

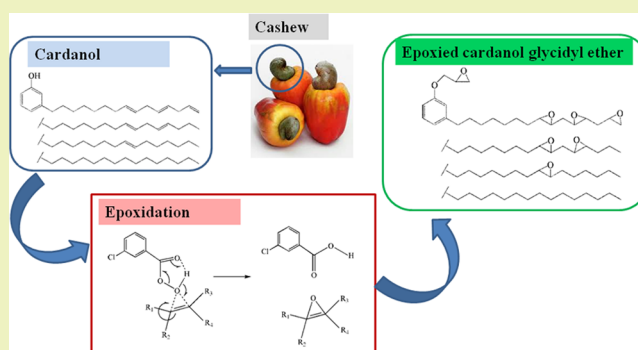
Synthesis and Application of Polyepoxide Cardanol Glycidyl Ether as Biobased Polyepoxide Reactive Diluent for Epoxy Resin

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Supporting Information

ABSTRACT: Polyepoxide cardanol glycidyl ether (PECGE), a novel cardanol derivative, was synthesized and used as reactive diluent for petroleum-based epoxy resin in this work. The synthetic condition was first optimized, and the resultant PECGE diluent was characterized using Fourier transform infrared spectroscopy, ¹H NMR, and ¹³C NMR. The influence of addition of this diluent on the viscosity of the diluent epoxy resin was also studied. Mechanical and heat-resistant properties of the cured epoxy resin containing PECGE were especially evaluated. By the addition of PECGE into the petroleum-based epoxy resin, the viscosity of the obtained epoxy resin was reduced. The tensile strength, elongation at break, and heat-resistant property of the obtained resin were all improved, while the flexural and compressive strengths of the resin only slightly decreased, implying the potential of PECGE as a very promising biobased reactive diluent for epoxy resin.

KEYWORDS: Reactive diluents, Cardanol, Epoxy resin, Mechanical properties, Thermal properties



INTRODUCTION

Epoxy resins, because of their fascinating mechanical, electrical, chemical, and thermal properties,^{1,2} have been tremendously used as engineering materials, including protective coatings, adhesives, matrixes of high performance composite materials, etc.^{3,4} Their high viscosity and poor process-ability, however, severely limits the range of other industrial and structural applications. An effective way to address the crucial issue of high viscosity is to add diluents into the epoxy resin.⁵

Generally, reactive diluents work in two ways within epoxy resin. They serve as solvents and/or react with oligomer monomers to form a network.⁶ Hence, reactive diluents are usually those low-viscosity compounds with multiple reactive functionalities that have good compatibility with epoxy resin.^{7,8} On the other hand, due to the concerns about environmental issues and pressures of using petroleum-based products, the demand for developing substitutes of chemical feed stocks from renewable resources is growing.^{9,10} A reactive diluent that is derived from a renewable resource would be promising for replacing the petrochemicals and supporting the development of global sustainability. Therefore, desirable reactive diluents should also distinguished themselves by low toxicity and low volatility.¹¹

Cashew nut shell liquid (CNSL), an abundant and low-cost agricultural byproduct, is one of the most commonly used renewable resources.^{12,13} Its extracted product, cardanol, is a natural alkyl phenol with a C₁₅ unsaturated hydrocarbon chain containing 1, 2, or 3 nonconjugated C=C bonds.¹⁴ Because of this versatile chemical structure, much interest has been drawn to cardanol derivatives.^{15,16} The major applications of cardanol derivatives lies in synthetic resins,^{17–20} epoxy curing agents,^{21,22} plasticizers,²³ coatings,^{24–26} biobased polymers,²⁷ and biocomposites.^{28–31} In recent years, researchers have studied the modification of the functional groups of hydroxyl and alkenyl by epoxidation. Jaillet et al.²⁰ studied the epoxy resins from commercial epoxidized cardanol and aromatic reactant, and the yield materials with good thermal and mechanical properties. Epoxidation of double bonds of alkenyl on the side chain of cardanol acetate was reported by Greco et al.²³ and used as a plasticizer. But epoxidation of both of the hydroxyl and alkenyl of cardanol was never reported in the literature as far as we know. Furthermore, the application of cardanol derivatives as reactive diluents in epoxy resin has rarely been reported.³² It

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was expected that the combination of the hard aromatic structure, long flexible alkyl chain, and the epoxy groups of polyepoxide cardanol derivatives would impart unique properties to the epoxy matrix.

