Preparation and Properties of Biocomposites Composed of Glycerol-Based Epoxy Resins, Tannic Acid, and Wood Flour

Mitsuhiro Shibata, Naozumi Teramoto, Yoshiro Takada, Satoru Yoshihara

Department of Life and Environmental Sciences, Faculty of Engineering, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino, Chiba 275-0016, Japan

ABSTRACT: After polyglycerol polyglycidyl ether (PGPE) and glycerol polyglycidyl ether (GPE) were mixed with tannic acid (TA) in ethanol and without solvent at epoxy/hydroxyl ratio 1/1, the obtained GPE-TA and PGPE-TA solutions were mixed with wood flour (WF), prepolymerized at 50°C, and subsequently compressed at 160°C for 3 h to give GPE-TA/WF and PGPE-TA/WF biocomposites with WF content 50–70 wt %, respectively. The storage moduli of the biocomposites in the rubbery state at more than 80°C were much higher than that of the control cured resins. The PGPE-TA/WF composites had higher tensile modulus and rather lower tensile strength than PGPE-TA. On the other hand, both the tensile modulus and strength of GPE-TA/WF were much higher than those of GPE-TA (2.4 GPa and 37 MPa). Those values of GPE-TA/WF increased with WF content, became maximal values (5.1 GPa and 51 MPa) at WF content 60 wt %, and were lowered at 70 wt %. FE-SEM analysis of the fractured surface of the biocomposites revealed that WF is tightly incorporated into the crosslinked epoxy resins. As a result of optimization of the epoxy/hydroxyl molar ratio for GPE-TA/WF composite with WF content 60 wt %, the composite prepared at the ratio of 1.0/0.8 showed the highest tensile modulus and strength. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2998–3004, 2010

Key words: biofibers; biopolymers; composites; renewable resources; tannic acid

INTRODUCTION

Because of increasing environmental concern and restricted availability of petrochemical resources, biocomposites composed of renewable resources-derived polymers (bio-based polymers), and natural/bio fibers have gained much attention in recent years.[1–6] For example, the biocomposites of bio-based polymers, such as poly(lactic acid),[7–15] poly(hydroxyalkanoate),[16–19] and cellulose acetate[20,21] with lignocellulosic natural fibers, such as flax, jute, hemp, kenaf, abaca, bamboo, and wood flour (WF) have been reported by several groups. However, the main problem encountered in using their bio-based polymers is its rather poor interfacial adhesion between the polar lignocellulose and the more hydrophobic characteristics of those polymeric matrices. The poor adhesion results in a poor strength, a relatively low stiffness and high moisture uptake. Another major shortcoming of this type of matrix is the relatively low fiber content, typically of less than 50–60 wt %. One way to improve the poor adhesion is a modification of the interface of matrix and

fiber.[7,9,10,13,16,17] However, the surface treatment normally increases both processing steps and its cost. We have already reported glycerol- and sorbitol-based epoxy resins cured with tannic acid (TA) as all bio-based and hydrophilic epoxy resin systems.[22]

This study describes the preparation and properties of the biocomposites composed of two types of glycerol-based epoxy resins with different viscosities and WF. The reason for the use of WF is as follows: Among the natural fibers, the use of waste wood generated from forest-thinning and wrecking of wooden building and soforth are very important for solving the severe environmental problem.[23,24] Also, a massive outbreak of damaged cedar trees infected by *Cercospora sequoiae* Ellis et Everhart ("Sugi-Mizogusare" disease), which cannot be used as log and lumber is becoming a serious problem in Chiba, Japan. The objective of this study is to propose the all bio-based resin system, which is suitable for the preparation of high performance biocomposite having a WF content not less than 60 wt % without special surface modification.

EXPERIMENTAL

Materials

Figure 1 shows the structure of main components of the reagents used in this study. Polyglycerol

Correspondence to: M. Shibata (shibata@sky.it-chiba.ac.jp).
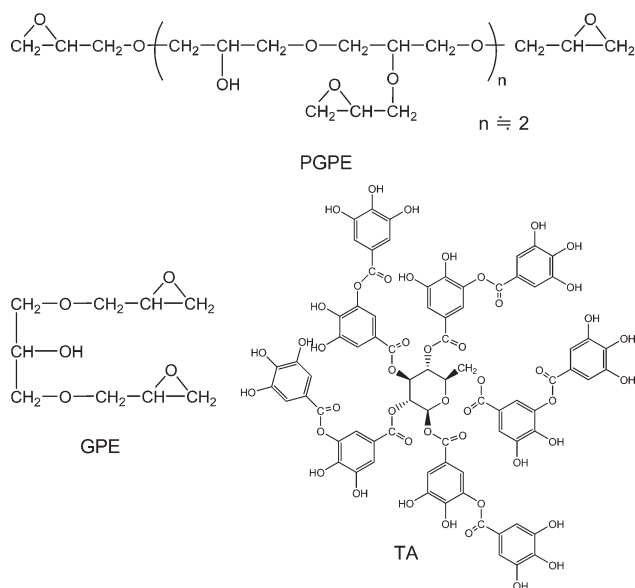
Figure 1 Main components of the reagents used in this study.

