

Preparation and Properties of Biocomposites Composed of Sorbitol-Based Epoxy Resin, Tung Oil-Pyrogallol Resin, and Wood Flour

Mitsuhiro Shibata, Naozumi Teramoto, Satoru Yoshihara, Yusuke Itakura

Department of Life and Environmental Sciences, Faculty of Engineering, Chiba Institute of Technology,
Narashino, Chiba 275-0016, Japan

Correspondence to: M. Shibata (E-mail: shibata@sky.it-chiba.ac.jp)

ABSTRACT: The biocomposites composed of sorbitol polyglycidyl ether (SPE), tung oil-pyrogallol resin (TPG), and wood flour (WF) were prepared by the compression molding at 190°C, and their thermal and mechanical properties were investigated in detail. The epoxy/hydroxy ratio was fixed to 1/1 in the curing reaction of SPE and TPG, based on the fact that the degree of addition of pyrogallol to each tung oil molecule for the TPG used as a flexible bio-based hardener is evaluated to be 2.3 by ¹H-NMR method. The SPE-TPG/WF biocomposites showed much higher storage moduli than SPE-TPG did, although tan δ peak temperatures of the biocomposites (44.5–45.6°C) were a little lower than that of SPE-TPG (53.5°C). Tensile moduli of the biocomposites increased with an increase of WF content in the range of 0–50 wt %. Furthermore, the biocomposites had a little higher tensile strength than the cured neat resin did. Field emission-scanning electron microscopy analysis of the biocomposites revealed that WF is tightly incorporated into the crosslinked epoxy resins. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: biopolymers and renewable polymers; composites; crosslinking; thermosets

Received 22 April 2012; accepted 16 October 2012; published online

DOI: 10.1002/app.38739

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 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.^{2–4} As examples of the bio-based epoxy resins, there are many references on epoxidized vegetable oils^{5–10} and lignin-based epoxy resins,^{11–14} etc. We have also reported on the preparation and properties of glycerol polyglycidyl ether (GPE)¹⁵ cured with tannic acid (TA) and sorbitol polyglycidyl ether (SPE) cured with quercetin,¹⁶ and their biocomposites with wood flour (WF). The GPE/TA/WF and SPE/TA/WF biocomposites had much higher tensile modulus than the cured GPE/TA and SPE/TA resins, respectively. However, the tensile strength and elongation at break of the WF biocomposites were rather lower than those of the cured resins. Therefore, in order to prepare the WF biocomposite with well-balanced tensile properties, it is necessary to use a multifunctional bio-based hardener containing a more flexible unit than TA did. Vegetable oils such as soybean oil and tung oil (TO) and bio-based

phenols such as cardanol and pyrogallol (PG) are promising raw materials for the preparation of flexible bio-based phenolic epoxy hardeners. TO is a triglyceride extracted from the seeds of the tung tree (*Aleurites fordii*), in which ~ 80% of the fatty acid chains is α -eleostearic acid, that is, 9-*cis*,11,13-*trans*-octadecatrienoic acid.^{17,18} Therefore, TO with the conjugated triene moiety shows a characteristic reactivity which is not seen in the convention soybean oil and linseed oil, etc. From the past studies, it was found that the reaction of soybean oil and phenol in the presence of a super acid such as trifluoromethanesulfonic acid or tetrafluoroboric acid produce a complex mixture of phenolated soybean oils oligomerized by Diels-Alder reaction.^{19,20} In contrast, the reaction of TO and phenol smoothly proceed in a mild acidic condition without the formation of oligomerized materials to produce a desired TO-phenol resin.^{21–24} On the other hand, cardanol is a phenol meta-substituted with a flexible unsaturated hydrocarbon chain, which is derived from cashew nutshell liquid.²⁵ There have been many studies on the utilization of cardanol to phenol resins^{26–28} and epoxy resins,^{28–31} and some of them have been already commercialized by Cardolite Corp. (Newark, NJ) and Shanghai Meidong Biomaterials Co. (Shanghai, China), etc. PG is obtained by decarboxylation of gallic acid which is a basic component of hydrolysable tannin. In the past studies, PG-formaldehyde resin³² and TO-PG resin³³ (TPG) have