In this work, we report the preparation of a novel multifunctionalized cardanol derivative as reactive diluent. The cardanol glycidyl ether (CGE) obtained via epoxidation of the cardanol hydroxyl group shown in Figure 1 was

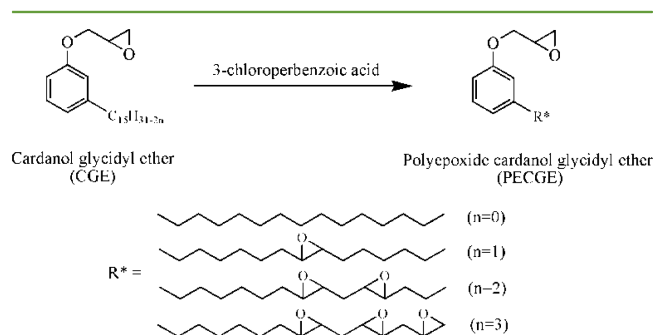


Figure 1. Scheme for the reaction of synthesizing PECGE.

employed as a reactive feedstock to synthesize the polyepoxide cardanol glycidyl ether (PECGE) diluent through further epoxidation of double bonds on the CGE side chain. In the curing system, the addition of this multifunctionalized cardanol derivative with additional cross-linking sites enhanced the flexibility and toughness of epoxy resins. Viscosity, mechanical and heat-resistant properties of the cured PECGE/epoxy resins were evaluated. In addition, the influence of contents of the reactive diluent on the diluent epoxy resin was also investigated.

EXPERIMENTAL SECTION

Materials. Cardanol glycidyl ether was synthesized and reported in our earlier work.³² Its physical properties are viscosity at 25 °C of 22 mPa·s, epoxy value at 0.273 mol/100 g⁻¹. 3-Chloroperbenzoic acid (MCPBA) was obtained from Wotu Chemical Co., Ltd. (Hefei, Anhui, China). The aromatic polyamine 934-type curing agent (amine hydrogen equivalent weight (AHEW) = 118.1 g/eq), with viscosity of 1400 mPa·s (25 °C), density of 0.88–0.92 g/mL, was purchased from Institute of Chemical Industry of Forest Products (ICIFP), Chinese Academy of Forestry (CAF), Nanjing Science and Technology Development Co., Ltd. (Nanjing, Jiangsu, China). Diglycidyl ether of bisphenol A (DGEBA) (epoxy equivalent weight (EEW) = 197 g/eq) was provided from Wuxi Epoxy Resin Factory of BlueStar New Chemical Materials Co., Ltd. (Wuxi, Jiangsu, China). Alkyl (C₁₂–C₁₄) glycidyl ether (AGE) and benzyl glycidyl ether (BGE) were obtained from Shenzhen Jiadida Chemical Co., Ltd. (Luo Hu Qu, Shenzhen, Guangdong, China). Sodium bicarbonate, sodium sulfite, anhydrous magnesium sulfate, and sodium oxide obtained from Nanjing Chemical Co., Ltd. (Nanjing, China) are reagent grade. All materials were used as received.

Synthesis of Polyepoxidized Cardanol Glycidyl Ether. 3.57 g (10 mmol) of cardanol glycidyl ether was added in a three-necked round-bottom flask equipped with a mechanical stirrer, thermometer sensor, and reflux condenser; then, the mixture of 15 g (176 mmol) of dichloromethane and 2.59 g (15 mmol) of MCPBA was added slowly into the flask. The resultant solution was allowed to react at 40 °C for 3 h. After the reaction was complete, the crude product was filtered and washed with a saturated solution of sodium sulfite several times until the color of the potassium iodide test paper did not change. Subsequently, a saturated sodium bicarbonate and sodium chloride solution was used to wash the product again, respectively. Finally, the organic phase was dried with anhydrous magnesium sulfate and then filtered. The filtrate was distilled under vacuum to recycle the

dichloromethane, and 3.35 g of a yellowish liquid was obtained (yield: 88% relative to CGE).

Formulations. Curing mixtures with different kinds and contents of diluents were used for a mechanical performance study. Several mixtures were obtained from diglycidyl ether of bisphenol A (EEW = 197 g/eq) with PECGE or CGE at different weight ratios of 0, 5, 10, 15, and 20%. The curing agent used was the 943-type. In all formulations, theoretically, the epoxy group and active H of amine should be prepared in 1:1 molar ratio. We used the data of EEW and AHEW to calculate the mass of curing agent:

$$m_1 = m_2 \times \frac{\text{AHEW}}{\text{EEW}} \quad (1)$$

where m_1 is the mass of curing agent, m_2 is the mass of epoxy resin, AHEW is the amine hydrogen equivalent weight, and the EEW is the epoxy equivalent weight.

After complete stirring, the mixture was charged into steel molds with cavity dimensions of 120 × 15 × 6 mm and 26 × 10 × 10 mm. Curing was performed at room temperature for 15 h, and then at 80 °C for 3 h. After being cooled to room temperature, the cured specimens were carefully removed from the mold and used for mechanical tests. The reported results of impact testing were an average of at least three samples.

