

## Wood-Derived Phenol Novolaks and Their Wood/Epoxy Biocomposites

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**ABSTRACT:** Guaiacol novolak (GCN) and wood-tar creosote novolak (WCN) were synthesized by the reactions of wood-derived guaiacol and creosote with formalin, respectively, and used as hardeners of sorbitol polyglycidyl ether (SPE). Thermal and mechanical properties of the cured resins (SPE-GCN and SPE-WCN) and their biocomposites with wood flour (WF) were compared with those of the materials prepared by using a petroleum-based phenol novolak (PN). Although  $\tan \delta$  peak temperatures of SPE-GCN and SPE-WCN were lower than that of SPE-PN, that (58.5–70.8°C) of SPE-GCN/WF(40–50 wt %) was higher than that (56.6–57.0°C) of SPE-PN/WF(40–50 wt %). Tensile moduli of all the biocomposites increased by the addition of WF, while tensile strengths were rather reduced. When the biocomposites with the same WF content were compared, tensile modulus of SPE-GCN/WF was higher than that of SPE-PN/WF. The 5% weight loss temperatures (346–291°C) of SPE-GCN and SPE-GCN/WF were comparable to those (338–284°C) of SPE-PN and SPE-PN/WF. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41347.

**KEYWORDS:** biopolymers and renewable polymers; cellulose and other wood products; composites; mechanical properties; thermosets

Received 1 May 2014; accepted 30 July 2014

DOI: 10.1002/app.41347

### INTRODUCTION

The soaring petroleum prices, concerns over the depletion of fossil resources in the near future, and increasing environmental concern have led to a growing interest in the use of alternative renewable resources for energy and materials.<sup>1,2</sup> Lignocellulosic biomass is a promising resource that can replace fossil oil without competition with food applications compared to starch or vegetable oils.<sup>3–5</sup> Lignocellulosic biomass is made up of three main components: cellulose, lignin, and hemicellulose. Lignin is of particular interest due to its phenolic nature from which a wide variety of phenols and phenol derivatives can be derived.<sup>6,7</sup> However, lignin and its derivatives are rarely exploited as raw materials for chemical production because of their unclear structure and its versatility according to the origin, separation, and fragmentation processes. We have interested in wood-tar creosote (WC), which is an industrially available and relatively cheap (\$1000–3000 per metric ton) phenolic mixture derived from lignin. The WC is produced by the distillation of wood tar which is obtained during the carbonization of beechwood or pine tree. The primary constituents of WC are guaiacol (2-methoxyphenol) and creosol (2-methoxy-4-methylphenol) (Figure 1). As other constituents, phenol, cresols (methylphenols), 4-ethylguaiacol and xylenols (dimethylphenols) etc. are contained.<sup>8,9</sup> Guaiacol (GC) is usually derived from WC or guaiacum.<sup>10</sup> The main uses of WC and GC are antiseptics,

gastric sedatives, flavorings, deodorants, fungicides, and parasitocides. There are very few reports on the polymer materials using WC or GC. Lindberg et al. reported the synthesis of guaiacol novolak (GCN) by the reaction of GC and paraformaldehyde using hydrochloric acid catalyst.<sup>11</sup> Liu et al.<sup>10</sup> and Stanzione et al.<sup>12</sup> reported the guaiacol unit branched polyacrylamide and polymethacrylate, respectively.

Most recently, bio-based thermosetting resins and their biocomposites have been gathering increasing attention as renewable resources-derived materials because their materials are hard to be recycled due to the infusible and insoluble properties.<sup>13–19</sup> Wood-tar creosote novolak (WCN) or GCN should be a promising hardener of fully bio-based thermosetting epoxy resin and its biocomposite with natural fiber. We had already reported on the preparation and properties of the bio-based epoxy resins such as sorbitol polyglycidyl ether (SPE), glycerol polyglycidyl ether (GPE) and polyglycerol polyglycidyl ether (PGPE) cured with tannic acid (TA) or quercetin (QC), and their biocomposites with wood flour (WF).<sup>20–22</sup> In this study, GCN and WCN were synthesized by the reactions of GC and WC with formalin, respectively (Figure 2). The thermal and mechanical properties of the cured resins of SPE with GCN and WCN and their biocomposites with WF were compared with those of the corresponding materials prepared by using a phenol novolak (PN) which is one of the most popular hardeners of epoxy resins (Figure 3).

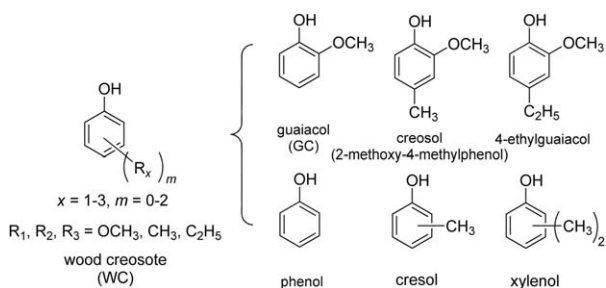


Figure 1. Main constituent phenols of WC.

## EXPERIMENTAL

### Materials

Sorbitol polyglycidyl ether (SPE, trade name: DENAKOL™ EX-614B, epoxy equivalent weight 172.2 g eq<sup>-1</sup>, average functional groups 3.6, chlorine content 9.8%, viscosity 4,740 mPa s<sup>-1</sup> at 25°C) was kindly supplied from Nagase ChemteX (Tokyo, Japan). Phenol novolak (PN, maker grade: PR-HF-3, softening point 82°C, weight per phenolic hydroxyl equivalent 104 g eq<sup>-1</sup>) was kindly supplied from Sumitomo Berklite (Tokyo, Japan). The structure of SPE and PN is shown in Figure 3. Wood-tar creosote (WC) and guaiacol (GC) were purchased from Wako Pure Chemical Industries (Tokyo, Japan) and Sigma-Aldrich Japan K. K. (Tokyo, Japan), respectively. Formaldehyde solution (*c* = 37% in water) and triphenylphosphine (TPP) were purchased from Tokyo Chemical Industry (Tokyo, Japan). *p*-Toluenesulfonic acid monohydrate (PTS) was purchased from Kanto Chemical (Tokyo, Japan). Wood flour (WF) was kindly supplied from Kowa Technos (Sammushu-shi, 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.

