European Polymer Journal 92 (2017) 165–173

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Fully biobased epoxy resin systems composed of a vanillin-derived epoxy resin and renewable phenolic hardeners

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ARTICLE INFO

Keywords:
Vanillin
Cyclopentanone
Biobased epoxy resins
Renewable hardeners
Quercetin
Thermal and mechanical properties

ABSTRACT

A new bio-based epoxy resin (DGEDVCP) was synthesized by the glycidylation of 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (DVCP) prepared by the crossed-aldol condensation of vanillin and cyclopentanone. The thermal and mechanical properties of DGEDVCP resins cured with renewable quercetin (QC) and guaiacol novolac (GCN) in addition to a petroleum-based phenol novolac (PN) were compared with those of bisphenol A diglycidyl ether (DGEBA) resins cured with QC, GCN and PN. Regarding the hardeners used for curing, the higher order of loss modulus (E'') peak temperature of cured products was QC > PN > GCN. The E'' peak temperatures of DGEDVCP/GCN and DGEDVCP/PN cured products were higher than and comparable to those of DGEBA/GCN and DGEBA/PN cured products, respectively. Thermal degradation temperatures of DGEDVCP-based products were slightly lower than those of DGEBA-based products. Char yields at 500 °C for DGEDVCP-based products were much higher than those of DGEBA-based products. The flexural strengths and moduli of the DGEDVCP/QC and DGEDVCP/GCN cured products were comparable to those of DGEBA/QC and DGEBA/GCN cured products, respectively.

1. Introduction

Thermosetting epoxy resins have been widely used in various fields such as printing circuit boards, semiconductor encapsulants, coatings, adhesives and composite materials because of their excellent chemical resistance, adhesion, electric insulation, heat resistance and mechanical properties [1,2]. Nowadays, almost 90% of the world production of epoxy resins is based on the reaction of petroleum-based bisphenol A and epichlorohydrin, producing diglycidyl ether of bisphenol A (DGEBA) [3]. In recent years, renewable resources-derived (bio-based) epoxy resins are attracting much attention from the viewpoints of petroleum resource saving and the control of carbon dioxide emissions that lead to global warming [1,3–10]. In addition, since bisphenol A is an endocrine disrupting and reprotoxic compound [11,12], it is strongly desired to produce epoxy resins from nonharmful and inexpensive biobased phenol derivatives such as vanillin (VN) [13], eugenol [14,15], guaiacol [16] and cardanol [17]. Among the biobased phenol derivatives, VN is especially interesting because it is the major aromatic compound produced commercially from lignin which is the second most abundant organic polymer after cellulose [13,18–24]. Ochi et al. reported the synthesis and properties of a diglycidyl compound by the reaction of epichlorohydrin and a bisphenol possessing a spiroacetal ring derived from VN and pentaerythritol [18,19]. Recently, Caillol et al. reported the synthesis of several diglycidyl compounds by the reactions of

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http://dx.doi.org/10.1016/j.eurpolymj.2017.05.007
Received 25 March 2017; Received in revised form 28 April 2017; Accepted 7 May 2017

methoxyhydroquinone, vanillyl alcohol and vanillic acid derived from VN with epichlorohydrin [20]. Aouf reported the synthesis of a stilbene-type diglycidyl ether by the cross metathesis of glycidyl-etherified 4-vinylguaiacol derived from VN [22]. Mar and Zhu et al. reported the synthesis and properties of flame retardant epoxy resins containing nitrogen and phosphorous atoms derived from VN [1]. Although the properties of some of their VN-derived epoxy resins cured with petroleum-based isophorone diamine and 4,4′-diaminodiphenylmethane (DDM) have been reported [1,21,23,24], those of the resins cured with biobased epoxy hardeners have never been reported, to the best of our knowledge. We have already reported the thermal and mechanical properties of the sorbitol-based polyglycidyl ether resins cured with biobased phenolic hardeners such as tannic acid [25], quercetin (QC) [26] and guaiacol novolac (GCN) [16].

Herein, we synthesized a new biobased epoxy resin (DGEDVCP) by the reaction of epichlorohydrin and 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (DVCP) prepared by the crossed-aldol condensation of VN and cyclopentanone (CPN) [27]. It was recently found that CPN can be produced by a selective hydrogenation of furfural [28–31]. As furfural is produced from a variety of agricultural byproducts such as corncobs, oat, wheat bran and sawdust, CPN can be derived from renewable resources. Furthermore, epichlorohydrin can be also produced from bio-based glycerol [32,33]. In this study, we report the synthesis of DGEDVCP and the thermal and mechanical properties of DGEDVCP resins cured with QC, GCN and a petroleum-based phenol novolac (PN), compared with those of DGEBA resins cured with QC, GCN and PN. As a result, the fully biobased epoxy-cured products exhibited the thermal and mechanical properties comparable to the petroleum-based DGEBA cured products.

2. Experimental

2.1. Materials

Vanillin (VN) and quercetin (QC) hydrate were purchased from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). Cyclopentanone (CPN), epichlorohydrin and triphenylphosphine (TPP) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Triethyl benzyl ammonium chloride (TEBAC) was purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA). Diglycidyl ether of bisphenol A (DGEBA, trade name: jER® 828, epoxy equivalent weight 185 g eq.$^{-1}$) was kindly supplied from Mitsubishi Chemical Corp. (Tokyo, Japan). Phenol novolac (PN, maker grade: PR-53195, softening point 110 °C, hydroxy equivalent weight 104 g eq.$^{-1}$) was kindly supplied from Sumitomo Berklite Co. Ltd. (Tokyo, Japan). Guaiacol novolac (GCN) was synthesized by the reaction of guaiacol and formalin according to the previously reported method [16]. The degree of polymerization of GCN measured by ^{1}H NMR method and hydroxy equivalent weight of GCN were 131 g eq.$^{-1}$ and 2.52, respectively. All of the commercially available reagents were used without further purification.