Orthogonal Experimental Design. In the present study, the epoxidation parameters were optimized by an orthogonal experimental design (L₉ matrix) where following three variables were analyzed: reaction temperature (factor A), reaction time (factor B), and CGE/MCPBA mole ratio (factor C). An L₉ (3³) matrix, which is an orthogonal array of three factors and three levels, was employed to assign the considered factors and levels as shown in Table 1. Nine

Table 1. Factors and Levels for Orthogonal Experiment

level	factors		
	reaction temperature A (°C)	reaction time B (h)	CGE/MCPBA mole ratio C
1	25	2	1:1
2	30	3	1:1.5
3	35	4	1:2

trials were carried out according to the L₉ matrix to complete the optimization process. Data analysis was carried out through the mean value (K_i , $i = 1, 2, 3$) and range analysis (R) to reflect the optimal reaction conditions and their magnitudes. Optimal conditions were obtained after the orthogonal experiments and subsequent data analysis. Finally, the experiment was repeated under the optimal conditions in order to verify the data.

Characterizations. Epoxy values of the synthesized diluents were determined according to the Chinese Standard GB/T 4612-2008. Viscosity measurements for the epoxy resin systems were performed on an NDJ-8S rotational viscometer from Shanghai Hangzhou Dizhi Instrument Company (Hangzhou, China).

Fourier-transform infrared spectroscopy (FT-IR) measurements of the samples were obtained on a Nicolet iS 10 spectrometer (Thermo Fisher Scientific, Inc., Waltham, MA, USA). The hot-deformation temperature (HDT) and vicat softening temperature (VST) of the resin products were determined by the measuring of both with a Vicat (RBW-300 heat distortion temperature tester (Testing Machine Co., Ltd., Jilin, Taihe, China)). Tensile properties, flexural performance, and compressive strength of the cured materials were examined using a CMT4303 SANS universal testing machine (MTS Systems (China) Co., Ltd., Shenzhen, China). Tensile strength and elongation at break were measured at a cross-head speed of 10 mm/min and a gauge length of 50 mm, in accordance with ASTM D638. Flexural performance and compressive properties were tested following Chinese Standard GB/T 2567-2008, respectively.