### Preparation of GCN

Formaldehyde solution 32.46 g (0.4000 mol) was dropwise added over a period of 0.5 h at 100°C to a mixture of GC 49.65 g (0.4000 mol) and PTS 0.477 g (2.51 mmol). After the resulting solution was stirred at 100°C for 3 h, the reaction mixture was cooled to room temperature. The product was extracted with chloroform, washed with water, dried over sodium sulfate, and concentrated *in vacuo* finally at 170°C for 2 h to give GCN 52.3 g as brown viscous liquid in 96.0% yield, based on an assumption that the novolak with an infinite molecular weight was produced.

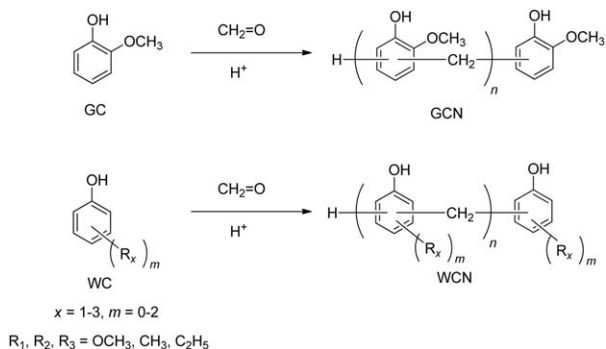


Figure 2. Synthetic scheme of GCN and WCN.

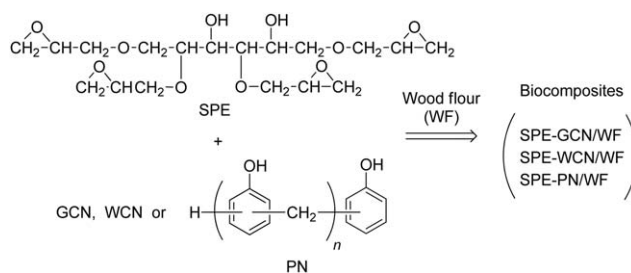


Figure 3. Preparation of the biocomposites of SPE, novolak and WF.

### Preparation of WCN

The average molecular weight of WC (119.27) was calculated from the composition of beechwood creosote identified by gas chromatography/mass spectrometry (guaiacol: 23.76%, creosol: 19.01%, phenol: 14.45%, *p*-cresol: 13.60%, 2-ethylguaiacol: 6.36%, *o*-cresol: 3.22%, 3,5-xyleneol: 2.94%, 2,4-xyleneol: 2.80%, 3-methylguaiacol: 1.85%, 5-methylguaiacol: 1.29%, 2,6-xyleneol: 1.04%, 3,4-xyleneol: 0.70%, 2,3-xyleneol: 0.70%, 2,5-xyleneol: 0.68%).<sup>8</sup> Formaldehyde solution 32.46 g (0.4000 mol) was dropwise added over a period of 0.5 h at 100°C to a mixture of WC 47.70 g (0.4000 mol) and PTS 0.477 g (2.51 mmol). After the resulting solution was stirred at 100°C for 3 h, the reaction mixture was cooled to room temperature. The product was extracted with chloroform, washed with water, dried over sodium sulfate, and concentrated *in vacuo* finally at 170°C for 2 h to give WCN 49.3 g as brown viscous liquid in 93.9% yield, based on an assumption that the novolak with an infinite molecular weight was produced.

### Preparation of Cured Resins

A mixture of SPE 5.67 g (epoxy 32.9 mmol), GCN 4.33 g (hydroxy 32.9 mmol) and TPP 20 mg (0.076 mmol) was stirred for 1 h at room temperature. The resulting viscous liquid was poured on a Petri dish made of stainless steel, and mixed by hand using a spatula on a hot plate of 150°C for 25 min to produce a gelatinous material. The obtained prepolymer was compression-molded at 10 MPa for 3 h using a Mini Test Press-10 (Toyo Seiki, Tokyo, Japan) which was beforehand set to 170°C to give a cured SPE/GCN (SPE-GCN) with the epoxy/hydroxy ratio of 1/1 as a pale brown plate. The thickness of the plate was controlled using a stainless steel spacer (thickness: 1.0 or 1.5 mm) during the compression molding. The samples for tensile test and dynamic mechanical analysis were cut off using an electric fret-saw. In a similar manner, cured SPE/WCN (SPE-WCN) and cured SPE/PN (SPE-PN) with the epoxy/hydroxy ratio of 1/1 were prepared from SPE 5.76 g (epoxy 33.5 mmol) and WCN 4.24 g (hydroxy 33.5 mmol), and SPE 6.23 g (epoxy 36.2 mmol) and PN 3.77 g (hydroxy 36.2 mmol), respectively.

### Preparation of Biocomposites

A mixture of SPE 3.97 g (epoxy 23.1 mmol), GCN 3.03 g (hydroxy 23.1 mmol), TPP 14 mg (0.053 mmol) and WF 3.00 g was stirred for 1 h at room temperature. In a similar manner to the preparation of cured epoxy resin, the resulting mixture was prepolymerized at 150°C for 30 min, and then compression-molded at 10 MPa and 170°C for 3 h to give a cured SPE-GCN/WF biocomposite with WF content 30 wt % (SPE-GCN/WF30) as a brown plate. The SPE-GCN/WF biocomposites with