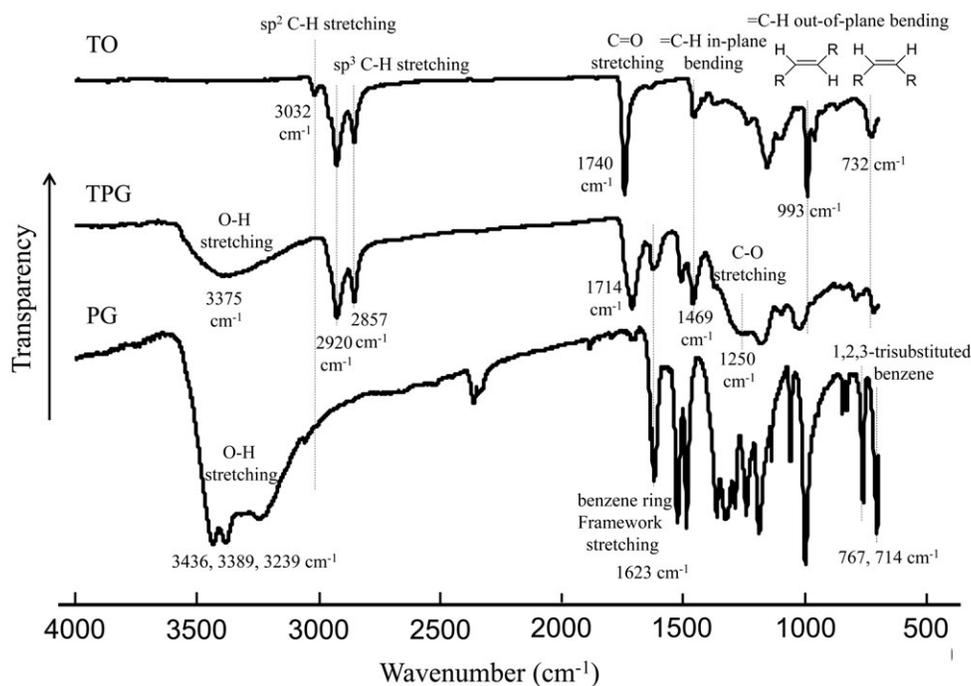


Figure 2. FTIR spectra of TO, TPG, and PG.

room temperature. To the obtained homogeneous solution, WF 4.00 g was added, and the mixture was stirred for 10 min at room temperature. After almost the solvent was vaporized at 80°C, the resulting compound was sandwiched between two sets of piled poly(tetrafluoroethylene) films ($250 \times 200 \times 0.10 \text{ mm}^3$) and stainless plates ($250 \times 250 \times 2 \text{ mm}^3$), and then compression-molded at 10 MPa for 3 h using Mini Test Press-10 (Toyo Seiki Co., Tokyo, Japan) which was beforehand set to 190°C to give a cured SPE-TPG/WF biocomposite with WF content 40 wt % (SPE-TPG/WF40) as a brown plate. In a similar manner, SPE-TPG/WF composites with WF content 50 and 60 wt % (SPE-TPG/WF50 and SPE-TPG/WF60) were prepared.

Measurements

Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded on a Bruker AV-400 (400 MHz) (Madison, WI) using CDCl_3 as a solvent. Fourier transform infrared (FTIR) spectra were measured on a FTIR 8100 spectrometer (Shimadzu Co., Kyoto, Japan) by the ATR method. The differential scanning calorimetry (DSC) measurement of SPE/TPG compound (ca. 10 mg) was performed on a Perkin-Elmer DSC Pyris 1 DSC in a nitrogen atmosphere. The sample was heated from room temperature to 230°C at a rate of 10°C/min. The 5% weight loss temperature was measured 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 1.0 mm) was performed on a Rheograph Solid (Toyo Seiki Co., 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 mm) was performed at 20°C using an Autograph AG-I (Shimadzu Co., Kyoto, Japan). Span length and testing speed were 25 mm and

10 mm/min, respectively. 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). The SPE-TPG/WF composites were fractured after immersion in liquid nitrogen for about 30 min. The surfaces of the fractures sample and WF were sputter coated with gold to provide enhanced conductivity.