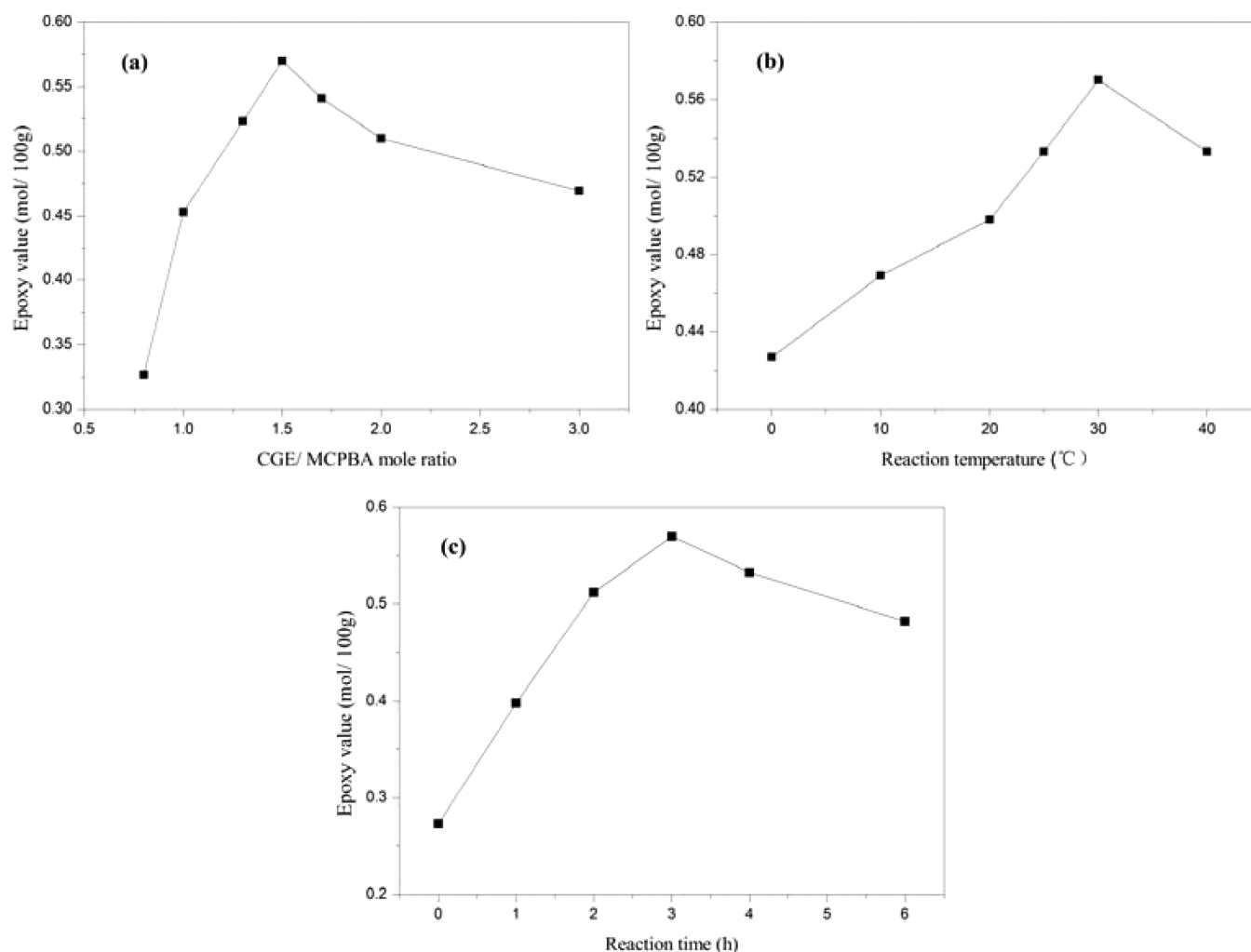


Figure 2. Results of single factor experiment: (a) CGE/MCPBA mole ratio, (b) reaction temperature, and (c) reaction time.

RESULTS AND DISCUSSION

Synthesis and Characterization. As shown in Figure 2, several experimental factors (i.e., reaction temperature, reaction time, CGE/MCPBA mole ratio) influenced the epoxy reaction of synthesizing the target product polyepoxide cardanol glycidyl ether (PECGE).

Figure 2a shows the effects of CGE/MCPBA mole ratio on epoxidation at 30 °C for 3 h. When the ratio was lower than 1:1.5, it was found that the epoxy value increased. According to the studies on the epoxidation mechanism,^{33–36} the possible mechanisms of the epoxidation of CGE using MCPBA as oxidant can be elucidated as Figure 3. It can be concluded that the appropriate excess of MCPBA is necessary for its partial decomposition. However, because of its acidity, the excess use of MCPBA will aggravate side reaction, leading to ring-opening reaction of the epoxy bond of PECGE, which also demoted the epoxy value.³⁷ On the other hand, when the ratio was higher than 1:1.5 the epoxy value decreased and the color of the product intensified. These results are likely attributed to the fact that excess MCPBA caused the ring-open reaction. Therefore, 1:1.5 was selected as the optimal MCPBA/CGE mole ratio in this study.

The relationship between temperature and epoxy value of the product is given in Figure 2 b, with the CGE/MCPBA mole ratio of 1:1.5 and the reaction time 3 h. The temperature was

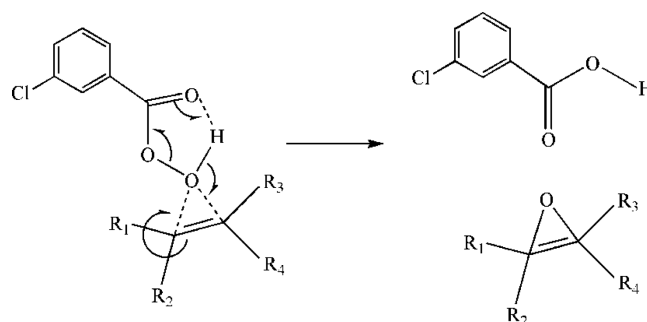


Figure 3. Mechanisms of the epoxidation of CGE using MCPBA as oxidant. R1, R2, R3, and R4: alkyl chain.

observed as an important factor for epoxidation reaction. The epoxy value kept increasing with the temperature in the range of 0–30 °C. However, further addition of heat inhibited the reaction and the epoxy value decreased significantly from 0.570 to 0.533 mol·100 g⁻¹. Because further increases of temperature beyond 30 °C led to an increased instability of epoxy group,³⁸ we chose 30 °C as the proper reaction temperature.

Figure 2c gives effect of reaction time on the epoxidation under the condition of reaction temperature 30 °C and CGE/MCPBA mole ratio 1:1.5. As can be clearly seen, the epoxy value of product increased as the reaction time increased,

reaching the maximum number of $0.57 \text{ mol}\cdot 100 \text{ g}^{-1}$ in 3 h. A presumable explanation is that, in a short reaction time, the reaction was incomplete and, thus, the product appeared to have a low epoxy value. On the other hand, the epoxy value decreased when the reaction time was longer than 3 h, indicating that the excess MCPBA caused ring-open reaction under acidic conditions. Hence, the suitable reaction time was 3 h.