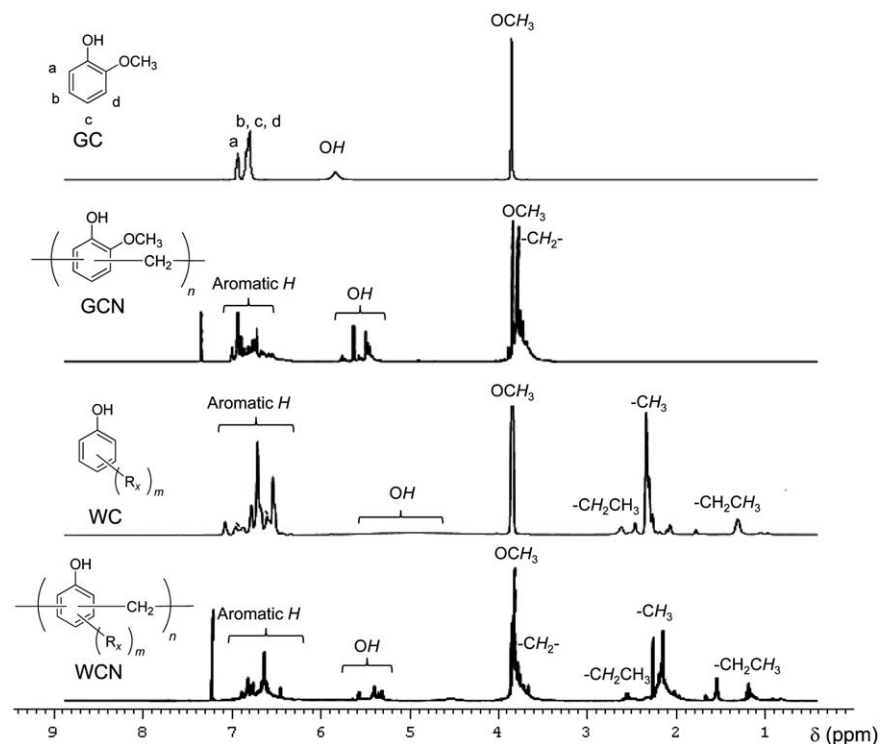


Figure 4.  $^1\text{H}$  NMR spectra of GC, GCN, WC, and WCN in  $\text{CDCl}_3$ .

the WF contents of 40 and 50 wt % (SPE-GCN/WF40 and SPE-GCN/WF50), SPE-WCN/WF biocomposites with the WF contents of 30, 40, and 50 wt % (SPEWCN/WF30, SPE-WCN/WF40, and SPE-WCN/WF50), and SPE-PN/WF biocomposites with the WF contents of 30, 40, and 50 wt % (SPE-PN/WF30, SPE-PN/WF40, and SPE-PN/WF50) were prepared in a similar manner to the preparation of SPE-GCN/WF30.

#### Measurements

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on a Bruker AV-400 (400 MHz) (Madison, WI) using  $\text{CDCl}_3$  as a solvent. Gel permeation chromatography (GPC) was carried out at  $60^\circ\text{C}$  on a Shodex GPC analysis apparatus equipped with two SB-806M HQ GPC columns (Showa Denko K. K., Tokyo, Japan) and an UV detector ( $\lambda = 280$  nm). DMF was used as an eluent at a flow rate of  $0.5$  mL  $\text{min}^{-1}$ . Polystyrene standards with a narrow distribution of molecular weights (580–377,400) were used for molecular weight calibrations. Thermogravimetric analysis (TGA) was carried out using a Shimadzu (Kyoto, Japan) TGA-50 thermogravimetric analyzer in a nitrogen atmosphere at a flow rate of  $50$  mL  $\text{min}^{-1}$ . Each sample (ca. 10 mg) was heated from room temperature to  $500^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}$   $\text{min}^{-1}$ . The 5 and 50% weight loss temperatures ( $T_5$  and  $T_{50}$ ) and residual weight percent at  $500^\circ\text{C}$  were obtained from the TGA curve. Dynamic mechanical analysis (DMA) of the rectangular specimen (length 30 mm, width 5 mm, thickness 1.5 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  $2^\circ\text{C}$   $\text{min}^{-1}$  in a tensile mode. Tensile test of the rectangular specimen (length 50 mm, width 7 mm, thickness 1.0 mm) was performed at  $20^\circ\text{C}$  using an Autograph AG-I (Shimadzu, Kyoto, Japan).

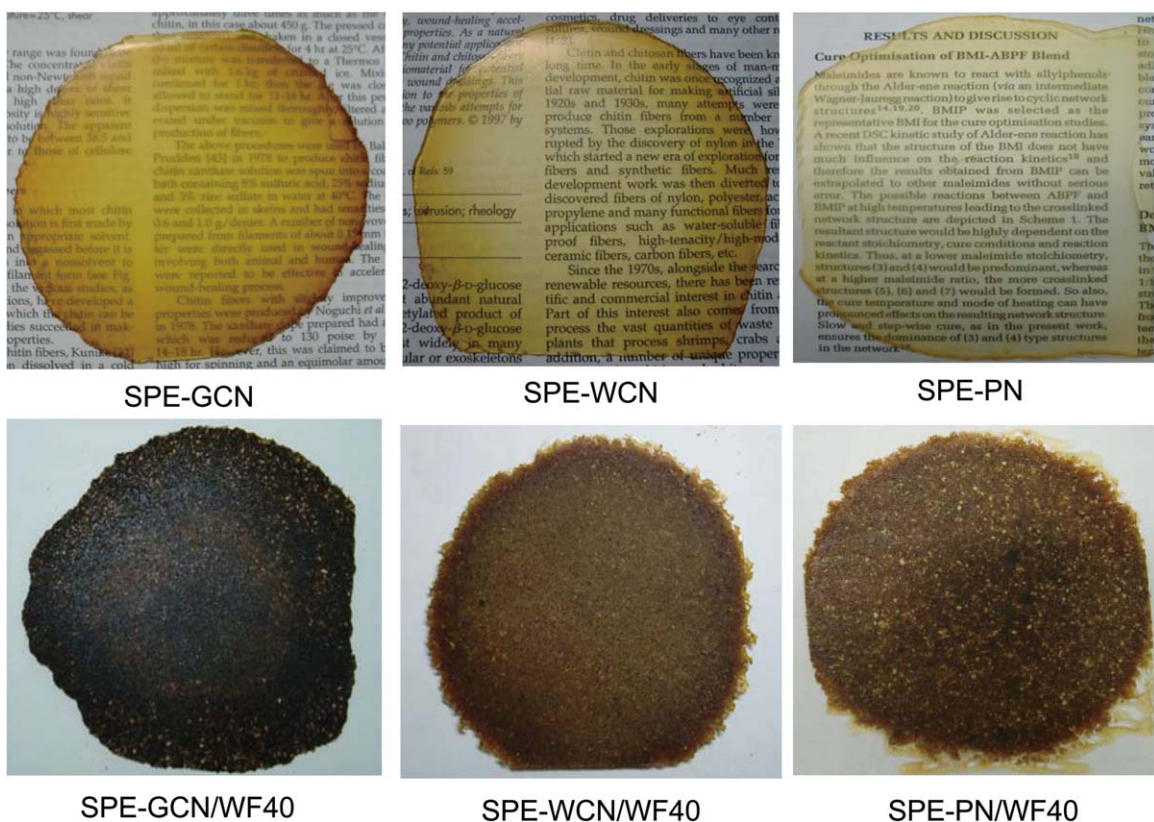
Span length and testing speed were 25 mm and  $10$  mm  $\text{min}^{-1}$ , respectively. Five specimens were tested for each set of samples, the mean value was calculated, and a difference between maximal and minimal values was displayed as an error bar in the graph. The morphology of the composites was observed by field emission-scanning electron microscopy (FE-SEM), using a Hitachi S-4700 machine (Hitachi High-Technologies Corporation, Tokyo, Japan). The fractured surface of the sample after tensile test and WF were sputter coated with gold to provide enhanced conductivity.