2.2. Synthesis of 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (DVCP)

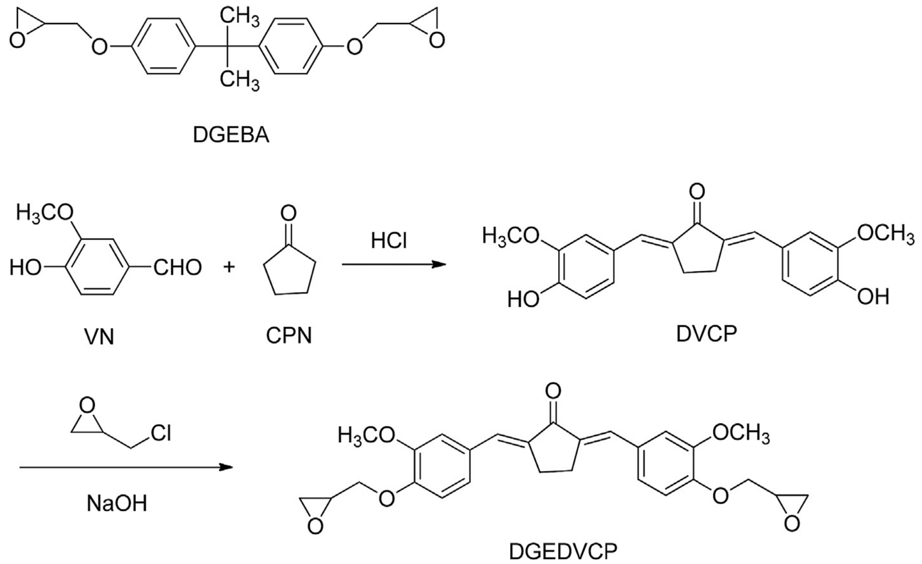
DVCP was synthesized by modifying the already reported method [27] as follows: Concentrated hydrochloric acid (3.0 mL) was added to a solution of VN (76.1 g, 0.500 mol) and CPN (21.0 g, 0.250 mol) in 1,4-dioxane (100 mL), and the solution was stirred at room temperature for 5 h. After the reaction mixture was allowed to stand at room temperature for 3 d, the product was treated with cold acetic acid/water (1/1). The formed precipitated was filtered and washed with cold water, then with hot water, and dried at 100 °C for 24 h in a vacuum oven to produce DVCP as a white crystals (68.8 g). Yield: 78%; mp. 178–179 °C (lit. 178–179 °C [25]); ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm) 3.10 (s, 4H, H-e), 3.88 (s, 6H, OCH_3), 6.93 (d, J = 8 Hz, 2H, H-c), 7.20 (brd, J = 8 Hz, 2H, H-b), 7.28 (brs, 2H, H-a), 7.40 (s, 2H, H-d), 9.69 (s, 2H, OH).

2.3. Synthesis of diglycidyl ether of DVCP (DGEDVCP)

A mixture of DVCP (28.1 g, 80.0 mmol), epichlorohydrin (74.0 g, 0.800 mol) and TEBAC (1.82 g, 8.00 mmol) was stirred at 80 °C until a clear solution was obtained, and then cooled to room temperature. An aqueous solution of TEBAC (1.82 g, 8.00 mmol) and sodium hydroxide (12.9 g, 0.320 mol, 5.0 mol L^{-1}) was added and the mixture was stirred for 1 h at room temperature. After the reaction mixture was neutralized with aqueous hydrochloric acid (2.0 mol L^{-1}), chloroform (300 mL) and water (200 mL) was added to the mixture. After the mixture was stirred for 0.5 h, the organic layer was separated, washed with water twice and dried over sodium sulfate. The dried organic layer was concentrated in vacuo, and dried at 60 °C for 24 h in a vacuum oven to produce DGEDVCP as a pale yellow powder (36.0 g). Yield 97%; (400 MHz, $CDCl_3$, δ, ppm) δ 2.76 (dd, J = 4.5 and 2.7 Hz 2H, H-h′), 2.90 (t, J = 4.5 and 2.5 Hz 2H, H-h), 3.08 (s, 4H, H-e), 3.39 (m, 2H, H-g), 3.90 (s, 6H, OCH_3), 4.06 (dd, J = 11.2 and 4.2 Hz 2H, H-f′), 4.31 (dd, J = 11.2 and 3.1 Hz, 2H, H-f), 6.97 (d, J = 8 Hz, 2H, H-c), 7.12 (brs, 2H, H-a), 7.18 (brd, J = 8 Hz, 2H, H-b), 7.51 (s, 2H, H-d); FT-IR (ATR) 3061, 2997, 2926, 2872, 2830, 1681, 1618, 1585, 1510, 1446, 1418, 1331, 1273, 1240, 1211, 1132, 1020, 999, 912, 849, 802 cm^{-1}; ESI-MS (m/z) calcd. for $[M+H]^+$ ($C_{27}H_{29}O_7$) 465.1913, found465.1904.