According to the L_9 matrix, which levels of factors are listed in Table 1, nine experiments were conducted and their epoxy value results are shown in Table 2. As mentioned above, for

Table 2. Results of Epoxidation Process in L_9 Orthogonal Experiment

trial no.	factors			results epoxy value (mol/100 g)
	reaction temperature A (°C)	reaction time B (h)	CGE/MCPBA mole ratio C	
1	25	2	1:1	0.412
2	25	3	1:1.5	0.453
3	25	4	1:2	0.398
4	30	2	1:1.5	0.512
5	30	3	1:2	0.510
6	30	4	1:1	0.467
7	35	2	1:2	0.504
8	35	3	1:1	0.486
9	35	4	1:1.5	0.473
K_1	1.263	1.428	1.365	
K_2	1.489	1.449	1.438	
K_3	1.463	1.338	1.412	
R	0.226	0.111	0.73	

each factor, the best level can be determined from the highest mean value of the experimental condition. In Table 2, the highest epoxy value of the epoxidation products for each level was clearly distinguished, as the reaction temperature was 30°C ($0.496 \text{ mol}/100 \text{ g}$), reaction time was 3 h ($0.483 \text{ mol}/100 \text{ g}$), and the CGE/MCPBA mole ratio was 1:1.5 ($0.479 \text{ mol}/100 \text{ g}$), because K_i was the highest at these combinations ($C_2A_2B_2$). Furthermore, the range value (R) indicates the significance of the factor's effect and a larger R implies the corresponding factor has a bigger impact on the epoxy value. Therefore, compared with the range values of the different factors, the factor's level of significance are as follows: CGE/MCPBA mole ratio (0.730) > reaction time (0.226) > reaction temperature (0.111). Among all range value, R_c is largest, indicating that a small change in CGE/MCPBA mole ratio can produce a significant change in epoxy value of the epoxidation products. To verify the data, a repeated experiment was performed under the optimal conditions and the results were presented in Table 3. Moreover, the results were in good agreement with the previous orthogonal experiment.

The physical characteristics such as viscosity, iodine value, and epoxy equivalent of the epoxidized product PECGE are shown in Table 4. It can be seen that after epoxidation the iodine and viscosity value decrease obviously, though the epoxy

Table 3. Results of Repeat Trail on Optimal Reaction Conditions

trial no.	1	2	3	average value
epoxy value (mol/100 g)	0.569	0.571	0.566	0.568

Table 4. Physical Characteristics of Cardanol and PECGE

property	cardanol	PECGE
viscosity at 25°C (mPa·s)	42	28
iodine value (g/100 g)	263.63	25.78
epoxy equivalent (g/eq)		175

value increase with the same. These results indicate that the phenolic hydroxyl group and unsaturated double bonds of cardanol are utilized for ester group and epoxy group formation.^{39,40} Furthermore, the epoxy equivalent value confirms the formation of epoxy group, which is also supported by FT-IR and NMR studies.

Figure 4 shows the FT-IR spectra of cardanol feedstock, CGE, and PECGE. The intense peaks at 2925 and 2854 cm^{-1}

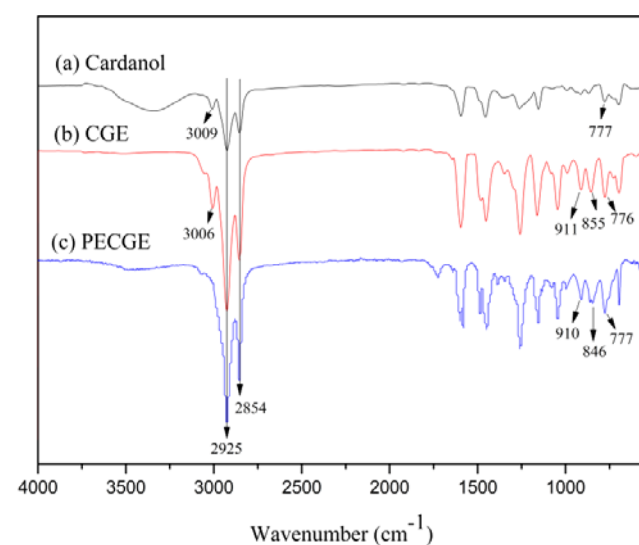


Figure 4. FT-IR spectra of (a) cardanol, (b) CGE, and (c) PECGE.

were indicative of the stretching vibrations of the C—H band for the methylene chain. The bands at 1449 – 1600 cm^{-1} were attributed to the C=C stretching mode of vibration for the benzenoid ring. The peaks at 777 , 846 , 855 , 910 , and 911 cm^{-1} were the characteristic peaks of epoxide.⁴¹ The peak at 855 cm^{-1} was the ring deformation of the terminal epoxy group, which differentiated from the vibration of epoxy group on the aliphatic chain at 846 cm^{-1} . Moreover, compared with CGE, the peak of 3006 cm^{-1} disappeared in PECGE, which means the double bonds on side chain were transformed to epoxy groups.