## RESULTS AND DISCUSSION

### Chemical Characterization of GCN and WCN

The reactions of GC and WC with formaldehyde at the molar ratio of 1 : 1 in the presence of PTS gave GCN and WCN, respectively (Figure 2). Figure 4 shows the  $^1\text{H}$  NMR spectra of GCN and WCN measured in  $\text{CDCl}_3$ . From the comparison with the assignment of the  $^1\text{H}$  signals of GC at 7.02 (m, 1H,  $\text{H}^a$ ), 6.89 (m, 3H,  $\text{H}^{b,c,d}$ ), 5.93 (bs, 1H, OH) and 3.93 ppm (s, 3H,  $\text{OCH}_3$ ), the  $^1\text{H}$  signals at 7.1–6.6 ppm (m,  $17.04x\text{H}$ ), 5.9–5.5 (m,  $5.5x\text{H}$ ), 3.95–3.70 (m,  $25.61x\text{H}$ ) for GCN were reasonably assigned to the aromatic, hydroxy, (methoxy + methylene) protons of GCN, respectively. Based on the structure of GCN shown in Figure 2, integral ratio of aromatic protons and (methoxy+methylene) protons,  $17.04x\text{H}/25.61x\text{H}$  is equal to  $(2n+4)/(5n+3)$ . Therefore,  $n$  is calculated to be 1.52. As the degree of polymerization (DP, or phenolic nucleus number) is expressed by the equation,  $\text{DP} = n+1$ , the DP becomes 2.52. The molecular weight ( $n\text{C}_8\text{H}_8\text{O}_2 + \text{C}_7\text{H}_8\text{O} = 331.03$ ) calculated from the  $n$  value was not contradictory to the number and weight average molecular weights ( $M_n$ : 200,  $M_w$ : 440) measured





**Figure 5.** Photographs of the cured resins and biocomposites with WF content 40 wt %. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

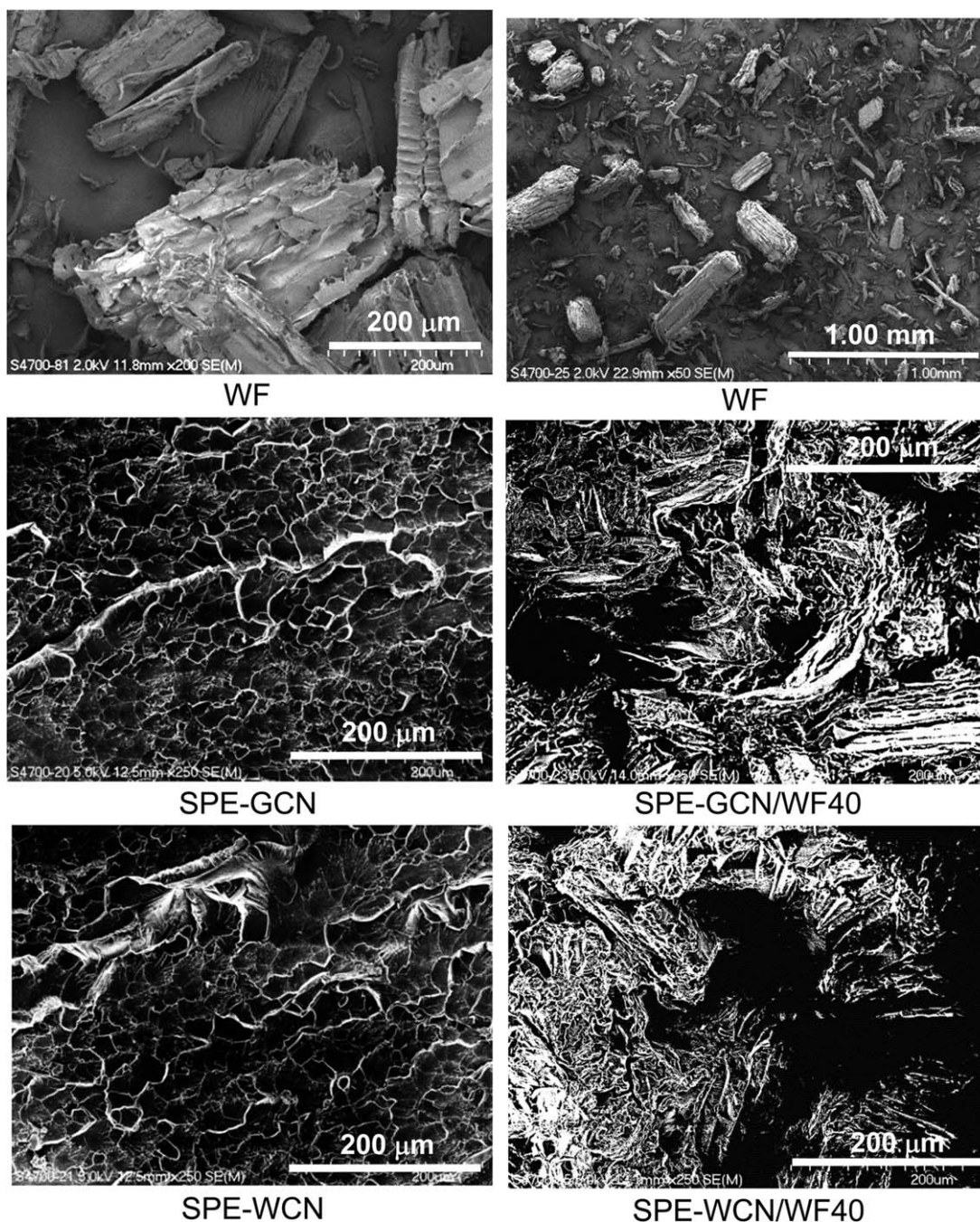
by GPC using polystyrene standards for GCN. This result is also consistent with the fact that molecular weight measured by vapor pressure osmometry for the GCN prepared by the reaction of GC and paraformaldehyde at GC/CH<sub>2</sub>O 1/1 using hydrochloric acid catalyst was 362 (DP = 2.73).<sup>11</sup> The reason why DP of GCN was not so high as that of phenol novolak prepared by a similar condition is explained by the facts that *ortho*-position of phenols has a higher reactivity toward electrophiles than the *para*-position, and that one *ortho*-position of GC is blocked by methoxy group. On the calculation of the molar amount of hydroxy group for GCN, the hydroxy equivalent (331.03/2.52  $\cong$  131.4) calculated from the molecular weight (331.03) and DP (2.52) evaluated by the NMR method was used.