2.4. Preparation of the cured epoxy resins

A mixture of DGEDVCP (3.19 g, epoxy: 13.7 mmol), GCN (1.80 g, OH: 13.7 mmol) and TPP (50 mg, 1 wt% of the total weight of resins) was mixed by hand using a spatula on a hot plate of 150 °C until the melted resin mixture became a gelatinous material (ca. 45 min). The obtained prepolymer was compression-molded at 10 MPa for 3 h using a Mini Test Press-10 (Toyo Seiki Co., Ltd, Tokyo, Japan) which was beforehand set to 180 °C to give a DGEDVCP/GCN cured product (DGEDVCP-GCN) with the epoxy/hydroxy ratio



Scheme 1. Chemical structure of DGEBA and synthetic route of DGEDVCP.

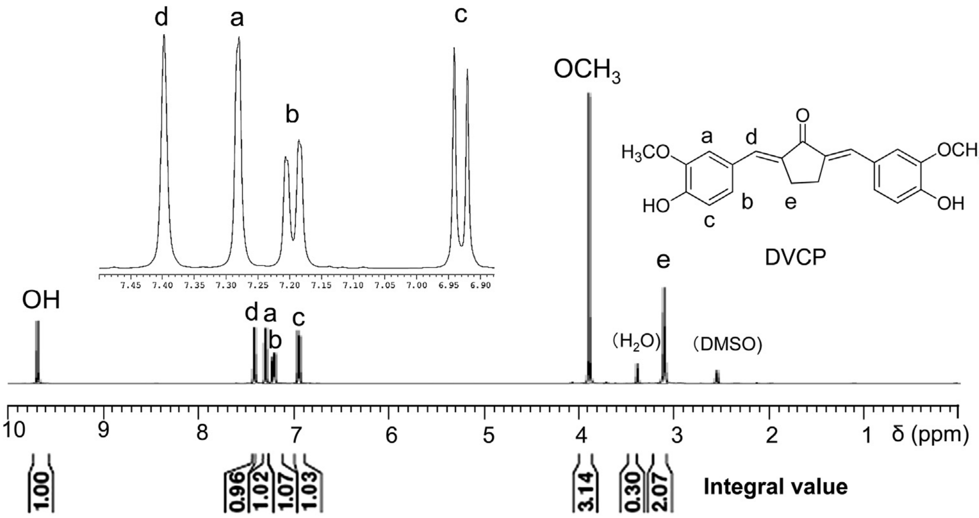


Fig. 1. ^1H NMR spectrum of DVCP in DMSO-d_6.

of 1/1 as a pale brown plate. The thickness of the plate was controlled using a stainless steel spacer (thickness: 1.0 mm) during the compression molding. The samples for flexural test and dynamic mechanical analysis were cut off using an electric fret-saw. DGEDVCP/QC, DGEDVCP/PN, DGEBA/GCN, DGEBA/QC and DGEBA/PN cured products (DGEDVCP-QC, DGEDVCP-PN, DGEBA-GCN, DGEBA-QC and DGEBA-PN) with the epoxy/hydroxy ratio of 1/1 were prepared by the similar procedure to the preparation of DGEDVCP-GCN except using acetone as a mixing solvent in the cases using QC and PN as hardeners.

2.5. Measurements

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker AV-400 (400 MHz) (Madison, WI, USA) using $CDCl_3$ or DMSO-d_6 as a solvent. Fourier transform infrared (FT-IR) spectra were recorded at room temperature in the range from 4000 to 700 cm^{-1} on a Shimadzu (Kyoto, Japan) IRAffinity-1S by the attenuated total reflectance (ATR) method. The IR spectra were acquired using 50 scans at a resolution of 4 cm^{-1}. The temperatures at which 5, 10 and 20% weight loss occurred (T_{d5}, T_{d10} and T_{d20}) and char yields at 500 °C were measured on a Shimadzu TGA-50 thermogravimetric analyzer using a sample of ca. 5 mg at a heating rate of 20 °C min^{-1} in a nitrogen atmosphere. Dynamic mechanical analysis (DMA) of a rectangular plate ($30 \times 5 \times 1$ mm^3) was performed on a Rheolograph Solid instrument (Toyo Seiki Co., Ltd, Tokyo, Japan) under air atmosphere with a chuck distance of 20 mm, a frequency of 1 Hz and a heating rate of 2 °C min^{-1}, based on ISO 6721-4:1994 (Plastics-Determination of dynamic mechanical properties, Part 4: Tensile vibration – Non-resonance method). Flexural testing of rectangular specimens

