

Thermal and Mechanical Properties of Sorbitol-Based Epoxy Resin Cured with Quercetin and the Biocomposites with Wood Flour

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ABSTRACT: After a bio-based epoxy resin, sorbitol polyglycidyl ether (SPE) was mixed with a flavonoid, quercetin (QC) in tetrahydrofuran at an optimized epoxy/hydroxy ratio 1/1.2, the obtained SPE/QC solution was mixed with wood flour (WF), prepolymerized at 150°C, and subsequently compressed at 170°C for 3 h to give SPE-QC/WF biocomposites (WF content:0, 20, 30, 40 wt %). The tan δ peak temperature of SPE-QC without WF (85.5°C) was higher than that of SPE cured with conventional phenol novolac (81.0°C). In addition, diglycidyl ether of bisphenol A cured with QC had a higher tan δ peak temperature (145.1°C) than that cured with PN (90.8°C). The tan δ peak temperatures (106–113°C) of SPE-QC/WF biocomposites were significantly higher than that of SPE-QC. The tensile modulus of SPE-QC/WF biocomposites increased with increasing WF content. A lower wavenumber shift of carbonyl stretching absorption peak in the FTIR spectrum of SPE-QC/WF as compared with that of SPE-QC suggested that hydroxy group of woody component forms hydrogen bonding with carbonyl group of quercetin moiety. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Renewable resources-derived polymers (bio-based polymers) and their composites with natural/bio fibers (biocomposites) have attracted attention in recent years due to increasing environmental concern and restricted availability of petrochemical resources.^{1–6} Most recently, much focus is being placed on bio-based thermosetting resins such as epoxy resins, phenol resins, unsaturated polyester resins, and their biocomposites, because their materials are hard to be recycled due to the infusible and insoluble properties.^{7–23} As examples of the bio-based epoxy resins, there are many references on epoxidized vegetable oils^{9–14} and lignin-based epoxy resins,^{15–18} etc. We have also reported on the preparation and properties of sorbitol polyglycidyl ether (SPE) or glycerol polyglycidyl ether (GPE) cured with tannic acid (TA) and its biocomposites with microfibrillated cellulose or wood flour (WF).^{22,23} The cured epoxy resins with high glass transition temperatures (T_g s) are required to retain the dimensional stability and rigidity at a high temperature in electrical and structural materials.^{24,25} However, T_g s of the cured bio-based epoxy resins and their biocomposites were still lower than those of cured materials based on popular diglycidyl ether of bisphenol A (DGEBA).²⁶ Therefore, when industrially available and inexpensive SPE is combined with a bio-based phenolic hardener, the hardener having a lower hydroxy value and a

higher aromatic content than TA should be used. Quercetin (3,3',4',5,7-pentahydroxyflavone) is one of the most abundant flavonoid found in glycosylated forms in plants such as onion, capers and tea. Quercetin can be obtained from plants via extraction of the quercetin glycosides followed by hydrolysis to release the aglycone and subsequent purification.²⁷ Although quercetin is used as an ingredient in supplements, beverages and foods, it has not been used as an ingredient of polymer materials to the best of our knowledge. When quercetin is used as an epoxy hardener, it is expected that the cured resin has a high T_g and superior adhesiveness to plant fibers because of the rigid and polar polyphenol moiety.

This study describes the preparation and properties of the SPE cured with QC and its biocomposites with WF. The thermal properties of the cured SPE/QC are also compared with those of SPE cured with PN, and DGEBA cured with QC or PN. Our attention is focused on the development of heat resistant bio-based epoxy resin/hardener/WF composites having a comparable T_g to conventional DGEBA/PN curing system.

