts of 25 carbons in GEMA and the corresponding structural assignments are labeled in Fig. 4. The CH_3 resonance is at 14 ppm. The CH_2 carbon peaks are in the 22.60–30.40 ppm range, which are assigned to number 2–8 and 14–17 carbons. The CH carbon between the two double bonds labeled as number 11 is at 33.65 ppm. The number 20–23 carbons are in range of 44.59–49.38 ppm. The CH_2 beside the epoxy ring is at 64.77 ppm. The chemical shifts are in a range of 127.14–133.68 ppm, and are attributed to carbons of double bonds. Three carboxyl carbons are in the range of 171.24–173.16 ppm.

To get more detailed structural information from GEMA, the DEPT ^{13}C NMR spectra (θ_{135}) should be an effective method to identify the methine (CH), methylene (CH_2) and methyl (CH_3) carbon types. Fig. 5 is the spectra acquired with a 135° proton pulse. It shows CH and CH_3 phased up while CH_2 are phased down [18]. The methine carbons of double bonds are C9, C10, C12 and C13. Other methine carbons are C11, C14, C20, C22 and C23. The methyl carbon is C18. The methylene carbons which total 12 carbons are C2–8, C15–17, C19 and C21. Except for the three carboxyl carbons that could not be displayed in the spectra, there are a total of 22 carbons of GEMA clearly indicated by Fig. 5. The DEPT ^{13}C NMR spectra fits well with the structure of GEMA.

3.3. Curing behavior

The curing behavior of GEMA was investigated through DSC and Soxhlet extraction. Curing kinetics were studied using a 2910 MDSC (TA Instruments) instrument. GEMA and 2-ethyl-4-methylimidazole (0.5 wt% on the basis of the weight of GEMA) were mixed. The sample was scanned from 25 to 250 °C at heating rates of 5, 10, 15, and 20 °C/min, respectively.

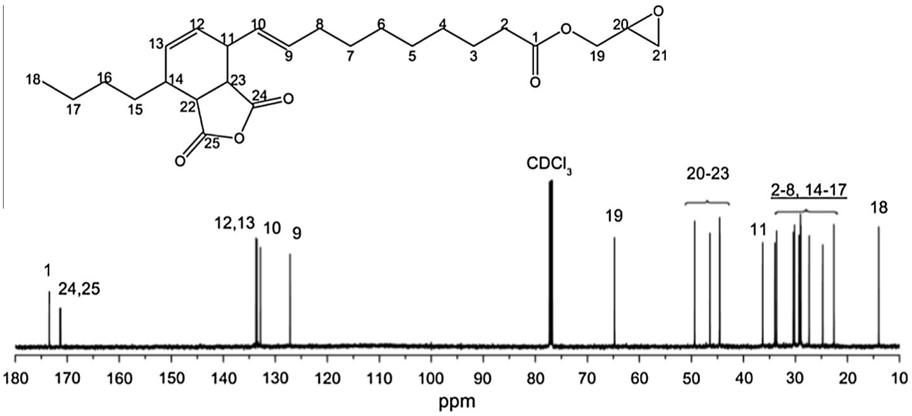


Fig. 4. The ^{13}C NMR of GEMA.