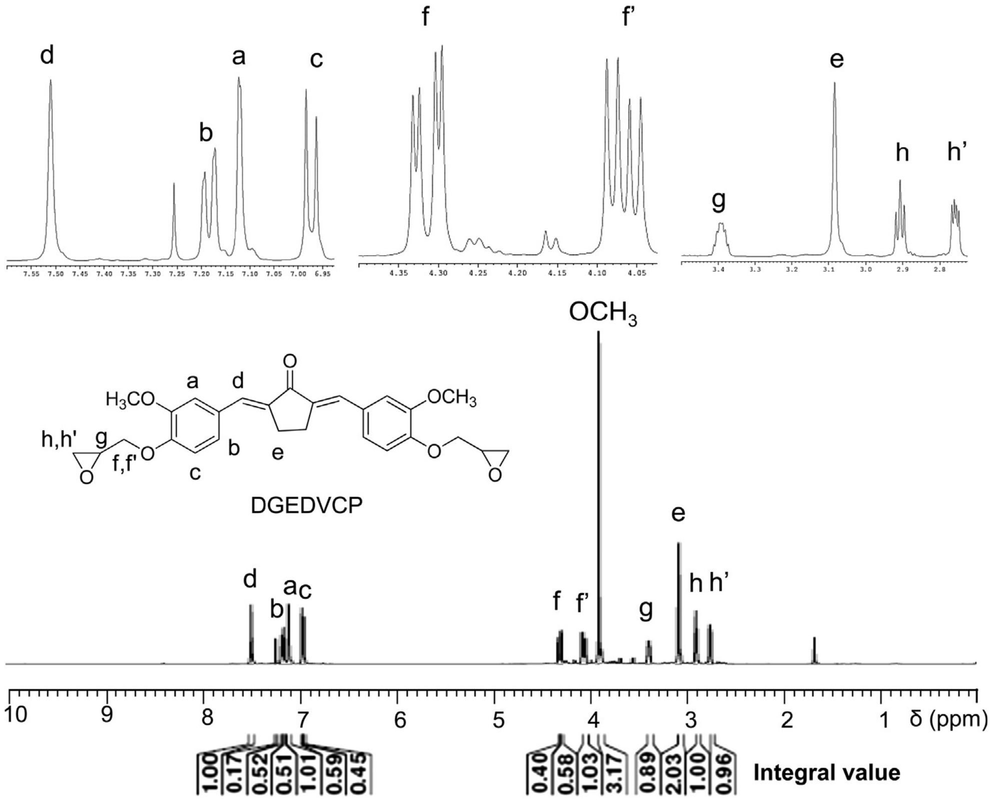


Fig. 2. ^{1}H NMR spectrum of DGEDVCP in $CDCl_3$.

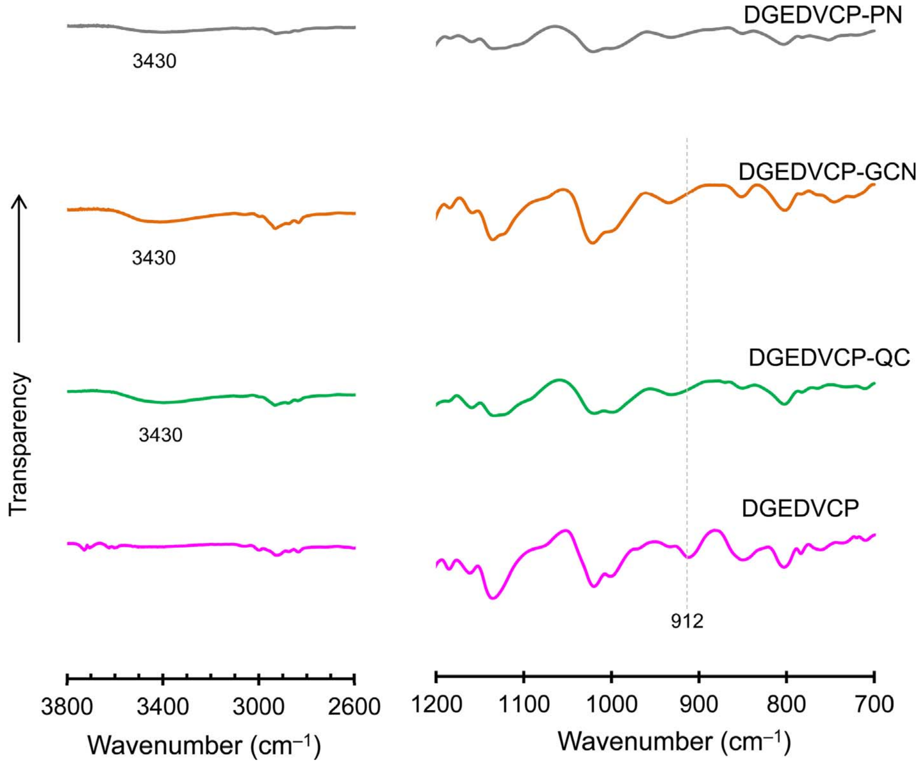
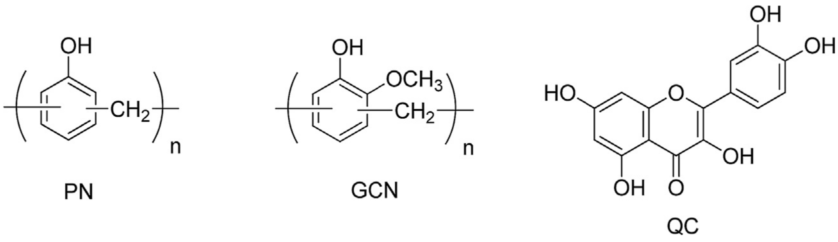


Fig. 3. FT-IR spectra of DGEDVCP, GCN, QC, DGEDVCP-GCN, DGEDVCP-QC and DGEDVCP-PN.



Scheme 2. Phenolic hardeners used in this study.