EXPERIMENTAL

Materials

Figure 1 shows the structure of the reagents used in this study. Sorbitol polyglycidyl ether (SPE, DENAKOL EX-614B (weight

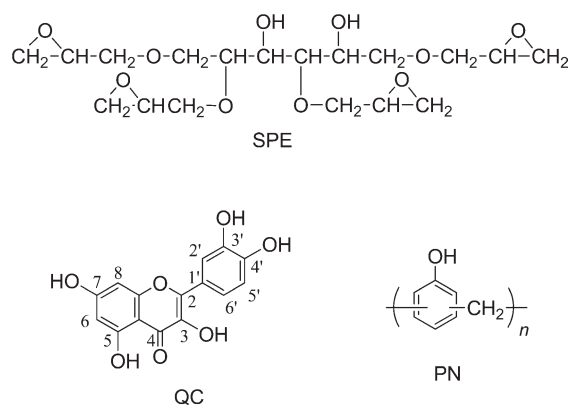


Figure 1. Chemical structure of SPE, QC, and PN.

per epoxy equivalent 172.2 g/eq., average functional groups 3.6, chlorine content 9.8%, viscosity 4740 mPa s at 25°C) was kindly supplied from Nagase ChemteX, (Tokyo, Japan). Quercetin (QC) was purchased from Sigma-Aldrich Japan (Tokyo, Japan). Wood flour (WF) was supplied by Kowa Technos (Sammushi, Chiba, Japan). The WF is made from Sanbu cedar crushed into powders through 3 mm screen mesh. It was dried at 105°C for 24 h before use. As petroleum-based epoxy resin and hardener, diglycidyl ether of bisphenol A (DGEBA, maker grade: jER[®] 828, weight per epoxy equivalent:185 g/eq.) and phenol novolac (PN, maker grade: PR-HF-3, softening point 82°C, weight per phenolic hydroxy equivalent 104 g/eq.) were kindly supplied from Mitsubishi Chemical Corporation (Tokyo, Japan) and Sumitomo Berklite (Tokyo, Japan). Triphenylphosphine (TPP) was purchased from Tokyo Chemical Industry (Tokyo, Japan).

Preparation of SPE-QC and SPE-PN

A mixture of SPE 8.61 g (epoxy 50.0 mmol), QC 3.63 g (hydroxy 60.0 mmol), and tetrahydrofuran 40 mL was stirred for 1 h at room temperature. After the obtained homogeneous

solution was poured onto stainless steel plate, almost the solvent was vaporized at 40°C for 24 h. The resulting viscous liquid was prepolymerized at 150°C for 2 h, and then compression-molded at 170°C for 3 h to give a cured resin of SPE/QC with the epoxy/hydroxy ratio of 1/1.2 (SPE-QC) as pale brown plate. The cured samples at epoxy/hydroxy ratios of 1/0.8, 1/0.9, 1/1, and 1/1.1 (SPE-QC 1/0.8, 1/0.9, 1/1, and 1/1.1) were similarly prepared by the compression-molding. If the epoxy/hydroxy ratio is not specified for SPE-QC, it means 1/1.2. For SPE-QC 1/1, the thermal properties of the resins cured at 150, 170, and 190°C for 3 h were compared. If the curing temperature is not specified, its curing temperature is 170°C. In a similar manner to the preparation of SPE-QC except for using PN, the cures SPE/PN resins at epoxy/hydroxy ratios of 1/0.8, 1/0.9, and 1/1 (SPE-PN 1/0.8, SPE-PN 1/0.9, and SPE-PN 1/1) were also prepared. If the epoxy/hydroxy ratio is not specified for SPE-PN, it means 1/0.8. The use of TPP as a catalyst for curing of SPE and QC (PN) little affected the thermal properties of the cure SPE/QC(PN), although the gelation time becomes shorter.