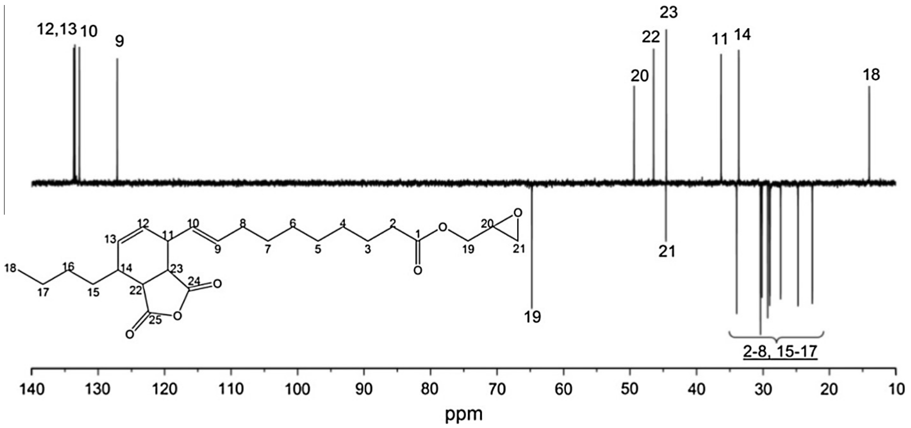


Fig. 5. The DEPT ^{13}C NMR of GEMA.

For detailed information on the curing procedure, the Ozawa method was used to determine the activation energy during the curing. The Ozawa method yields a simple relationship between the activation energy (E_a), the heating rate, and peak temperature at different heating rates, giving the E_a as [19]:

$$E_a = \frac{-R}{1.052} \frac{\Delta \ln \phi}{\Delta(1/T_p)}$$

where ϕ is the heating rate, T_p the peak temperature (absolute temperature) at different heating rates and R the universal gas constant.

Fig. 6 shows the DSC thermograms of the curing of the four epoxies at different heating rates and Fig. 7 shows the plots of $1/(T_p)$ versus $\ln(\phi)$ and the slopes are used to calculate E_a. The curing of each epoxy exhibited only one exothermic peak during the non-isothermal test. As the heating rate (ϕ) increased, the peak exothermic temperature (T_p) shifted to a higher temperature, which is a typical methodological phenomenon for non-isothermal curing. Fig. 6 showed that the T_p at different heating rates are 146 °C, 161 °C, 170 °C, and 176 °C, respectively. It indicated that the curing temperatures of GEMA fell within the same range of the glycidyl ester epoxies curing temperatures [20]. On the other hand, the E_a of curing GEMA was 68.7 kJ/mol which was nearly identical to that of two glycidyl esters curing with anhydride: DGEC21/NMA (67.2 kJ/mol) and TGEC22/NMA (69.2 kJ/mol) [16]. These results suggested that GEMA followed the conventional mechanism of curing reactions for epoxy resin with anhydride in the presence of tertiary amine catalysts.

After curing, the cured GEMA was scanned by DSC once again. The DSC curve (Fig. 8) showed that no exotherm peak appeared. This result confirmed that GEMA obtained almost complete crosslinking. The cured GEMA (4.891 g) was smashed into powder by the pulverizer, then extracted with acetone in a Soxhlet extractor for 2 h. The residual powder was dried in an oven at 120 °C for 6 h, then was weighed. The dry residual powder was 4.744 g, which indicated that there was 97% non-soluble powder due to the self-crosslinking of GEMA.

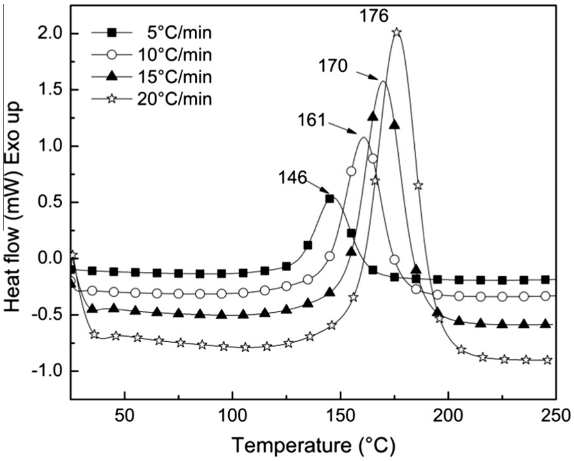


Fig. 6. The representative DSC thermograms of non-isothermal curing of the epoxies at different heating rates.