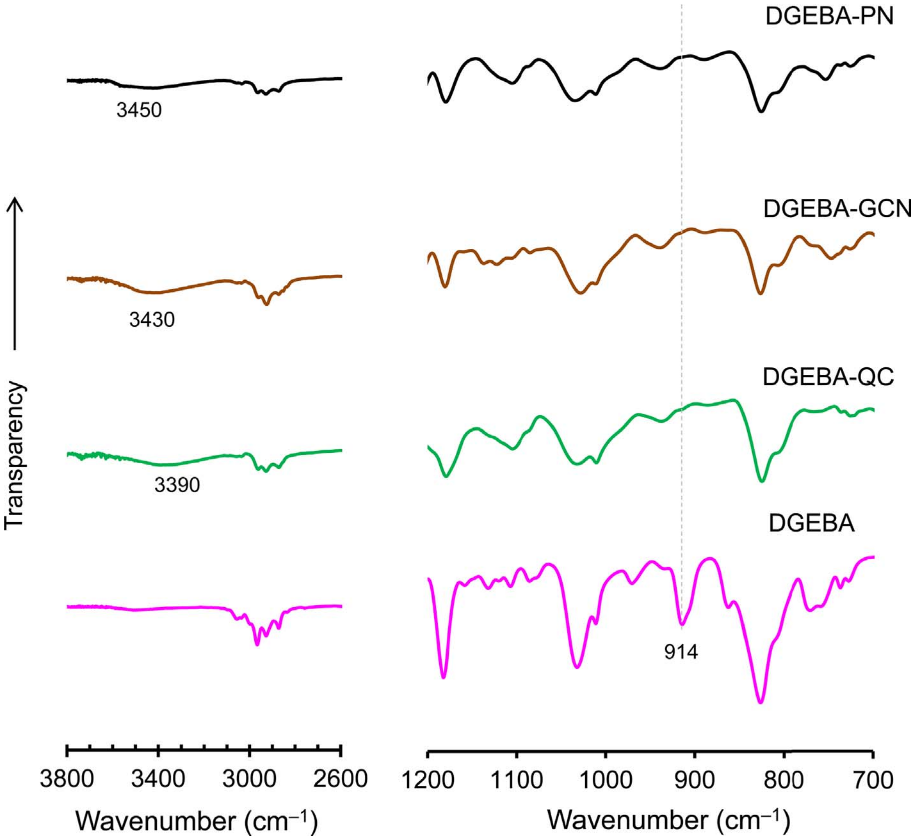


Fig. 4. FT-IR spectra of DGEBA, GCN, QC, DGEBA-GCN, DGEBA-QC and DGEBA-PN.

($50 \times 7 \times 1$ mm^3) was performed at room temperature (23 ± 2 °C) using an Autograph AG-1 (Shimadzu Co., Ltd.). The span length was 20 mm, and the testing speed was 10 mm min^{-1}. Five specimens were tested for each set of samples, and the standard deviation was calculated.

3. Results and discussion

3.1. Synthesis and Characterization of DGEDVCP

DVCP was synthesized by the crossed-aldol condensation and subsequent dehydration reactions of VN and CPN in a convenient one-pot process basically according to the already reported method [27]. DGEDVCP was quantitatively synthesized by a general glycidylation reaction of DVCP with excess epichlorohydrin in the presence of sodium hydroxide and TEBAC as a base and a phase transfer catalyst, respectively (Scheme 1).

Fig. 1 shows ^{1}H NMR spectrum of DVCP in DMSO-d_6. In the ^{1}H NMR spectrum of DVCP, the ^{1}H-signal of olefinic protons (H-d) which were formed by the dehydration reaction after the cross-aldol condensation was observed at 7.40 ppm (s, 2H). Concerning the ^{1}H-signals of benzene ring, broad singlet, broad doublet (J_{bc} = 8 Hz) and doublet (J_{bc} = 8 Hz) peaks at 7.28, 7.20 and 6.93 ppm were assigned to H-a, H-b and H-c, respectively based on their coupling patterns. Also, hydroxy, methoxy and methylene ^{1}H-signals of DVCP were observed at 9.69, 3.88 and 3.10 ppm, respectively.

Fig. 2 shows ^{1}H NMR spectrum of DGEDVCP in CDCl$_3$. In the case of DGEDVCP, the ^{1}H-signals of benzene ring at 7.18 (broad

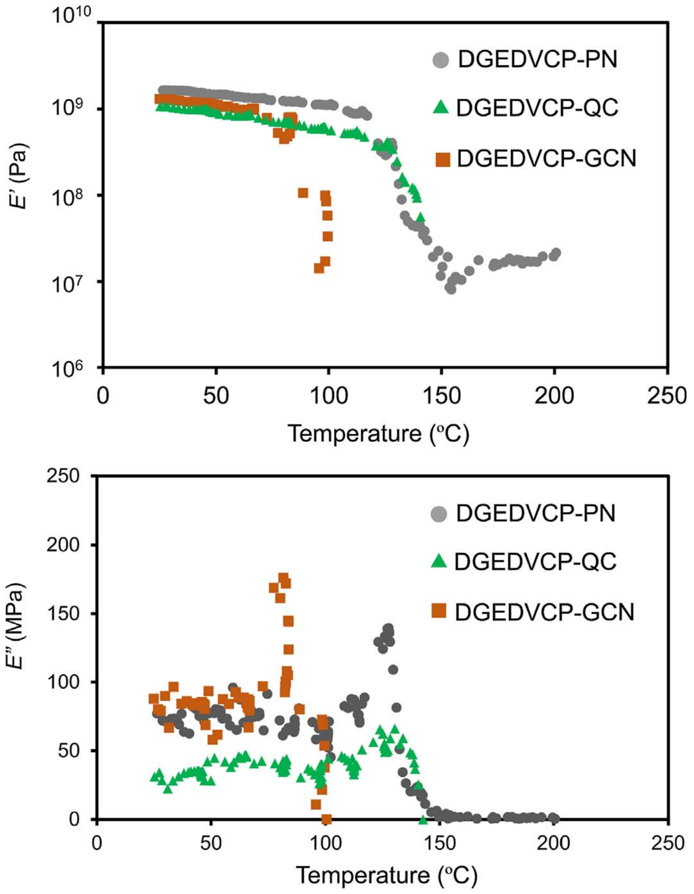


Fig. 5. DMA curves of DGEDVCP-GCN, DGEDVCP-QC and DGEDVCP-PN.