Preparation of DGEBA-QC and DGEBA-PN

A mixture of DGEBA 9.25 g (epoxy 50.0 mmol), QC 3.63 g (hydroxy 60.0 mmol), TPP 64 mg (0.24 mmol) and tetrahydrofuran 45 mL was stirred for 1 h at room temperature. After the obtained homogeneous solution was poured onto stainless steel plate, almost the solvent was vaporized at 40°C for 24 h. The resulting viscous liquid was prepolymerized at 150°C for 0.5 h, and then compression-molded at 170°C for 3 h to give a cured resin of DGEBA/QC with the epoxy/hydroxy ratio of 1/1.2 (DGEBA-QC 1/1.2) as pale brown plate. The sample cured at epoxy/hydroxy ratio of 1/1 (DGEBA-QC 1/1) was also prepared by the compression-molding. In a similar manner to the preparation of DGEBA-QC except for using PN, the DGEBA cured with PN at epoxy/hydroxy ratio of 1/1 (DGEBA-PN 1/1) was also prepared.

Table I. Thermal Properties of Epoxy Resins Cured with QC and PN at Various Conditions

Sample	Epoxy/hydroxy ratio	Curing temperature (°C)	tan δ peak temperature (°C)	5% Weight loss temperature (°C)
SPE/QC	1/1	150	58.7	330.1
		170	78.4	335.4
		190	75.3	329.5
SPE/QC	1/0.8	170	84.9	342.2
		170	79.8	344.9
		170	78.4	335.4
		170	79.5	335.8
		170	85.5	342.5
SPE/PN	1/0.8	170	81.0	346.3
		170	80.6	
		170	78.1	
DGEBA/QC	1/1	170	130.2	385.2
		170	145.1	407.4
DGEBA/PN	1/1	170	90.8	395.5

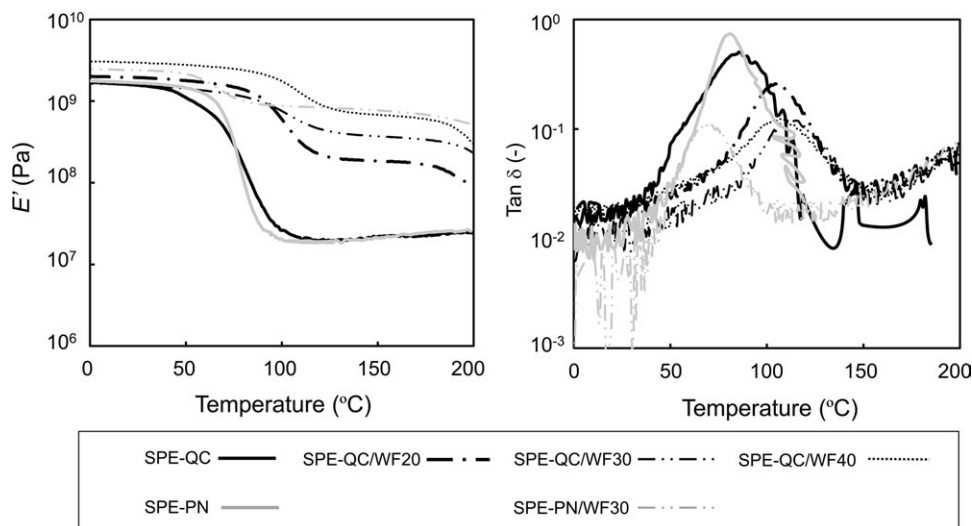


Figure 2. DMA curves of SPE-PN, SPE-QC, SPE-PN/WF, and SPE-QC/WF biocomposites.

Preparation of SPE-QC/WF and SPE-PN/WF Biocomposites

A mixture of SPE 8.61 g (epoxy 50.0 mmol), QC 3.63 g (hydroxy 60.0 mmol) and tetrahydrofuran 40 mL was stirred for 1 h at room temperature. After the obtained homogeneous solution was poured onto stainless steel plate, almost the solvent was vaporized at 40°C for 24 h. The resulting viscous liquid was prepolymerized with WF 3.00 g at 150°C for 2 h, and then compression-molded at 170°C for 3 h to give a cured SPE-QC/WF biocomposite with WF content 20 wt % (SPE-QC/WF20) as a brown plate. In a similar manner, SPE-QC/WF composites with WF content 30 and 40 wt % (SPE-QC/WF30 and SPE-QC/WF40) were prepared. As a comparison, SPE-PN/WF composite with WF content 30 wt % (SPE-PN/WF30) was similarly prepared.