RESULTS AND DISCUSSION

Preparation and Characterization of TPG

The reaction of TO and PG in the presence of *p*-toluenesulfonic acid in dioxane at 80°C for 3 h gave TPG as a brown viscous liquid in 37% yield (Figure 1). The fact that a considerable amount of TPG is lost during the repeated washing with hot water for the removal of unreacted PG is a reason for the low yield. So, there is a possibility that the yield is improved by the optimization of purification method. As PG has a high reactivity at both the 4- and 6-positions to an electrophile, it is supposed that crosslinking reaction should occur in the reaction with a multifunctional reagent such as TO. Actually, the reaction at a higher temperature than 80°C or the use of other acid catalysts such as hydrochloric acid and borontrifluoride diethyl etherate resulted in a formation of gelatinous materials. The obtained TPG was soluble to ethanol, acetone, ethyl acetate, tetrahydrofuran, diethyl ether, *N,N*-dimethylformamide, and dimethylsulfoxide, and insoluble to water, chloroform, and hexane.

Figure 2 shows FTIR spectra of TO, TPG, and PG. The band at 3375 cm^{-1} due to O—H stretching vibration and that at 1623 cm^{-1} due to benzene ring framework stretching vibration in addition to the band at 1714 cm^{-1} due to C=O stretching