In the <sup>1</sup>H NMR spectrum of WC, the <sup>1</sup>H signals of methyl and ethyl groups attached to benzene ring were observed at 2.35 ppm (—CH<sub>3</sub>) and 2.62 (—CH<sub>2</sub>CH<sub>3</sub>), 1.30 ppm (—CH<sub>2</sub>CH<sub>3</sub>) in addition to the aromatic and methoxy protons of GC which is a primary constituent of WC, because WC contains creosol, cresols, xylenols and 4-ethylguaiaicol (Figure 1). The <sup>1</sup>H signals of hydroxy groups of WC were observed as a very broad and weak peak, probably due to the H—H exchange of hydroxy groups between various phenols and/or contaminated water. The new <sup>1</sup>H signals of the novolak methylene protons, which were not observed for WC, were observed at 4.0–3.7 ppm as the multiplet peaks overlapped with methoxy protons for WCN. We could not evaluate the DP of WCN from the integral ratio of proton signals, because WC itself is a complex mixture of phenols. The

$M_n$  measured by the GPC method for WCN was 220, which is comparable to that (200) of GCN, suggesting that WCN has a similar DP to GCN. The hydroxy equivalent (126.5) of WCN was calculated using the estimated average molecular weight (119.3) of WC in the assumption that WCN has the same DP (2.52) as GCN, considering that hydroxy equivalent does not largely change by the DP. However, the  $M_w$  (900) by GPC for WCN is much higher than that (440) of GCN, indicating that the molecular weight distribution of WCN is broader than that of GCN. This result can be explained by the fact that phenol contained in WC produces the novolak with a higher molecular weight, while *ortho*- and *para*-disubstituted phenols (e.g., creosol and 4-ethylguaiaicol) contained in WC cannot produce the novolak with the DP higher than 2.

#### Morphologies, Thermal, and Mechanical Properties of Cured Resins, and Biocomposites

The wood-derived novolaks, GCN and WCN were used as hardeners of SPE and the biocomposite with WF. Their mixtures with the epoxy/hydroxy ratio of 1 : 1 were prepolymerized at 150°C and subsequently compression-molded at 170°C for 3 h. When 0.2 phr (parts per hundred parts by weight of resin) of TPP was used as a curing catalyst, the cured material with a little higher tan  $\delta$  peak temperature was obtained. Thermal and mechanical properties of the cured resins (SPE-GCN and SPE-WCN) and their biocomposites (SPE-GCN/WF and SPE-WCN/WF) were compared with those of SPE-PN and SPE-PN/WF.