Measurements

FTIR spectra were measured in the wavenumber range of 700–400 cm^{-1} on a FTIR 8100 spectrometer (Shimadzu, Kyoto, Japan) by the KBr method (sample 1 mg, KBr 0.3 g). The spectra were acquired using 50 scans at a resolution of 4 cm^{-1} . The

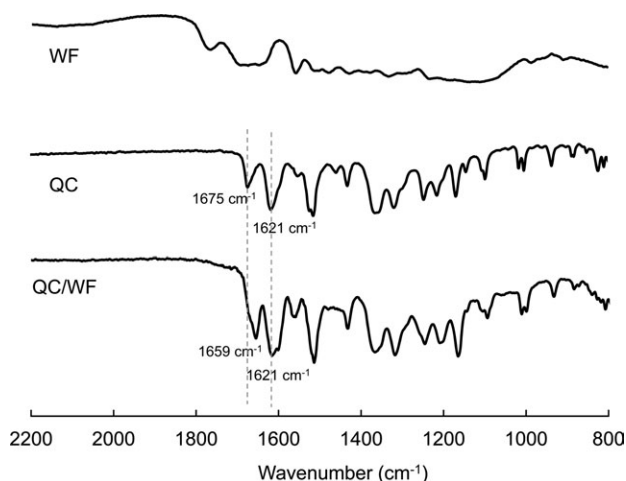


Figure 3. FTIR spectra of WF, QC, and QC/WF.

5% weight loss temperature of the sample (8–12 mg) was measured over the temperature range of room temperature to 500°C on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 20°C/min in a nitrogen atmosphere. Dynamic mechanical analysis (DMA) of the rectangular specimen (length 30 mm, width 5 mm, thickness 1.2–1.9 mm) was performed on a Rheograph Solid (Toyo Seiki, Tokyo, Japan) with a chuck distance of 20 mm, a frequency of 1 Hz and a heating rate of 2°C/min. Tensile test of the rectangular specimen (length 50 mm, width 7 mm, thickness 1.0–1.2 mm) was performed at 25°C using an Autograph AG-I (Shimadzu, Kyoto, Japan) based on the standard method for testing the tensile properties of plastics [JIS K7161:1994 (ISO527-1:1993)]. Span length and testing speed was 25 mm and 10 mm/min. Five specimens were tested for each set of samples, and the mean values and the standard deviation were calculated. The morphology of the composites was observed by field emission-scanning electron microscopy (FE-SEM), using a Hitachi S-4700 machine (Hitachi High-Technologies Corporation, Japan). All samples were fractured after immersion in liquid nitrogen for about 30 min. The fracture surfaces were sputter coated with gold to provide enhanced conductivity.

RESULTS AND DISCUSSION

Properties of Cured Epoxy Resins

In order to optimize the curing condition of SPE and QC, the curing temperature and epoxy/hydroxy ratio were changed. Table I summarizes the $\tan \delta$ peak temperature measured by DMA and 5% weight loss temperature of SPE-QC cured at various conditions. When the curing temperature was changed

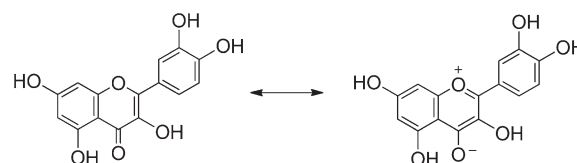


Figure 4. Resonance structure of QC.