polyglycidyl ether (PGPE, DENAKOL EX-512, epoxy equivalent weight 169 g/eq., viscosity 1,300 cps at 25°C) and glycerol polyglycidyl ether (GPE, DENACOL EX-313, epoxy equivalent weight 140 g/eq. viscosity 150 cps at 25°C) were supplied from Nagase ChemteX, Corp. (Tokyo, Japan). TA was supplied from Kanto Chemical (Tokyo, Japan). WF was supplied by Kowa Technos, (Sammu-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 PGPE-TA/WF biocomposites

The mixture of PGPE 20.00 g (epoxy 0.118 mol), TA 8.05 g (hydroxyl 0.118 mol), and ethanol 12 g was stirred for 10 min at 50°C. To the homogeneous solution was added WF 28.05 g (fiber content 50 wt %) and mechanically stirred for 10 min. The obtained mixture was dried at 50°C for 1 h in a vacuum oven and then compressed at 160°C and 15 MPa for 3 h to give a cured PGPE-TA/WF biocomposite at epoxy/hydroxyl ratio 1/1 with WF content 50 wt % (PGPE-TA(1/1)/WF50) as a brown sheet. In a similar manner, PGPE-TA cured at epoxy/hydroxyl ratio 1/1 without WF (PGPE-TA(1/1)), PGPE-TA cured at epoxy/hydroxyl ratio 1/1 with WF content 60 wt % (PGPE-TA(1/1)/WF60), and PGPE-TA cured at epoxy/hydroxyl ratio 1/1 with WF content 70 wt % (PGPE-TA(1/1)/WF70) were also prepared.

Preparation of GPE-TA/WF biocomposites

The mixture of GPE 20.25 g (epoxy 0.145mol), TA 9.84 g (hydroxyl 0.145 mol) was stirred for 30 min at

room temperature. To the homogeneous solution was added WF 30.09 g (fiber content 50 wt%) and mechanically stirred for 10 min, and then compressed at 160°C and 15 MPa for 3 h to give a cured GPE-TA/WF biocomposite at epoxy/hydroxyl ratio 1/1 with WF content 50 wt % (GPE-TA(1/1)/WF50) as a brown sheet with. In a similar manner, GPE-TA cured at epoxy/hydroxyl ratio 1.0/0.6, 1.0/0.8, and 1.0/1.2 without WF (PGPE-TA(1/0.6, 1/0.8, and 1/1.2)), GPE-TA/WF cured at epoxy/hydroxyl ratio 1.0/0.6, 1.0/0.8, and 1.0/1.2 with WF content 50 wt % (GPE-TA(1/0.6, 1/0.8, and 1/1.2)/WF50), GPE-TA/WF cured at epoxy/hydroxyl ratio 1.0/0.6, 1.0/0.8, 1.0/1.0, and 1.0/1.2 with WF content 60 and 70 wt % (PGPE-TA(1/0.6, 1/0.8, 1/1, and 1/1.2)/WF50 and WF70) were also prepared.

Measurements

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 1.2 mm) was performed on a Rheolograph 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 5 mm, thickness 1.2 mm) was performed at 25°C using an Autograph AG-I (Shimadzu Co. Ltd., Kyoto, Japan). 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