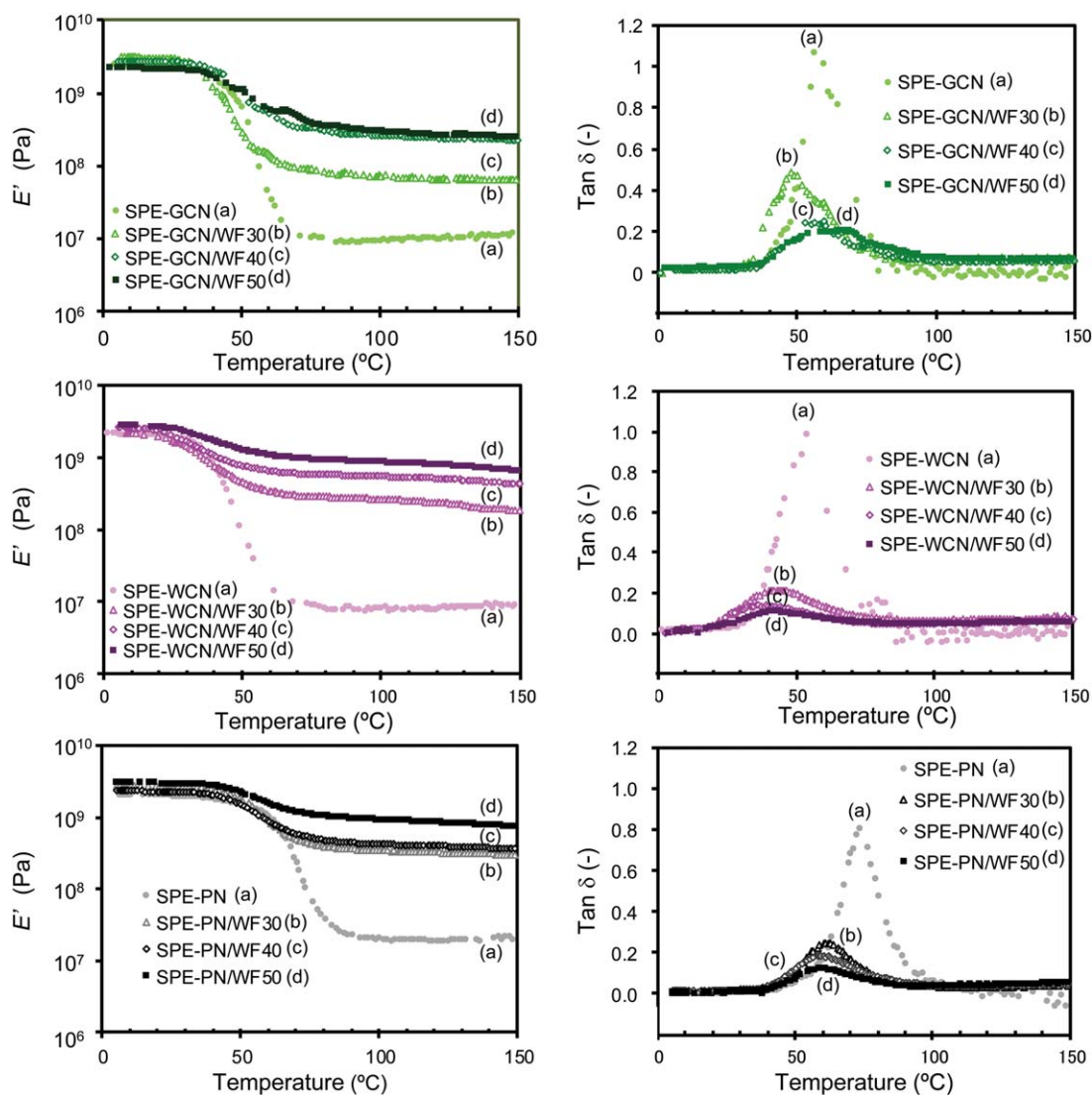


**Figure 6.** FE-SEM images of WF and the fractured surfaces of SPE-GCN, SPE-WCN, SPE-GCN/WF40 and SPE-WCN/WF40.

Figure 5 shows the photographs of the cured resins and biocomposites. All the cured resins were obtained as transparent rigid plates of a pale brown to brown color. The brown color of SPE-GCN/WF40 was much deeper than that of SPE-WCN/WF40 or SPE-PN/WF40. We do not know a clear reason, but it may be related to the fact that the color of SPE-GCN itself is a little darker than that of SPE-WCN or SPE-PN, and the possibility that the lignin with a relatively low crosslinking density of WF is partially eluted into the SPE-GCN because GCN has a similar structure to lignin. When the WF content is more than 50 wt % for all the biocomposites, visually homogeneous biocomposites were not obtained.

Figure 6 shows SEM images of WF (higher and lower magnifications) and fracture surfaces of SPE-GCN, SPE-WCN and their biocomposites (a higher magnification). The photograph of WF shows that the fiber length and width of WF are about 0.2–0.4 mm and 40–200  $\mu\text{m}$ , respectively. For the cured resins (SPE-GCN and SPE-WCN), the continuous pattern with the size of about 20  $\mu\text{m}$  was observed. In the case of biocomposite, such a fractured pattern characteristic to the cured resin was not observed and the interface between the cured resin and WF was obscure. Also, no hole which was generated by pull-out of WF was observed. It appeared





**Figure 7.** DMA curves of the cured resins and biocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

that the interfacial adhesion between the cured resin and WF is good.

Figure 7 shows the temperature dependency of storage modulus ( $E'$ ) and  $\tan \delta$  for the cured resins and biocomposites measured by DMA.  $\tan \delta$  peak temperatures related to glass transition for all the samples are summarized in Table I. Regarding the cured resins,  $\tan \delta$  peak temperatures (56.5 and 52.5°C) for SPE-GCN and SPE-WCN were lower than that of SPE-PN (72.8°C). This result is attributable to the fact that molecular weights of GCN and WCN are much lower than those of PN (softening point: 82°C), considering that  $M_n$  and  $M_w$  of a general phenol novolak with a similar softening point (85°C) are reported to be 631 and 2028, respectively.<sup>23</sup> Also, the fact that  $T_g$  of SPE-WCN was a little lower than that of SPE-GCN may be related to the fact that bisphenols derived from creosol and 4-ethylguaiaicol contained in WCN produce the polymer with a very low crosslinking density. The  $\tan \delta$  peak temperatures of all the WF biocomposites except for SPE-GCN/WF40 and SPE-