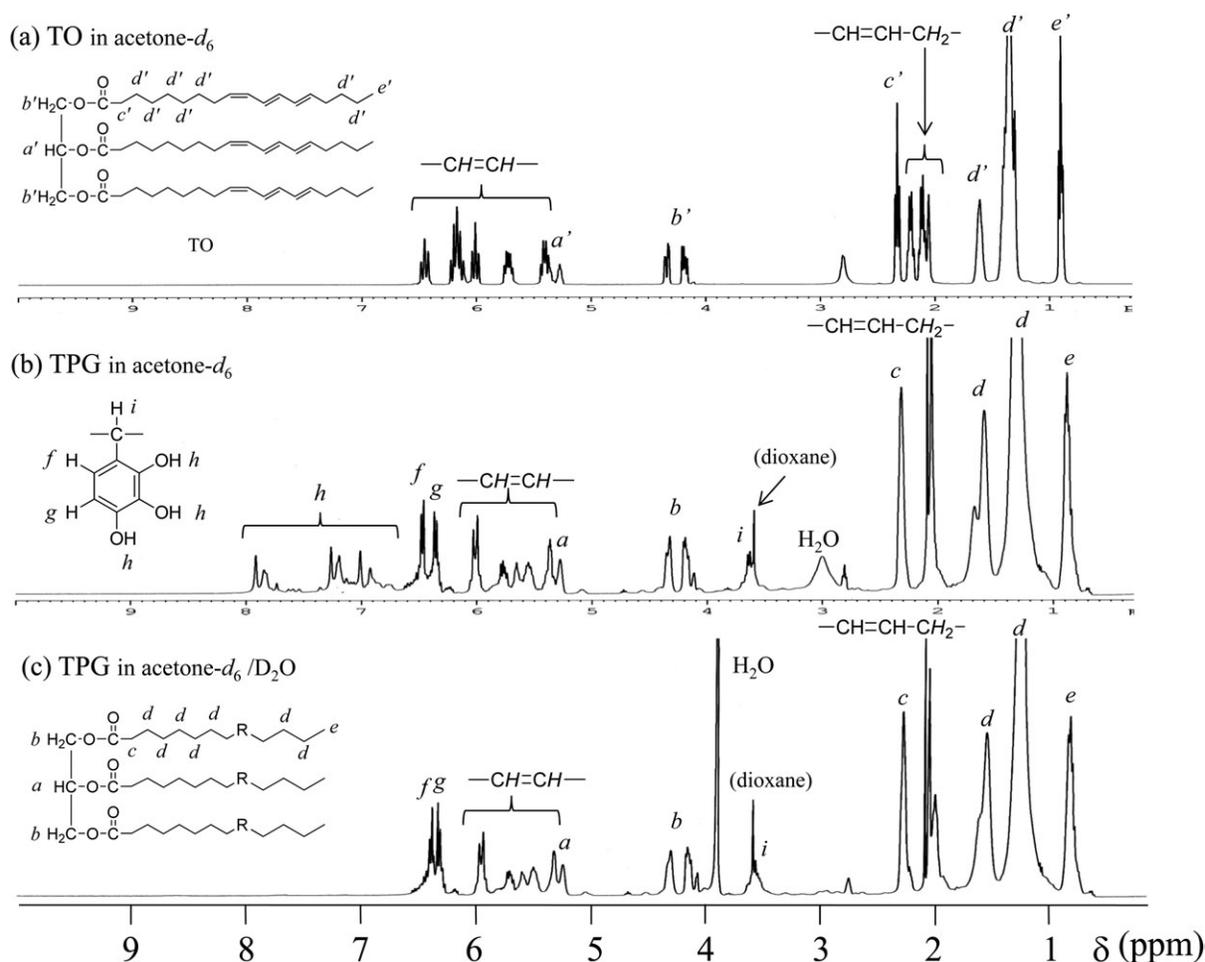


Figure 3. $^1\text{H-NMR}$ spectra of TO and TPG in acetone- d_6 , and TPG in acetone- $d_6/\text{D}_2\text{O}$.

vibration and those at $2950\text{--}2840\text{ cm}^{-1}$ due to $\text{sp}^3\text{ C-H}$ stretching vibration were observed for the spectrum of TPG, indicating that PG moiety and TO moiety certainly bonded. Also, the fact that the bands at 993 cm^{-1} and 732 cm^{-1} due to

=C-H out-of plane bending vibrations of *trans*- and *cis*-olefinic moieties, respectively, observed for TO considerably diminished for TPG, suggesting that the addition reaction of PG to the olefinic moieties of TO certainly proceeded.

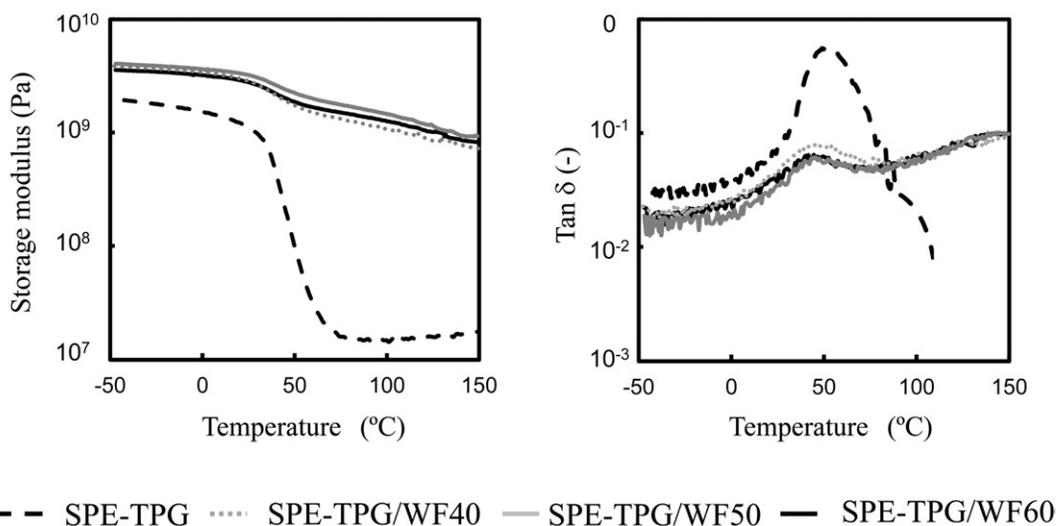


Figure 4. DMA curves of SPE-TPG and SPE-TPG/WF composites.

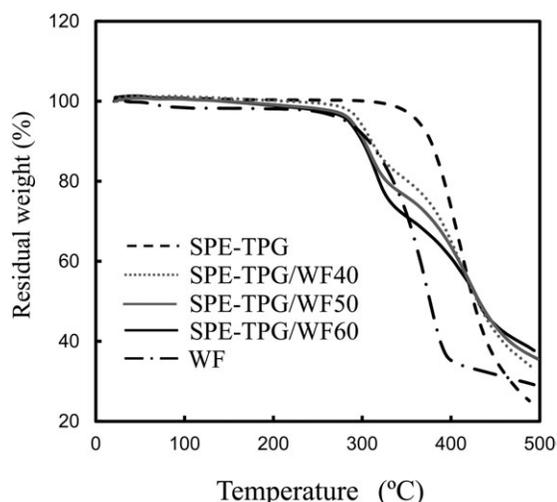


Figure 5. TGA curves of SPE-TPG, SPE-TPG/WF composites, and WF.