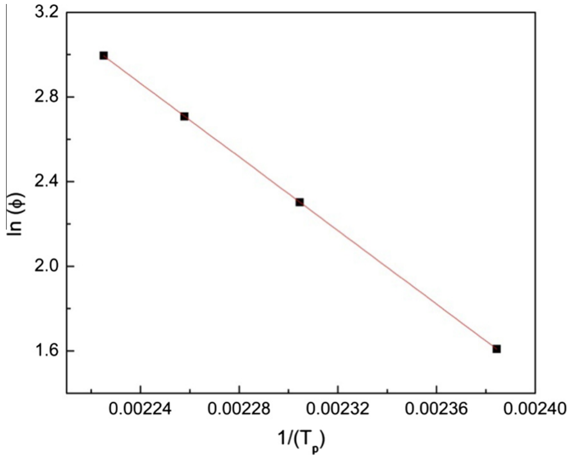


Fig. 7. The plots of $1/(T_\mathrm{p})$ versus $\ln(\phi)$.

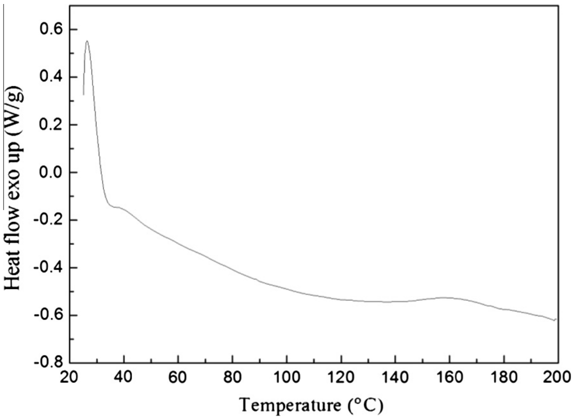


Fig. 8. The DSC thermograms of cured GEMA.

3.4. Stability of GEMA

Stability is very important for a single-component epoxy resin. Good stability benefits the storage, transportation and applicability of the products. The change in viscosity of a resin during storage is an important parameter, from both a

Table 1
The viscosity of GEMA determined after different storage periods.

Storage time (hour, 25 °C)	0	168	360	720	1440	2160
Viscosity (mPa s, 25 °C)	1331	1334	1333	1336	1337	1344

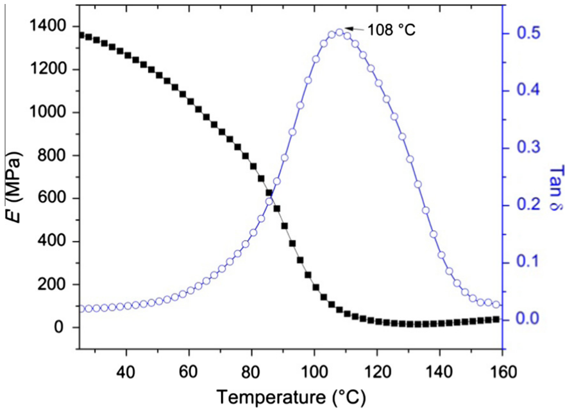


Fig. 9. The storage modulus (E') and damping (tan δ) of the cured GEMA.

Table 2
The tensile properties and T_g of GEMA and other comparing cured system.

Cured sample	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)	T_g (°C)
GEMA	42.5 ± 3.6	3.2 ± 0.5	1930.3 ± 205.1	108
GEEA/MA [16]	42.4 ± 1.1	3.1 ± 0.5	1949.1 ± 152.5	106
Epon 825/NMA [22]	60.2 ± 1.7	2.09 ± 0.26	3620 ± 70	136

practical and a theoretical viewpoint. An increase in viscosity indicates an early reaction, leading to an increase in the molecular chain length of the polymer in the stored mixture [21]. In order to evaluate the stability of GEMA, the viscosity of GEMA was determined after different storage periods (Table 1). GEMA was sealed in a glass bottle which was conditioned at 50% humidity and 23 °C. It is evident that after a period of 2160 h, the viscosity of GEMA was almost constant. Table 1 indicates that GEMA has very good storage stability, at least within 3 months.