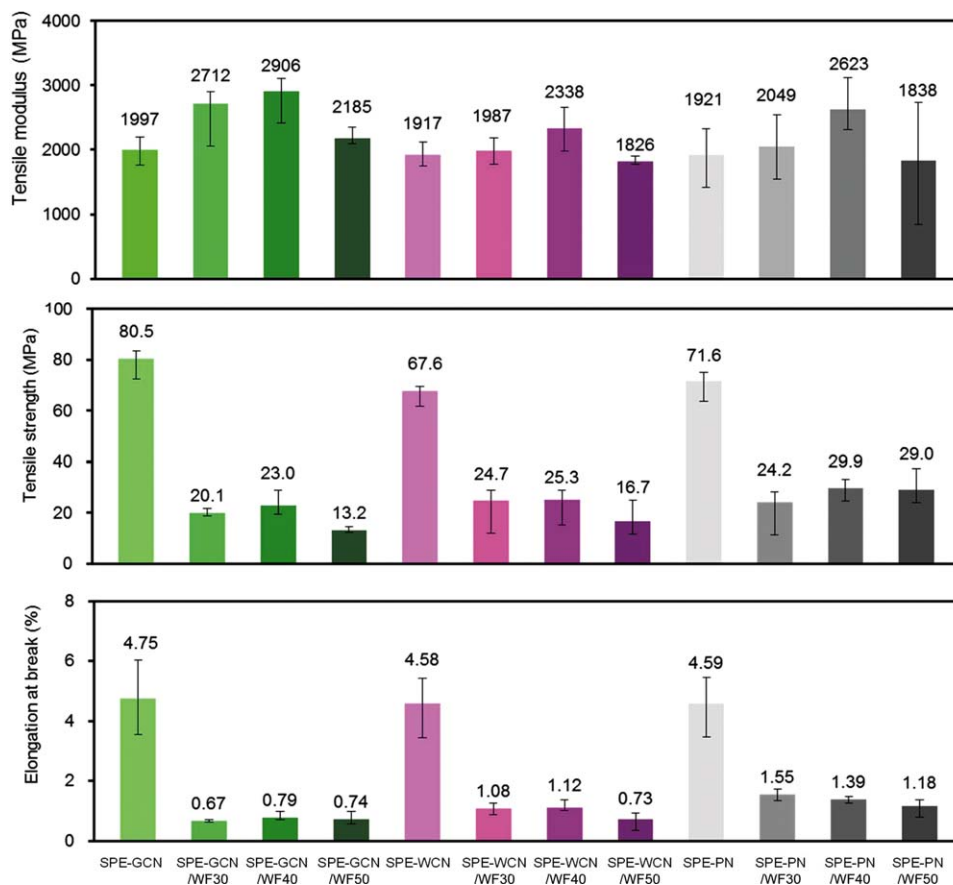
GCN/WF50 were lower than those of the corresponding cured resins without WF. The reason is not clear, but it is thought that hydroxy groups of cellulose, hemicellulose and lignin components of WF reacted with epoxy groups of SPE and the stoichiometry of epoxy and hydroxy is deviated. A similar decline of  $T_g$  by the addition of WF was also observed for the GPE-TA/WF biocomposites.<sup>20</sup> On the other hand, the  $\tan \delta$  peak temperatures (58.5 and 70.8°C) of the SPE-GCN/WF40 and SPE-GCN/WF50 were higher than that (56.5°C) of SPE-GCN. For all the WF biocomposites, the  $\tan \delta$  peak height decreased with increasing WF content in accordance with a decrease of matrix polymer content involved with glass transition. When the biocomposites with the same WF content were compared,  $\tan \delta$  peak height for SPE-GCN/WF was higher than those of SPE-WCN/WF and SPE-PN/WF. These results suggest that the lignin of WF eluting into the matrix caused the increase of  $\tan \delta$  peak temperature and its height for SPE-GCN/WF, considering the deep coloration of the biocomposite. The  $E'$ s at the rubbery

**Table I.** Tan  $\delta$  Peak Temperatures and  $T_5$ 's,  $T_{50}$ 's and Residue at 500°C for the Cured Resins and Biocomposites

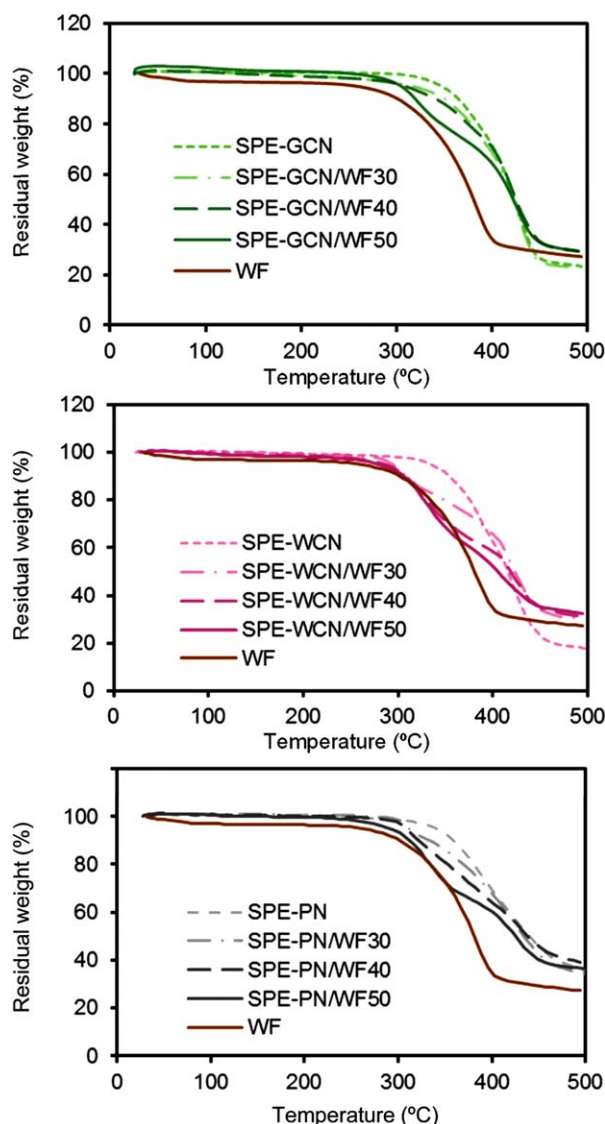
Sample	Tan $\delta$ peak Temperature (°C)	$T_5$ (°C)	$T_{50}$ (°C)	Residual weight at 500°C (%)
SPE-GCN	56.5	345.5	423.5	23.4
SPE-GCN/WF30	48.9	313.9	423.1	22.9
SPE-GCN/WF40	58.5	301.6	424.8	29.6
SPE-GCN/WF50	70.8	291.1	419.3	29.4
SPE-WCN	52.5	332.4	415.0	17.9
SPE-WCN/WF30	42.9	293.7	423.0	29.8
SPE-WCN/WF40	38.3	284.2	418.6	31.0
SPE-WCN/WF50	41.3	278.9	405.0	32.6
SPE-PN	72.8	338.0	439.6	35.6
SPE-PN/WF30	58.0	308.3	432.4	34.2
SPE-PN/WF40	56.6	305.0	435.9	39.2
SPE-PN/WF50	57.0	284.0	420.3	36.3
WF	-	263.5	382.3	27.3

plateau region over 50°C for all the biocomposites were much higher than those of the corresponding cured resins, suggesting a superior reinforcement effect due to the wood fibers. When the  $E'$  at 100°C reflecting the crosslinking density of the matrix polymer were compared, a higher order among the cured resin

was SPE-PN (20.2 MPa) > SPE-GCN (9.2 MPa) > SPE-WCN (8.0 MPa), while that among the biocomposites with WF content 50 wt % was SPE-PN/WF50 (937 MPa) > SPE-WCN/WF50 (849 MPa) > SPE-GCN/WF50 (298 MPa). It is supposed that the crosslinking reaction of SPE and the lignin eluted into the



**Figure 8.** Tensile properties of the cured resins and biocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 9.** TGA curves of the cured resins and biocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

matrix did not so much proceed from the fact that SPE-GCN/WF50 exhibited the lowest  $E'$  at 100°C. Therefore, the increase of  $\tan \delta$  peak temperature for SPE-GCN/WF should be caused by the structural characteristics of lignin such as a high aromatic character and high molecular weight.