Figure 3 shows the ^1H -NMR spectra of TO and TPG measured in acetone- d_6 . The ^1H signal of methine proton of glyceride unit (H_a and H_a') in TPG and TO was observed at 5.29 ppm (s) and 5.27 ppm (s), respectively. The integral values of other proton signals were evaluated relative to those of H_a and H_a' signal (1H). Because we could not specify the phenolic hydroxy groups of PG unit in TPG, the H-D exchange reaction was performed by the addition of D_2O in a NMR tube. As a result, the ^1H signals from 7.92 to 6.71 ppm (6.8H) in acetone- d_6 disappeared in the spectrum of TPG in acetone- $d_6/\text{D}_2\text{O}$, indicating 2.3 PG units are added to a TO triglyceride moiety. This number is in agreement with the integral values of ^1H signals at 6.45 ppm (d, 2.3H, H_f , $J = 8.3$ Hz) and 6.34 ppm (d, 2.2 H, H_g , $J = 8.3$ Hz) in the PG ring of TPG. The fact that coupling constant of two protons (H_f and H_g) of the PG ring is 8.3 Hz indicates that electrophilic substitution reaction of the TO-derived carbocation occurred at 4-position of PG (1,2,3-trihydroxybenzene), because the product obtained by the reaction at 5-position should have the coupling constant at around 3 Hz. The PG-substituted methine proton (H_i) is also observed at 3.65 ppm (m, 2.3H). The number of olefins of TO per triglyceride is estimated to be 7.6 from the integral value of the olefinic ^1H signals at 6.45–5.41 ppm relative to that of H_a . Similarly, the

number of olefins of TPG is estimated to be 4.3 from the integral value of the olefinic ^1H signals at 6.07–5.35 ppm relative to that of H_a . From their values, the number of diminished olefins of TPG relative to TO is estimated to be 3.3, which is a little higher than the degree of addition of PG (2.3). This discrepancy may be attributed to the possibility that some components of TO with lower olefinic number are eliminated by the purification. Four structural formulae (R) of TPG in Figure 1 are capable as the structures of the PG-substituted hexadiene moiety of TPG, considering the stability of the carbocation of reaction intermediate, if the horizontally flipped structures of R are omitted. In addition, there is a possibility that the original *cis-trans-trans* configuration of triene part of TO is transformed to other configurations by the migration of π -bond in the carbocation intermediates. Among the olefinic proton signals of TPG, the signal at a lower magnetic field (6.07 ppm) is assigned to inner protons ($-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$) of conjugated diene moiety, and that at a higher magnetic field (5.35 ppm) is related to the protons of isolated olefin moiety. However, we could not assign the olefinic proton signals of TPG more precisely because many structural and configurational isomers are contained.

Thermal Properties of SPE-TPG/WF Biocomposites

The onset and peak temperatures of the exothermic curve on the first heating DSC thermogram for the SPE/TPG compound with a standard epoxy/hydroxy ratio of 1/1 were 142.3 and 192.9°C, respectively. Based on the DSC data, the curing temperature of the SPE/TPG was changed between 150 and 190°C. The $\tan \delta$ peak temperature (43.0, 43.5, and 53.5°C) measured by DMA increased with an increase of curing temperature (150, 170, and 190°C). Also, the 5% weight loss temperature (344.3, 344.8, and 361.1°C) increased with an increase of curing temperature. When the mixture was cured at a temperature higher than 190°C, the cured material considerably colored. The curing temperature was fixed to 190°C, considering the stability of SPE/TPG and WF which is subsequently added.