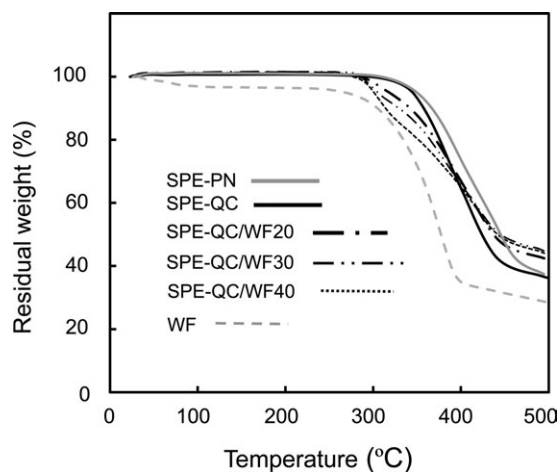


Figure 5. TGA curves of SPE-PN, SPE-QC, and SPE-QC/WF biocomposites.

from 150°C to 190°C for SPE/QC at a typical epoxy/hydroxy ratio of 1/1, the SPE/QC cured at 170°C had the highest $\tan \delta$ peak temperature (78.4°C) and 5% weigh loss temperature (335.4°C). Because SPE is an aliphatic epoxy resin, it is presumed that some thermal degradation starts to occur at around 190°C. Therefore, the curing temperature was fixed to 170°C. When the epoxy/hydroxy ratio was changed from 1/0.8 to 1/1.2 at the curing temperature of 170°C, the SPE-QC 1/1.2 had the highest $\tan \delta$ peak temperature (85.5°C) and 5% weigh loss temperature (342.5°C). This result suggests that four hydroxy groups of QC with five hydroxyl groups per molecule actually reacted with SPE. Although it is not clear why SPE-QC 1/0.8 had a higher $\tan \delta$ peak temperature than SPE-QC 1/0.9-1/1.1, it is supposed that cationic homopolymerization of SPE occurs by the action of acidic hydroxy proton at α -position of carbonyl group of QC. Consequently, the epoxy/hydroxy ratio of 1/1.2 and curing temperature of 170°C were selected as the optimized curing condition for SPE/QC. Table I also summarizes the thermal properties of the cured resins of SPE/PN, DGEBA/QC and DGEBA/PN. As a result of optimization of the epoxy/hydroxy ratio for SPE/PN, SPE-PN 1/0.8 showed the highest $\tan \delta$ peak

temperature (81.0°C), which was still lower than that of SPE-QC 1/1.2 (85.5°C). Although we did not fully optimize the epoxy/hydroxy ratio for DGEBA/QC and DGEBA/PN, DGEBA-QC 1/1 and DGEBA-QC 1/1.2 showed higher $\tan \delta$ peak temperature than DGEBA-PN 1/1. These results indicate that QC is a superior epoxy hardener to produce the cured resin with a high glass transition temperature (T_g).

Properties of SPE-QC/WF Biocomposites

Figure 2 shows the temperature dependency of storage modulus (E') and $\tan \delta$ for SPE-QC, SPE-PN, SPE-QC/WF, and SPE-PN/WF biocomposites measured by DMA. The $\tan \delta$ peak amplitude for the biocomposites became weaker with increasing WF content, indicating that amorphous content of the biocomposites certainly decreased with WF content. The E' curve of at the rubbery plateau region over 120°C for all the biocomposites was much higher than those of control SPE-QC and SPE-PN, suggesting a superior reinforcement effect due to the wood fibers. The $\tan \delta$ peak temperatures (SPE-QC/WF20, 30, 40:106.2, 112.7, 107.2°C) related to T_g for the SPE-QC/WF biocomposites were significantly higher than that of SPE-QC (85.5°C). This trend is marked contrast to the fact that SPE-PN/WF30 had a lower $\tan \delta$ peak temperature (69.9°C) than that of SPE-PN did (81.0°C). Similar lowering of $\tan \delta$ peak temperature of WF biocomposite relative to the corresponding cured neat resin had been also observed for GPE/TA/WF biocomposites as was reported by our group.²² Also, the E' of the SPE-QC/WF biocomposites declined at around 90–120°C due to the glass transition, and then again decreased at around 180–200°C, probably due to the disappearance of specific interaction between WF and the cured SPE/QC resin. Figure 3 shows FTIR spectra of WF, QC, and a mixture of QC/WF 1/1 (w/w) prepared by mixing in THF and drying at 40°C for 24 h. The band at 1621 cm^{-1} for QC due to C=C stretching vibration at C-2 and 3 did not shift for QC/WF. In contrast, the band at 1675 cm^{-1} for QC due to unsaturated carbonyl (C=O) stretching vibration significantly shifted to a lower wavenumber region for QC/WF (1659 cm^{-1}), indicating that there is a hydrogen bonding interaction between unsaturated carbonyl group of quercetin moiety and hydroxyl group of lignocellulose component of WF.