#### Preparation and morphology of PGPE-TA/WF and GPE-TA/WF biocomposites

All the bio-based materials used in this study (PGPE, GPE, and TA) are water-soluble and hydrophilic substances. The average number of epoxy groups per molecule of PGPE and GPE is 4.1 and 2.0, respectively. Because the viscosity of GPE (150 cps at 25°C) was much lower than that of PGPE (1,300 cps at 25°C), a mixture of GPE, TA, and WF can be compounded without solvent. However, it was necessary to add a solvent in case of a mixture
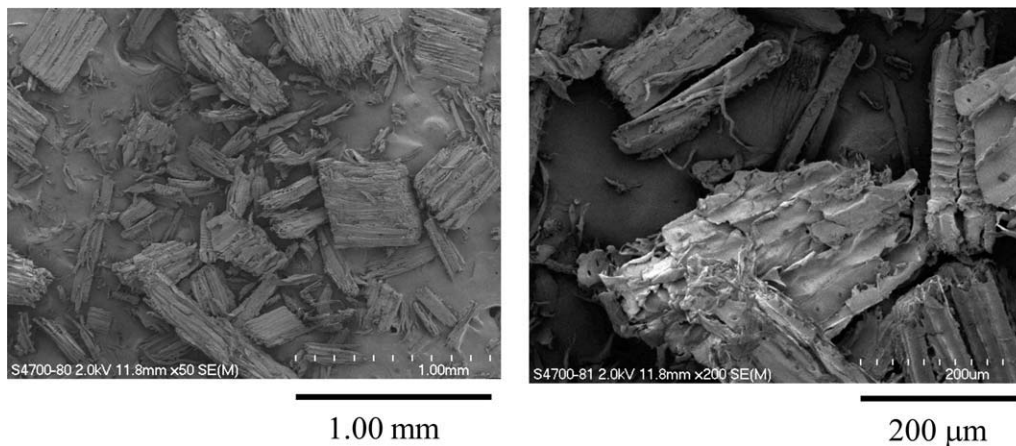
Figure 2   FE-SEM photographs of WF.

of PGPE, TA, and WF. As some precipitate was liberated when aqueous solutions of PGPE and TA were mixed, ethanol was used as a mixing solvent. The mixture of PGPE, TA, and WF or GPE, TA, and WF was cured at the condition of 160°C for 3 h with epoxy/hydroxyl ratio of 1/1, at which most balanced thermal and mechanical properties were attained for the cured products of GPE and TA in the previous literature.[22] Although the biocomposites with WF content higher than 70 wt % can be prepared, the obtained composites became brittle and