Figure 4 shows DMA curves of the SPE-TPG/WF biocomposites cured at 190°C. The storage modulus (E') at the rubbery plateau region over 50°C for the composites was much higher than that of SPE-PGT, suggesting a superior reinforcement effect due to the wood fibers. The $\tan \delta$ peak temperature related to T_g for the composites (WF40 : 45.6°C; WF50 : 45.7°C; WF60 :

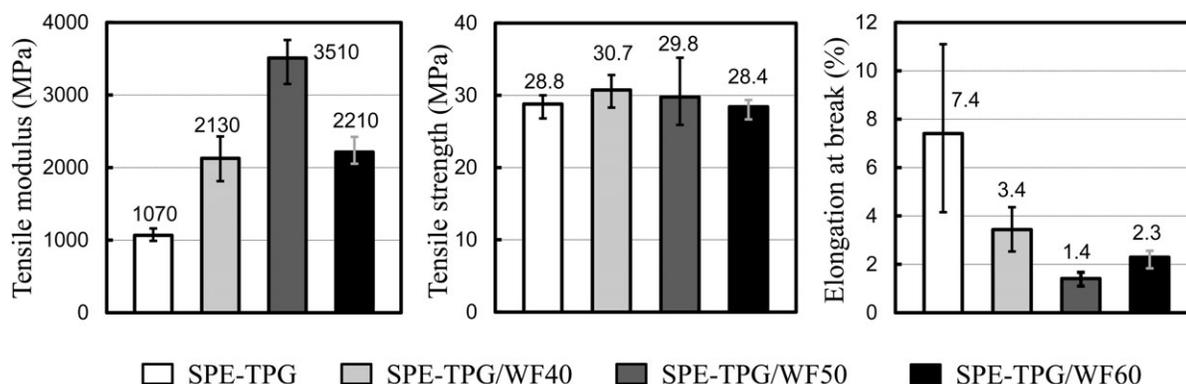


Figure 6. Tensile properties of SPE-TPG and SPE-TPG/WF composites.

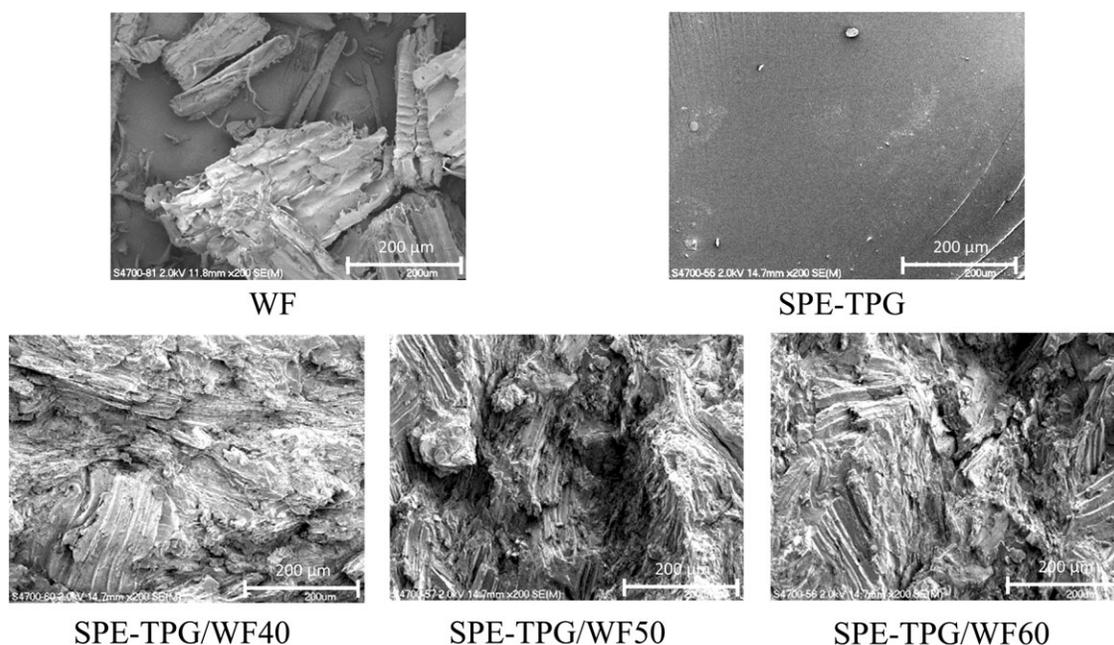


Figure 7. FE-SEM images of WF and the fracture surface of SPE-TPG and SPE-TPG/WF composites.