doublet, J_{bc} = 8 Hz), 7.12 (broad singlet) and 6.97 (doublet J_{bc} = 8 Hz) were assigned to H-b, H-a and H-c, respectively. The two protons ($H_{f,f'}$) of a phenoxymethylene unit were separately observed at 4.31 (dd, $J_{ff'}$ = 11.2 Hz, J_{fg} = 3.1 Hz, H-f) and 4.06 (dd, $J_{ff'}$ = 11.2 Hz, $J_{f'g}$ = 4.2 Hz, H-f′). Also, the two protons ($H_{h,h'}$) of an epoxy methylene group were separately observed at 2.90 (t, $J_{hh'}$ = 4.5 Hz, J_{hg} = 2.5 Hz, H-h) and 2.76 (dd, $J_{hh'}$ = 4.5 Hz, $J_{h'g}$ = 2.7 Hz, H-h′), and the proton (H-g) of an epoxy methine group was observes at 3.39 (m, H-g). Other ^{1}H-signals at 7.51 (s), 3.90 (s) and 3.08 ppm (s) were assigned to H-d, methoxy protons and H-e, respectively.

In the FT-IR spectrum of DGEDVCP, the absorption band characteristic of epoxy group was observed at 912 cm^{-1} as is shown in Fig. 3. The band due to epoxy group was used for the confirmation of curing reactions in the next section. Also, a band due to O-H stretching vibration was not observed in the wavenumber region of 3200–3500 cm^{-1}, indicating that phenolic hydroxy groups of DVCP were completely glycidylated. The chemical formula ($C_{27}H_{28}O_7$) of DGEDVCP elucidated from the ^{1}H NMR and FT-IR spectral data was confirmed by the electrospray ionization mass spectroscopy (ESI-MS) analysis, as is described in the experimental section.

3.2. Characterization and properties of the DGEDVCP and DGEBA resins cured with GCN, QC and PN

DGEDVCP was prepolymerized at 150 °C with GCN and QC as biobased phenolic hardeners, and PN as a petroleum-based popular hardener, and then compression-molded at 180 °C to produce cured products (DGEDVCP-GCN, DGEDVCP-QC and DGEDVCP-PN) (Scheme 2). For comparison, a petroleum-based DGEBA was similarly cured with GCN, QC and PN to produce DGEBA-GCN, DGEBA-QC and DGEBA-PN, respectively. Figs. 3 and 4 show FT-IR spectra of DGEDVCP- and DGEBA-based cured products compared with those of DGEDVCP and DGEBA, respectively. The absorption bands at 912 and 914 cm^{-1} characteristic of epoxy groups which were observed for DGEDVCP and DGEBA, respectively, were nonexistent for all the cured resins, indicating that the epoxy groups were certainly consumed. Furthermore, broad absorption bands due to OH stretching vibration were observed at 3390–3450 cm^{-1} for all the cured resins, suggesting that hydroxy propyl moieties generated by the ring-opening reaction of epoxy and phenolic hydroxy groups. The gel contents measured by the extraction with hot chloroform for DGEDVCP-GCN, DGEDVCP-QC and DGEDVCP-PN were 98.1, 99.4 and 99.7 wt%, respectively, indicating that the reactants were almost completely incorporated into the polymer networks. The fact that DGEDVCP-GCN exhibited a little lower gel content should be caused by the lower hydroxy functionality (2.52) of GCN.

Figs. 5 and 6 show DMA curved of DGEDVCP- and DGEBA-based products, respectively. Table 1 summarizes loss modulus (E″)

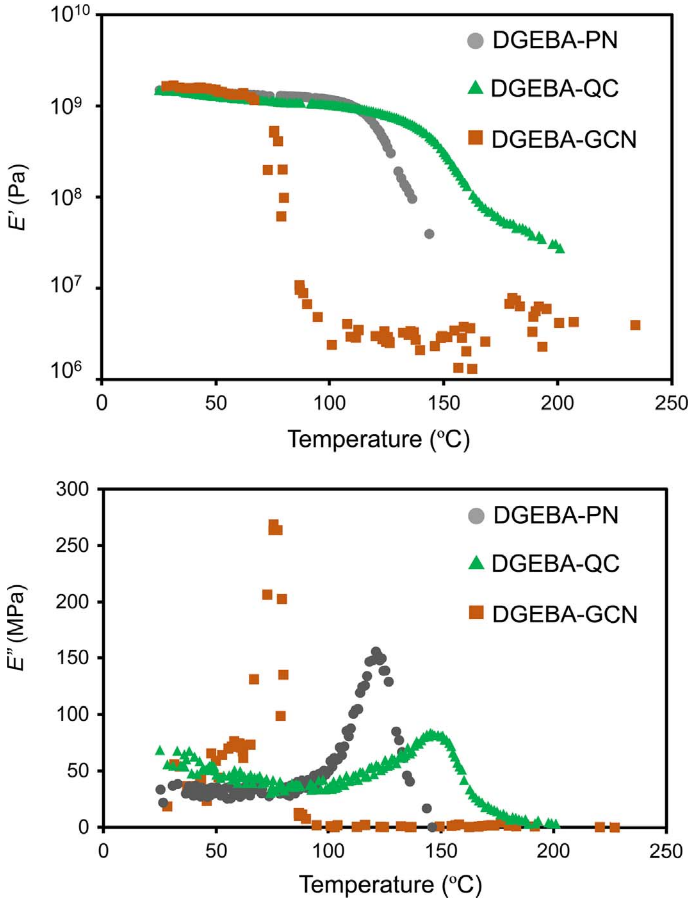


Fig. 6. DMA curves of DGEBA-GCN, DGEBA-QC and DGEBA-PN.