Figure 8 shows the tensile properties for the cured resins and biocomposites with WF. Tensile moduli of all the biocomposites increased with WF content until 40 wt % and declined at the WF content of 50 wt %. Some aggregation of WF is presumed for the biocomposites with WF content of 50 wt %. When cured resins and the biocomposites with the same WF content are compared, tensile moduli of the SPE-GCN and SPE-GCN/WF biocomposites were a little higher than those of the other cured resins and biocomposites, respectively. The tensile modulus (2.9 GPa) of SPE-GCN/WF40 was the highest among all the biocomposites. This result should be caused by the elution of lignin in a manner similar to the increase of  $\tan \delta$  peak temper-

ature. However, the tensile strengths and elongations at break for all the biocomposites were much lower than those of the corresponding cured resins. Similar tendency for tensile modulus and strength was also observed for the biocomposites composed of SPE-QC/WF.<sup>22</sup> Tensile strength and modulus of a general cedar lumber is reported to be about 80 MPa and 8 GPa, respectively.<sup>24,25</sup> Although the tensile modulus of cedar lumber is much higher than those of SPE-GCN and SPE-WCN (ca. 2 GPa), the former tensile strength is comparable to the latter strength (70–80 MPa). Therefore, tensile strength of the biocomposite should not be improved by the addition of WF, as is easily estimated from the rule of mixture. Furthermore, the critical fiber length of WF for this biocomposite is estimated to be much higher than the fiber length (0.2–0.4 mm) of WF, considering that tensile strength of the biocomposite is much lower than that of the cured resin without WF. The tensile modulus (2.9 GPa) and strength (23 MPa) of SPE-GCN/WF40 in this study were higher than those of SPE-QC/WF40 (1.6 GPa and 16 MPa).<sup>22</sup> As a whole, the tensile properties of SPE-GCN/WF and SPE-WCN/WF biocomposites were comparable to those of SPE-PN/WF composites.

Figure 9 shows TGA curves of WF, cured resins and composites. The  $T_5$ 's,  $T_{50}$ 's and residual weight percent at 500°C for all the samples are summarized in Table I. All the cured resins had much higher  $T_5$  and  $T_{50}$  than WF. Although a higher order of  $T_5$  for the cured resins was SPE-GCN > SPE-PN > SPE-WCN, that of  $T_{50}$  was SPE-PN > SPE-GCN > SPE-WCN. All the WF biocomposites showed two-step degradation curve related to the decomposition of WF and cured resin. Therefore, the  $T_5$ 's of all the WF biocomposites were lower than those of the corresponding cured resins. Although  $T_5$  of SPE-WCN/WF was lower than that of SPE-PN/WF, SPE-GCN/WF exhibited a comparable  $T_5$  to that of SPE-PN/WF. There was little difference of  $T_{50}$  between the cured resin and WF biocomposite. A higher order of  $T_{50}$  for the biocomposites was SPE-PN/WF > SPE-GCN/WF > SPE-WCN/WF. The residual weight percent at 500°C for PN-based cured resins and biocomposites were a little higher than those of GCN- and WCN-based ones, suggesting that PN has a little higher carbonization efficiency.

## CONCLUSIONS

As wood-derived phenol novolaks, GCN and WCN were synthesized by the reactions of GC and WC with formalin at the phenol/formaldehyde ratio of 1/1, respectively. The DP measured by <sup>1</sup>H NMR method for GCN was 2.52. Although DP of WCN could not be evaluated, the average molecular weight of WCN by GPC was comparable to that of GCN. Fully bio-based cured resins (SPE-GCN and SPE-WCN) and biocomposites (SPE-GCN/WF and SPE-WCN/WF) were prepared by the prepolymerization at 150°C and subsequent compression molding at 170°C. Their thermal and mechanical properties were compared with those of SPE-PN and SPE-PN/WF prepared by a similar method.  $\tan \delta$  peak temperatures (56.5 and 52.5°C) of SPE-GCN and SPE-WCN were lower than that (72.8°C) of SPE-PN. Although  $\tan \delta$  peak temperature was reduced by the addition of WF for most of the composites, those of SPE-GCN/WF40 and SPE-GCN/WF50 were rather higher than that of SPE-GCN.



As a result,  $\tan \delta$  peak temperature (70.8°C) of SPE-GCN/WF50 was higher than that (57.0°C) of SPE-PN/WF50. Tensile moduli of all the biocomposites increased with WF content until 40 wt % and declined at the WF content of 50 wt %. All the composites showed much lower tensile strengths and elongations at break than the cured resins. When the biocomposites with the same WF content were compared, tensile modulus of SPE-GCN/WF was higher than that of SPE-PN/WF. The  $T_g$ 's of SPE-GCN (346°C) and SPE-GCN/WF (314–291°C) were comparable to those of SPE-PN (338°C) and SPE-PN/WF (308–284°C), respectively. Wood-derived GCN is a promising hardener of epoxy resins which can be substituted for petroleum-based PN, especially when used as a hardener for wood-epoxy composites. Additionally, wood adhesives and wood preservatives should be potential applications of the SPE/GCN or SPE/WCN curing system.

#### ACKNOWLEDGMENTS

The authors thank Dr. Naozumi Teramoto and Dr. Toshiaki Shimasaki of their department for their helpful suggestions. They are also grateful to Mr. Ryusuke Osada of the Material Analysis Center at the Chiba Institute of Technology for assisting in measuring the FE-SEM analysis reported here.

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