The NMR technique is employed to investigate the structure of the obtained products of PECGE. Figure 5 and Figure 6 display the ^1H NMR and ^{13}C NMR of cardanol, CGE, and PECGE, respectively. The characteristic peaks at 6.7 – 7.3 ppm are corresponding to the proton on benzene ring. Compared to the spectra of cardanol (Figure 5a) and CGE (Figure 5b), it can be clearly seen that the peak at 5.2 – 5.5 ppm of PECGE (Figure 5c) corresponding to the proton of $-\text{CH}=\text{CH}-$ and $-\text{OH}$ almost disappeared. It indicated that the phenolic hydroxyl group and unsaturated double bonds on the side chain have been converted. Additionally, the new peaks at 2.76 , 3.38 , 4.00 , and 4.20 ppm indicate the existence of glycidyl ester in CGE and PECGE.⁴² Furthermore, the peaks at 2.9 – 3.1 ppm corresponding to the proton of the $-\text{CH}-\text{O}-\text{CH}-$ groups have appeared on the ^1H NMR spectrum of PECGE, also

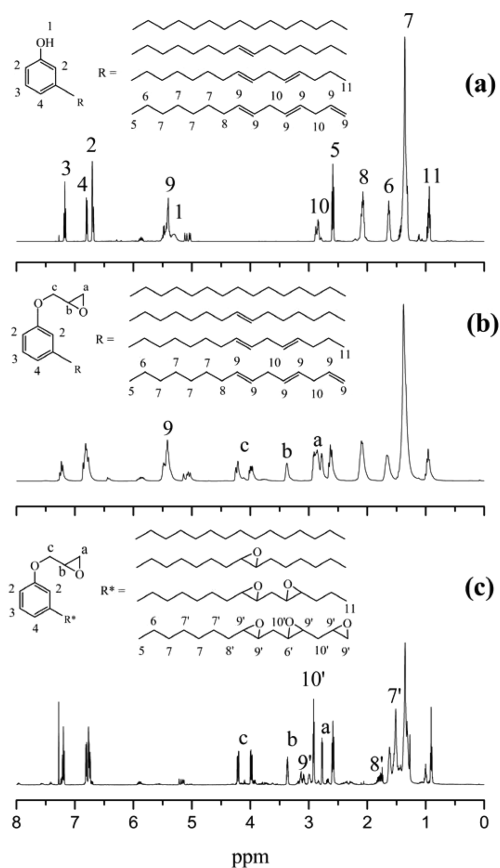


Figure 5. ^1H NMR spectra of (a) cardanol, (b) CGE, and (c) PECGE.

indicating the occurrence of epoxidation. The changed chemical shift of the peaks at 1.2–1.8 ppm also supports the production of epoxidized groups after the epoxidation reaction. The ^{13}C NMR chemical shifts peaks at 126.4–137.1 ppm disappeared in Figure 6c. Likewise, the glycidyl ester group and $-\text{CH}-\text{O}-\text{CH}-$ groups made a distinction between cardanol (Figure 6a), CGE (Figure 6b), and PECGE. The chemical shifts of the three carbons in the glycidyl ester group of CGE and PECGE occurred near 44.90, 50.24, and 68.60 ppm, respectively.⁴³ The new peaks at 56.91 ppm of PECGE are corresponding to the carbons in the $-\text{CH}-\text{O}-\text{CH}-$ groups.

Effect of PECGE Content on Viscosity of the Obtained Resin System. Generally, epoxy resin has a high viscosity and a poorer mixing property; thus, a diluent needs to be added to reduce the viscosity of the initial mixture and to improve the processability of the resin. This behavior was observed when the samples were studied for evaluation of the epoxy groups in the epoxy resin dilution process.

As can be seen in Figure 7, with the increase of the reactive diluent content, the viscosity values decreased. By diluting with PECGE, to 10 and 20%, the samples exhibited significantly reduced viscosity values of 4780 and 2150 mPa·s, respectively. For reference, in the case of the CGE curing samples, viscosity values gradually decreased from 14 700 to 1892 mPa·s, with the increase of the CGE content from 0 to 15%. The similar remarkable reduction of viscosity values was found in the sample with a CGE content of 15% and the sample with a PECGE content of 20%.