44.5°C) was a little lower than that of the corresponding neat resins (53.5°C). The reason is not clear, but it is thought that hydroxy groups 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.¹⁵

Figure 5 shows TGA curves of WF, SPE-TPG, and SPE-TPG/WF composites. Because the thermal decomposition temperature of WF was lower than that of SPE-TPG, the SPE-TPG/WF composite exhibited two-step thermo-degradation, and the 5% weight loss temperature decreased with increasing WF content (0 wt % : 361.1°C, 40 wt % : 294.7°C, 50 wt % : 286.3°C, 60 wt % : 279.6°C).

Mechanical Properties and Microscopic Analysis of SPE-TPG/WF Biocomposites

Figure 6 shows the tensile properties for SPE-TPG/WF composites. The tensile modulus of SPE-TPG/WF increased with increasing WF content in the range of 0–50 wt %. However, the tensile modulus of SPE-TPG/WF60 was lower than that of SPE-TPG/WF50 in agreement with the influence of WF content on the E' measured by DMA. Also, the tensile strength of the composites with WF content 40–50 wt % was a little higher than the corresponding neat resin (SPE-TPG). The fact that the improvement of tensile strength is not so high as that of tensile modulus is related to the decrease of elongation at break for the WF biocomposites. In the previous our study on GPE-TA/WF and SPE-quercetin/WF biocomposites, the tensile strength considerably decreased by the addition of WF.^{15,16} When TPG was used as an epoxy-hardener, the tensile strength of the WF composite did not decrease.

Figure 7 shows SEM images of WF and the fractured surfaces of SPE-TPG and SPE-TPG/WF composites. The micrograph of SPE-TPG showed no phase separation, indicating that SPE is homogeneously cured with TPG. The micrograph of WF shows that the fiber length and width of WF are about 0.2–0.4 mm

and 40–200 μm , respectively. All the micrographs of SPE-TPG/WF biocomposites show that WF is tightly incorporated into the crosslinked epoxy resin and their interfacial adhesion is good. The fact that tensile strength did not decrease by the addition of WF is related to the good affinity of SPE-TPG and WF. The good affinity is inferred from what TO is widely used as a coating material for woody surface and the structure of PG moieties of TPG resembles that of lignin of WF.

CONCLUSIONS

Bio-based epoxy hardener, TPG was synthesized by the reaction of TO and PG in the presence of *p*-toluenesulfonic acid. The ¹H-NMR spectrum of TPG showed that the degree of addition of PG to the olefin units of TO per triglyceride is 2.3. After SPE was mixed with TPG in ethanol at epoxy/hydroxy ratio 1/1, the obtained SPE/TPG solution was mixed with WF, dried at 80°C, and subsequently compressed at 190°C for 3 h to give SPE-TPG/WF biocomposites. The DMA measurement revealed that E' of SPE-TPG/WF is much higher than that of SPE-TPG and that the $\tan \delta$ peak temperature of SPE-TPG/WF is around 46°C. The tensile test revealed that the tensile modulus of the cured resin was much improved by the addition of WF without reduction of tensile strength. FE-SEM analysis of the biocomposites revealed that WF is tightly incorporated into the crosslinked epoxy resins.

ACKNOWLEDGMENTS

The authors thank Mr. Ryusuke Osada of Material Analysis Center of our university for assisting in measuring FE-SEM.

REFERENCES

1. Sun, X. S. In *Bio-Based Polymers and Composites*; Wool, R. P.; Sun, X. S., Eds.; Elsevier Academic Press: Burlington, 2005; Chapter 1, p 1.