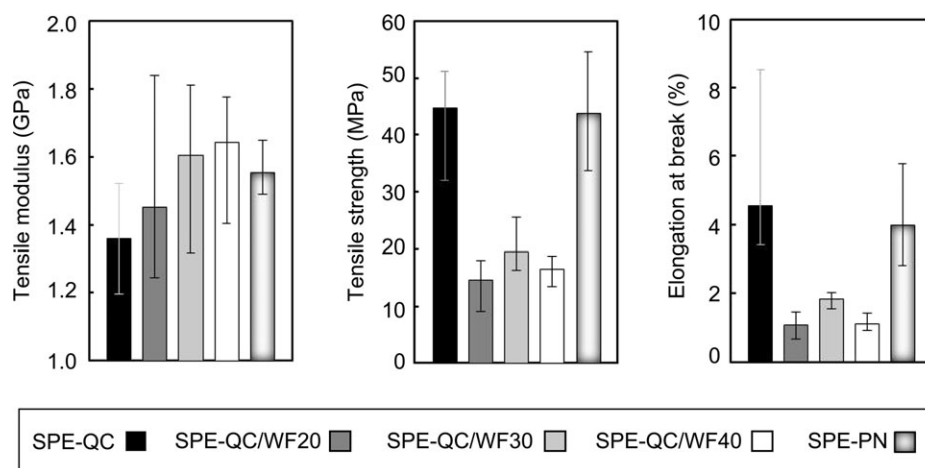


Figure 6. Tensile properties of SPE-PN, SPE-QC, and SPE-QC/WF biocomposites.