Mechanical Properties. Table 5 shows the effect of different content of the reactive diluent on mechanical properties of the cured resins. The neat DGEBA exhibited a

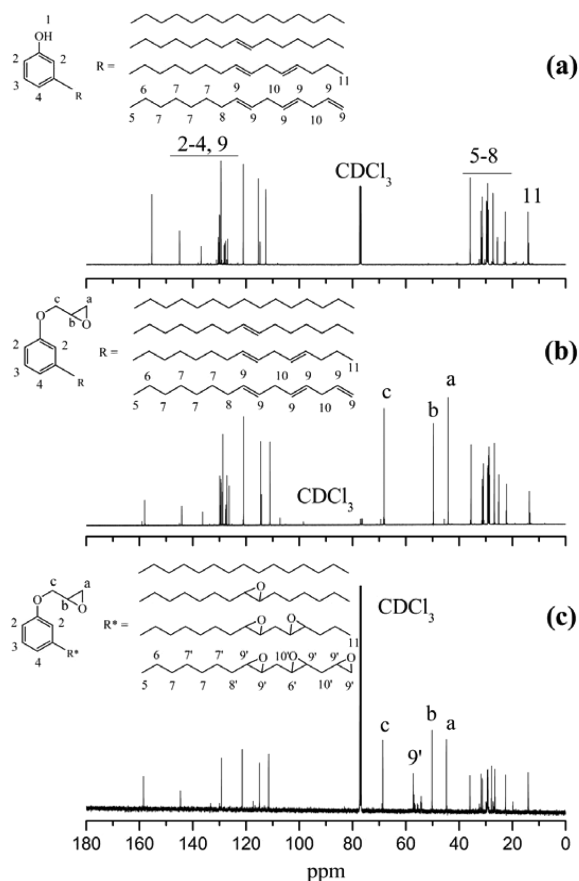


Figure 6. ^{13}C NMR spectra of (a) cardanol, (b) CGE, and (c) PECGE.

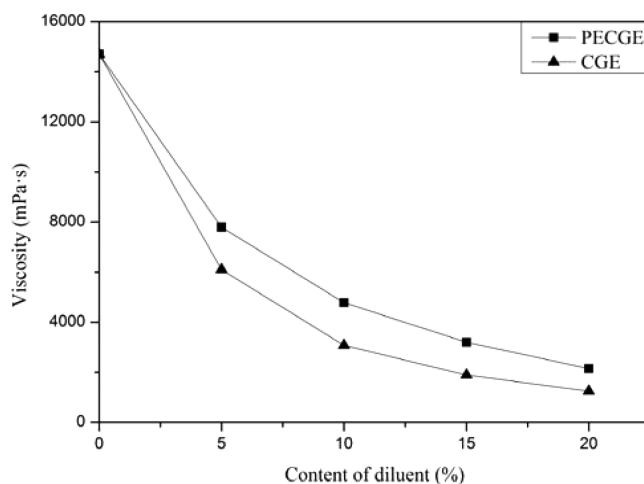


Figure 7. Effect of reactive diluent addition on viscosity of resin system at 25 °C.

tensile strength of 50.78 MPa, which was much lower than that of PECGE-5 (80.26 MPa). It was noticed that the tensile strength decreased as the content of PECGE increased, which is also observed for the high BGE content cases.⁴³ By gradually increasing the diluents content to 20 wt %, the tensile strength was still higher than that of neat DGEBA. Moreover, it also can be seen that the tensile strengths of the samples with PECGE were generally better than that with CGE. The reason for this probably lies in the fact that PECGE has more epoxy groups,

Table 5. Mechanical Properties of Cured Epoxies with PECGE and CG Reactive Diluents

samples	reactive diluents content (%)	tensile strength (MPa)	elongation at break (%)	flexural strength (MPa)	compressive strength (MPa)
neat DGEBA	0	50.78	1.42	107.70	95.32
PECGE-5	5	80.26	1.65	106.74	93.42
PECGE-10	10	73.55	2.67	100.69	93.00
PECGE-15	15	71.80	3.72	99.50	92.36
PECGE-20	20	57.45	4.80	93.13	89.23
CGE-5	5	72.12	3.07	102.90	87.43
CGE-10	10	69.72	3.70	93.56	82.80
CGE-15	15	54.91	6.28	79.50	77.90
CGE-20	20	42.31	9.96	57.95	63.90