2. Kim, J. R.; Sharma, S. *Ind. Crop. Prod.* **2012**, *36*, 485.
3. Raquez, J. M.; Deléglise, M.; Lacrampe, M. F.; Krawczak, P. *Prog. Polym. Sci.* **2010**, *35*, 487.
4. Effendi, A.; Gerhauser, H.; Bridgwater, A. V. *Renew. Sustain. Energy Rev.* **2008**, *12*, 2092.
5. Shibata, M.; Teramoto, N.; Makino, K. *J. Appl. Polym. Sci.* **2011**, *120*, 273.
6. Gupta, A. P.; Ahmad, S.; Dev, A. *Polym. Eng. Sci.* **2011**, *51*, 1087.
7. Gupta, A. P.; Dev, A.; Ahmad, S. *Polym. Plast. Technol. Eng.* **2010**, *49*, 657.
8. Sithique, M. A.; Ramesh, S.; Alagar, M. *Int. J. Polym. Mater.* **2008**, *57*, 480.
9. Takahashi, T.; Hirayama, K.; Teramoto, N.; Shibata, M. *J. Appl. Polym. Sci.* **2008**, *108*, 1596.
10. Warth, H.; Muelhaupt, R.; Hoffmann, B.; Lawson, S. *Angew. Makromol. Chem.* **1997**, *249*, 79.
11. Koike, T. *Polym. Eng. Sci.* **2012**, *52*, 701.
12. Kishi, H.; Akamatsu, Y.; Noguchi, M.; Fujita, A.; Matsuda, S.; Nishida, H. *J. Appl. Polym. Sci.* **2011**, *120*, 745.
13. Sun, G.; Sun, H.; Liu, Y.; Zha, B.; Zhu, N.; Hu, K. *Polymer* **2007**, *48*, 330.
14. Kishi, H.; Fujiuta, A.; Miyazaki, H.; Matsuda, S.; Murakami, A. *J. Appl. Polym. Sci.* **2006**, *102*, 2285.
15. Shibata, M.; Teramoto, N.; Takada, Y.; Yoshihara, S. *J. Appl. Polym. Sci.* **2010**, *118*, 2998.
16. Shibata, M.; Yashiro, M.; Ohno, Y. *J. Appl. Polym. Sci.* **2012**, DOI: 10.1002/app.38438.
17. Oyman, Z. O.; Ming, W.; Linde, R. *Prog. Org. Coat.* **2005**, *54*, 198.
18. Blayo, A.; Gandini, A.; Nest, J. F. L. *Ind. Crop. Prod.* **2001**, *14*, 155.
19. Nanaumi, K.; Horiuchi, T.; Nomoto, M.; Inoue, M. (to Hitachi Chemical Co.). U.S. Pat.5,380,789 (**1995**).
20. Ionescu, M.; Petrovič, Z. S. *J. Serb. Chem. Soc.* **2011**, *76*, 591.
21. Yoshimura, Y. *J. Appl. Polym. Sci.* **1984**, *29*, 1063.
22. Yoshimura, Y. *J. Appl. Polym. Sci.* **1984**, *29*, 2735.
23. Ziebarth, G.; Singer, K.; Gnauck, R.; Raubach, H. *Angew. Makromol. Chem.* **1989**, *170*, 87.
24. Singer, K.; Ziebarth, G.; Schulz, G.; Gnauck, R.; Raubach, H. *Angew. Makromol. Chem.* **1989**, *170*, 103.
25. Sharma, V.; Kundu, P. P. *Prog. Polym. Sci.* **2006**, *31*, 983.
26. Yadav, R.; Devi, A.; Tripathi, G.; Srivastava, D. *Eur. Polym. J.* **2007**, *43*, 3531.
27. Santos, R. S. S.; Souza, A. A.; Paoli, M. A.; Souza, C. M. L. *Compos. A* **2010**, *41*, 1123.
28. Devi, A.; Srivastava, D. S. *Mater. Sci. Eng. A* **2007**, *458*, 336.
29. Kim, Y. H.; An, E. S.; Park, S. Y.; Song, B. K. *J. Mol. Catal. B* **2007**, *45*, 39.
30. Campaner, P.; D'Amico, D.; Longo, L.; Stifani, C.; Tarzia, A. *J. Appl. Polym. Sci.* **2009**, *114*, 3585.
31. Yadav, R.; Srivastava, D. *J. Appl. Polym. Sci.* **2009**, *114*, 1670.
32. Garro-Galvez, J. M.; Riedl, B. *J. Appl. Polym. Sci.* **1997**, *65*, 399.
33. Yu, S.; Gu, J.; Fang, W.; Fu, X. *J. Photopolym. Sci. Technol.* **1989**, *2*, 51.