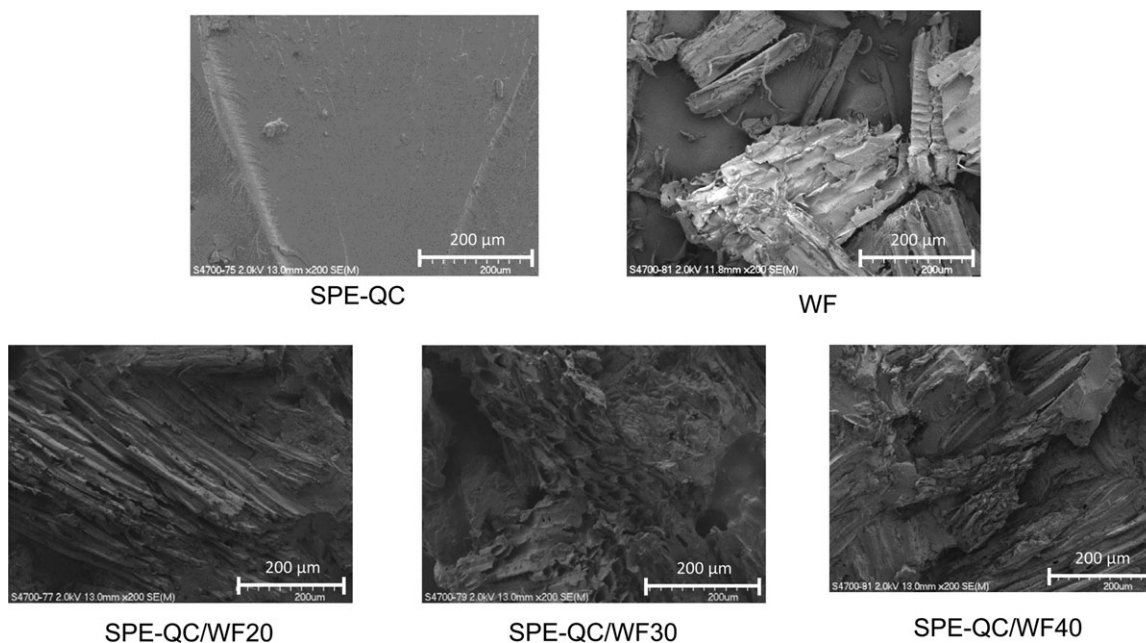


Figure 7. FE-SEM images of WF and the fracture surface of SPE-QC and SPE-QC/WF biocomposites.

This interaction is based on the resonance structure of QC generating highly polarized carbonyl group as is shown in Figure 4.

Figure 5 shows typical TGA curves of SPE-PN, SPE-QC, SPE-QC/WF biocomposites, and WF. Since the thermal decomposition temperature of WF was lower than that of SPE-QC, the SPE-QC/WF composite exhibited two-step thermodegradation. The 5% weight loss temperatures of SPE-QC, SPE-QC/WF20,30,40, and WF were 342.5, 311.4, 300.8, 299.2, and 295.5°C, respectively. The SPE-QC showed a comparable 5% weight loss temperature to SPE-PN (346.3°C) in agreement with the fact that both QC and PN are aromatic polyphenols. In addition, the cured resin of DGEBA and GC, both of which are aromatic compounds had a superior 5% weight loss temperature (407.4°C) as is shown in Table I.

Figure 6 shows the relationship between tensile properties and fiber content for SP-QC/WF composites. The tensile modulus of SPE-QC/WF biocomposites increased with increasing WF content, and SPE-QC/WF40 had a higher tensile modulus than SPE-PN. However, tensile strength and elongation at break of the biocomposite were lower than those of SPE-QC. Figure 7 shows the FE-SEM images of the fractured surface of SPE-QC/WF biocomposites. The micrograph of WF shows that the fiber length and width of WF are ca. 0.2–0.4 mm and 40–200 μm, respectively. It appeared that the composites are fractured at the interface between WF and the cured resin. As SPE-QC itself has a high tensile strength (43 MPa), a considerably high interfacial adhesiveness between WF and SPE-QC is necessary to obtain the biocomposite with a higher tensile strength than the cured resin.

CONCLUSIONS

The curing condition of bio-based SPE/QC was optimized and the thermal properties of the cured resin were compared with

those of the SPE cured with petroleum-based PN. As a result, SPE-QC showed a higher $\tan \delta$ peak temperature than SPE-PN. When petroleum-based DGEBA was also used as an epoxy resin, DGEBA-QC showed a higher $\tan \delta$ peak temperature and 5% weight loss temperature than those of DGEBA-PN. These results indicate that QC is a superior epoxy hardener to generate the cured resin with high heat resistance. The SPE-QC/WF biocomposites showed higher $\tan \delta$ peak temperature, storage modulus and tensile modulus than SPE-QC. The high $\tan \delta$ peak temperature of the biocomposites was attributed to the interfacial hydrogen bonding interaction between unsaturated carbonyl group of quercetin moiety and lignocellulose component of WF. The all-bio-based SPE-QC/WF composites are expected to be environmentally benign materials for the replacement of petroleum-based fiber-reinforced epoxy composites.

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