Table 1

Peak temperatures of tan δ and *E″*, thermal degradation temperatures and char yields at 500 °C for all the cured resins.

Sample	Tan δ peak temperature (°C)	*E″* peak temperature (°C)	T_{d5} (°C)	T_{d10} (°C)	T_{d20} (°C)	Char yield at 500 °C (%)
DGEDVCP-GCN	100	82	387	422	438	48
DGEDVCP-QC	141	130	386	419	431	61
DGEDVCP-PN	131	128	394	428	440	59
DGEBA-GCN	77	76	408	431	440	30
DGEBA-QC	155	144	394	420	439	39
DGEBA-PN	133	121	413	432	450	35

peak temperatures corresponding to glass transition temperatures (T_gs) in addition to tan δ peak temperatures for all the cured resins. The higher order of *E″* peak temperature was QC-cured resins > PN-cured resins > GCN-cured resins. This result should be attributed to the fact that QC has a rigid flavonoid framework with five hydroxy groups, and that the hydroxy functionality of GCN is much lower than those of PN and QC. It can be said that QC is an excellent epoxy hardener to produce the cured resins with high glass transition temperatures. It is noteworthy that the *E″* peak temperatures (130 and 128 °C) of DGEDVCP-QC and DGEDVCP-PN are higher than that (121 °C) of the conventional DGEBA-PN, whereas that (144 °C) of DGEBA-QC was the highest among those of all the cured resins. The fact that DGEDVCP-PN exhibited a higher *E″*peak temperature than DGEBA-PN should be caused by a more rigid structure of the 2,5-bis(exomethylene)cyclopentanone moiety of DGEDVCP than the isopropylidene moiety of DGEBA. Also, the tan δ peak temperatures (141 and 131 °C) of DGEDVCP-QC and DGEDVCP-PN were much higher than those (113–117 °C) of the cured products of epoxy resins derived from model mixtures of the lignin-to-vanillin process and isophorone diamine [21]. Although there was not a big difference in the storage modulus (*E′*) value at 30 °C for the DGEBA-cured resins, the *E′* of DGEDVCP-QC (1.06 GPa) was apparently lower than those (1.64 and 1.29 GPa) of DGEDVCP-PN and DGEDVCP-GCN. It is considered that some hydroxy groups of QC did not react with epoxy groups of DGEDVCP due to the steric hindrance. Considering that the *E′* at 30 °C of DGEBA-QC (1.47 GPa) was comparable to that of DGEBA-PN (1.48 GPa), the glycidyl *o*-methoxyphenyl ether moiety of DGEDVCP should be more congested than glycidyl phenyl ether moiety of DGEBA.