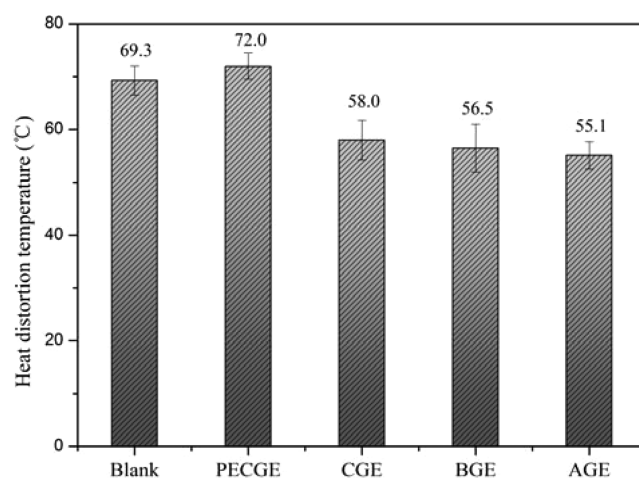
which increased the cross-link density of the cured system, and the binding forces between molecules will be stronger.⁴⁴

Furthermore, Table 5 shows that an increase in the PECGE content led to a progressive enhancement in break elongation of the modified epoxy resin. This break elongation could reach up to 2.4 times more than that of the neat DGEBA as the PECGE content increased to 20%. This is because PECGE is a soft phase that has a lower modulus than the epoxy matrix phase.⁴² In addition, the tendency of the break elongation of epoxy resins with varying PECGE and CGE contents was also observed. The break elongation of composite with CGE is higher than that with PECGE. This is because the PECGE possessed more epoxy groups on the long aliphatic chain, which can react with curing agent and make the composite become stiffer.⁴³ However, when the contents of PECGE and CGE change to 15 and 10%, respectively, similar toughness performances can be obtained.

The influence of the incorporation of reactive diluents on flexural properties of cured resins can be seen from the continuous decrease of strength with PECGE and CGE content. In PECGE-5, the cured epoxy resin exhibited similar flexural strength (106.74 MPa) with neat DGEBA (107.7 MPa), but higher than that of CGE-5 (102.9 MPa). As the PECGE content further increased to 20%, the sample showed a flexural strength of 93.13 MPa, which was close to the value of CGE-10. Indeed, due to the presence of PECGE, the increase of the cross-linking density of cured system would have a negative effect on the flexural strength of cured systems.¹ Therefore, PECGE could reduce the brittleness of the epoxy network and stabilize the flexural properties simultaneously when its addition content was less than 20%. The usage of CGE, however, should be lower than 10%. Likewise, the compressing effect of reactive diluents was reflected in the change of compressive strength. In the PECGE-15, the compressive strength exhibited 3.11% lower than that of neat DGEBA. By contrast, CGE-15 showed an 18.28% decrease. From an application viewpoint, the epoxy resin containing 10–15 wt % of PECGE displayed the best mechanical property and utility, and generally better than epoxy resin with the same amount of CGE.

Heat-Resistant Analysis. Polymer materials normally become deformed at an elevated temperature, which limits their application range.⁴⁵ The heat deflection temperature is a measurement of the heat-resistant performance of polymer

materials. Figure 8 shows the heat deflection temperature of the cured resins modified with different diluents (DGEBA:diluents

**Figure 8.** Effect of reactive diluents on the heat deflection temperature of the cured resin.

= 90:10). It can be seen that the neat DGEBA sample (Blank in Figure 8) had a heat deflection temperature of 69.3 °C. However, after adding the CGE, BGE, and AGE diluents into DGEBA, heat deflection temperatures of the cured resin samples decreased to 58.0, 56.5, and 55.1 °C, respectively. In contrast, the sample diluted with PECGE had a heat deflection temperature of 72.0 °C, which is higher than that of the neat DGEBA. This is because the PECGE with phenyl rigid group and multiple epoxy groups have provided additional cross-linking sites that improve the heat-resistant performance of the PECGE/DGEBA resin.

CONCLUSIONS

The renewable polyepoxide cardanol reactive diluent was synthesized and characterized. The optimized synthetic conditions were confirmed through orthogonal experiment and the product with a high epoxy value was achieved. Incorporation of the reactive diluent into epoxy resin formulations showed that the new multifunctionalized cardanol derivative is a very effective diluent for epoxy resin. The viscosity of the diluent epoxy resin significantly decreased with the increase of the content of the diluent, although the maximum reduction was less than that of monocardanol derivative diluent CGE. The PECGE provided additional cross-linking sites that influenced the values of tensile, flexural, compressive, and heat-resistant properties. However, the addition of PECGE showed no significant change in elongation at break as compared with CGE. Additionally, the thermal properties indicate that the addition of PECGE could significantly improve the heat-resistant performance. The enhanced processability and overall improved performance of the epoxy resins were obtained when less than 20 wt % of the PECGE reactive diluent was added. These results imply that PECGE is a very promising biobased reactive diluent with the potential to replace those reactive diluents from petrochemicals.

■ ASSOCIATED CONTENT

5 Supporting Information

The synthetic sequence for the obtainment of PECGE. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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The authors declare no competing financial interest.

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