3.5. DMA tensile properties and TGA of cured GEMA

Fig. 9 is the temperature dependence of the storage modulus (E') and loss factor (tan δ) for cured GEMA. During the curing of GEMA, it polymerized with its own epoxy and anhydride groups. The glass transition temperature (T_g) of cured GEMA occurred at 108 °C which was indicated by tan δ peak at that temperature. The cyclohexenyl of GEMA definitely contributes to the stiffness of the polymer. The tensile strength, elongation and modulus of cured GEMA listed in Table 2 are 42.5 MPa, 3.2% and 1930.3 MPa, respectively. Recently we made a novel biobased epoxy monomer with conjugated double bonds, i.e. GEEA from tung oil fatty acids [16]. The properties of cured GEMA are quite similar to that of GEEA cured by maleic anhydride (MA). GEMA and GEEA/MA systems have the same crosslink structures, the only difference is the former is a self-crosslinking monomer, while the GEEA/MA system is a two-component system. Meeks reported the tensile properties and T_g of bisphenol A epoxy resin (Epon 825) cured by nadic methyl anhydride (NMA) [22], as seen in Table 1. Because of the flexible nature of fatty chains, the tensile strength, modulus and T_g of cured GEMA are still lower than that of Epon 825/NMA. However, GEMA is a one-component thermosetting monomer which could cure by itself and, when compared to the two-coponent monomers, GEMA is more convenient to use.

TGA results were displayed in Fig. 10 including the cured GEMA (a) and a commercial bisphenol A epoxy resin DER332 cured with NMA (b). Obviously, GEMA has a better thermal stability than DER332/NMA. The 95% weight loss temperature ($T_{95\%}$) of GEMA was 386.5 °C which was much higher than the $T_{95\%}$ of DER332/NMA. The cured epoxies with higher crosslink density usually show better thermal stabilities, therefore, the result was attributed to the good homogeneity of GEMA which is a one-component epoxy monomer. DER332/NMA is a two-component system, during the mixing procedure of the resins and curing agents, the unavoidable nonuniformity, bubbles and insolubility always negatively affect the crosslink density of the network.

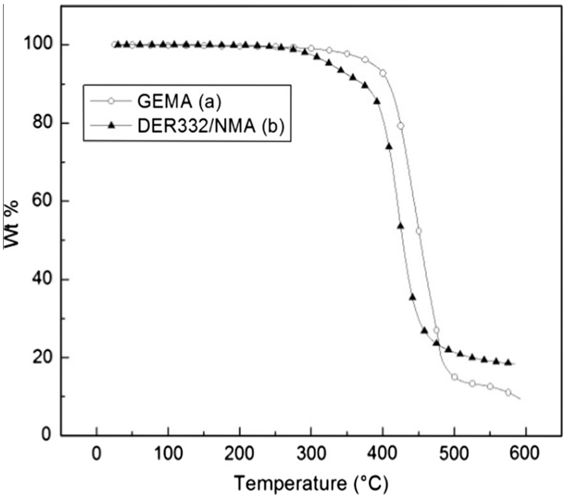


Fig. 10. Temperature dependence of the weight percent for cured samples: (a) GEMA and (b) DER332/NMA.

4. Conclusions

A self-crosslinking compound with both epoxy group and anhydride group (GEMA) was successfully synthesized from tung oil fatty acid by reacting with MA via the Diels–Alder reaction. GEMA has very good storage stability at least within 3 months, it could be cured by itself with trace amounts of tertiary amine like conventional epoxy resin/anhydride mixtures do. This advantage avoided the nonuniformity, bubbles and insolubility during the mixing procedure of the epoxy resins and curing agents. Compared to commercial bisphenol A epoxy resins, GEMA has relatively lower mechanical properties and thermal properties. However, in view of its renewable properties, GEMA still is a very promising potential bio-based epoxy which may replace bisphenol A epoxy resins in some applications.

Acknowledgement

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