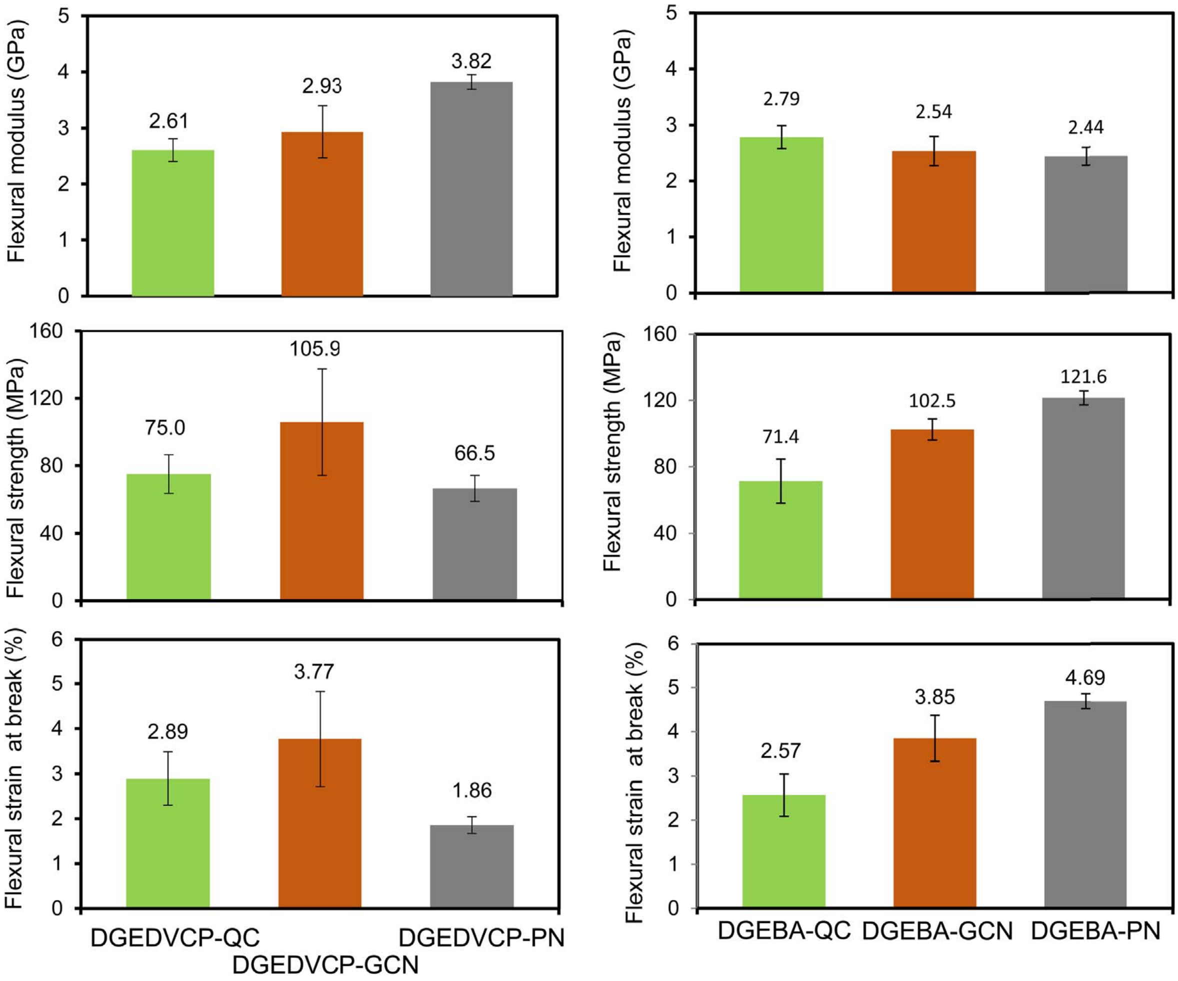


Fig. 7. Flexural properties of all the cured resins.

Table 1 also summarizes thermal degradation temperatures (T_ds) evaluated by 5, 10 and 20 wt% weight loss temperatures (T_{d5}, T_{d10} and T_{d20}) and char yields at 500 °C measured by TGA. The T_ds of DGEDVCP-based products were a little lower than those of DGEBA-based products. However, the former products exhibited much higher char yields at 500 °C than the latter ones. Although we did not measure the fire-retardancy, there is a possibility that DGEDVCP-based products are more flame-retardant than DGEBA-based products. Regarding the influence of the hardeners on T_ds of the cured resins, the higher order was PN > GCN > QC.

Fig. 7 shows flexural properties of all the cured resins. In agreement with the trend on the E' value at 30 °C, a higher order of flexural modulus at room temperature for the DGEDVCP-based products was DGEDVCP-PN > DGEDVCP-GCN > DGEDVCP-QC, and there was not a big difference in flexural modulus for the DGEBA-based products. The lowest flexural modulus of DGEDVCP-QC should be caused by the factor that five hydroxy groups of QC did not completely react with epoxy groups of DGEDVCP, as was discussed above. Although the epoxy/hydroxy ratio was fixed to 1/1 for the purpose of comparison of products cured with the same condition, the improvement of the flexural properties for DGEDVCP-QC is expected by the optimization of the epoxy/hydroxy ratio in a similar manner to the sorbitol-based polyglycidyl ether resins cured with QC [26]. It is noteworthy that the flexural modulus (3.82 GPa) of DGEDVCP-PN is much higher than that (2.44 GPa) of DGEBA-PN, reflecting that the framework of DGEDVCP is more rigid than that of DGEBA. However, the flexural strength and strain at break of DGEDVCP-PN was the lowest among the DGEDVCP-based cured resins, suggesting that DGEDVCP-PN is a relatively brittle material with a high crosslinking density. On the other hand, DGEDVCP-GCN exhibited the highest flexural strength and strain at break (105.9 MPa and 3.77%) among the DGEDVCP-based products, which were comparable to those (102.5 MPa and 3.85%) of DGEBA-GCN. This result should be attributed to the lowest hydroxy functionality (2.52) of GCN leading to a low crosslinking density. Also, the flexural strength, modulus and strain at break (75.0 MPa, 2.81 GPa and 2.80%) of DGEDVCP-QC were comparable to those (71.4 MPa, 2.79 GPa and 2.57%) of DGEBA-QC. In the past studies on VN-derived epoxy resins, it was reported that the tensile strength and modulus of cured products of a diglycidyl ether of methoxyhydroquinone were 14.9 MPa and 2.01 GPa [24]. Although the tensile and flexural properties cannot be simply compared, it can be said that the DGEDVCP-based products in this study possess excellent mechanical properties in comparison with those of the biobased VN-derived epoxy cured resins.

4. Conclusions

A new biobased aromatic epoxy resin (DGEDVCP) was synthesized by the glycidylation of the crossed-aldol condensation product (DVCP) of vanillin and cyclopentanone. The thermal and mechanical properties of the DGEDVCP resins cured with biobased hardeners (QC and GCN) and a petroleum-based hardener (PN) were compared with those of the DGEBA resins cured with the same hardeners. The E'' peak temperatures of DGEDVCP-QC and DGEDVCP-PN are higher than that of the conventional DGEBA-PN. Although the T_ds of DGEDVCP-based products were a little bit lower than those of the corresponding DGEBA-based products, the difference in T_{d5} between DGEDVCP-QC and DGEBA-QC was only 8 °C. Char yields at 500 °C for DGEDVCP-based products were much higher than those of DGEBA-based products. The flexural strengths and moduli of the DGEDVCP/QC and DGEDVCP/GCN cured products were comparable to those of DGEBA/QC and DGEBA/GCN cured products, respectively. Consequently, the fully biobased epoxy resin systems utilizing renewable phenolic compounds in this study are promising materials which can replace the conventional petroleum-based epoxy resin systems.

Acknowledgements

We gratefully acknowledge financial support from the Chiba Institute of Technology. We thank Dr. Naozumi Teramoto and Dr. Toshiaki Shimasaki of our department for their helpful suggestions.

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