the surface was rough. Figure 2 shows the FE-SEM micrographs of the used WF. The photograph at a low magnification shows that the WF particles are mainly composed of fibrous substance of about 0.2–1.0 mm in length. The average length and aspect ratio of the WF fibers were about 0.7 mm and 4.2, respectively. The photograph at a high magnification revealed that each particle is composed of fiber bunch with a rough surface. Figure 3 shows FE-SEM photographs of the fractured surface of PGPE-TA(1/1)/WF and GPE-TA(1/1)/WF composites with WF
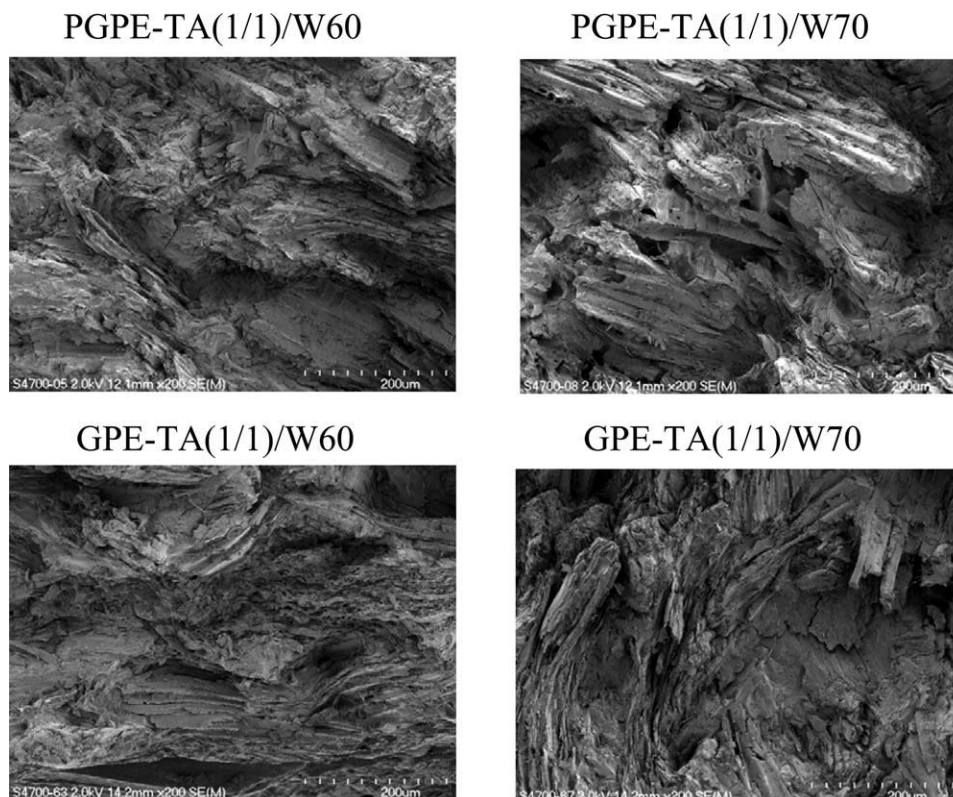
Figure 3   FE-SEM photographs of the fractured surface of GPE-TA(1/1)/WF and PGPE-TA(1/1)/WF composites with WF contents of 60 and 70 wt %.
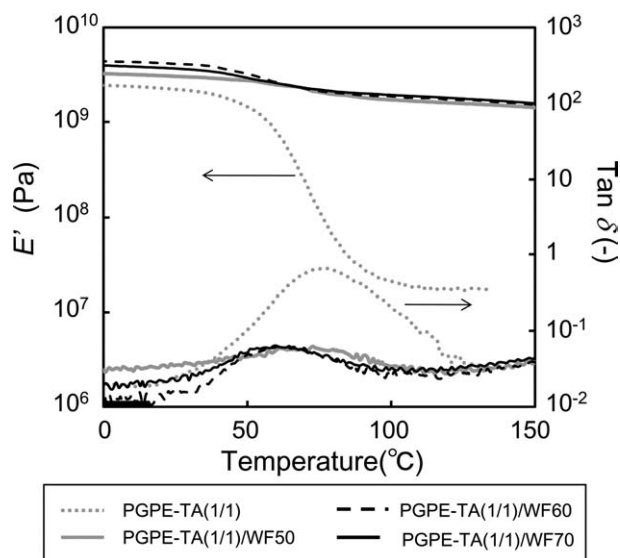
Figure 4 Temperature dependency of E' and tan δ for PGPE-TA(1/1)/WF biocomposites.
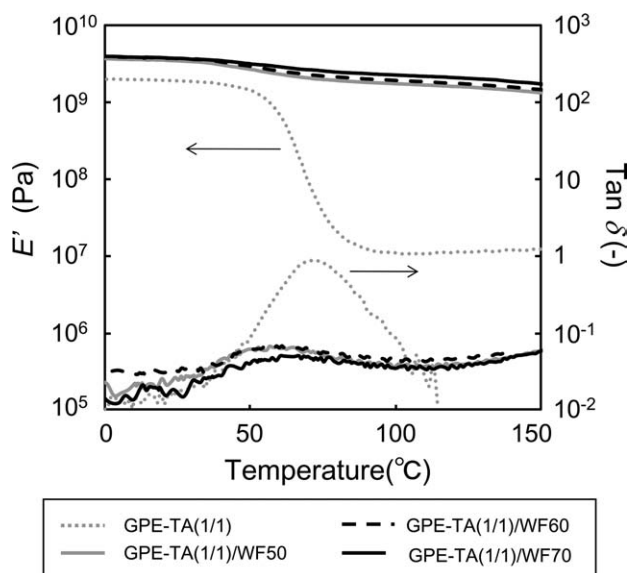
Figure 5 Temperature dependency of E' and tan δ for GPE-TA(1/1)/WF biocomposites.

contents of 60 and 70 wt %. It appeared that WF is tightly incorporated into the cross-linked epoxy resins and their interfacial adhesion is good. This result may be attributed to the fact that the polyphenol moiety of TA and lignocellulose moiety of WF resemble each other. There are some voids on the fractured surface of PGPE-TA(1/1)/WF, probably generated during the evaporation of ethanol when compared with GPE-TA/WF.

Properties of PGPE-TA/WF and GPE-TA/WF biocomposites

Figures 4 and 5 show the temperature dependency of storage modulus (E') and tan δ for PGPE-TA (1/1)/WF and GPE-TA(1/1)/WF measured by DMA, respectively. The E' at the rubbery plateau region over 80°C for all the composites was much higher than that of control cured resins, suggesting a superior reinforcement effect because of the wood fibers. The tan δ peak temperature related to T_g for the composites was a little lower than that of the corresponding neat resins. The reason is not clear, but it is thought that WF disturbs the cross-linking reaction and/or that specific components of GPE, PGPE, and TA are absorbed into the wood fibers and the stoichiometry of epoxy and hydroxyl is deviated.

Figure 6 shows typical TGA curves of GPE-TA(1/1), WF, and GPE-TA(1/1)/WF60. As the thermal decomposition temperature of WF was lower than that of GPE-TA, the GPE-TA/WF composite exhibited two-step thermodegradation. The 5% weight loss temperatures of all the composites are summarized in Table I. Consequently, the 5% weight loss

temperatures of all the composites were lower than those of the corresponding cured neat resins.

Figures 7 and 8 show the relationship between tensile properties and fiber content for PGPE-TA(1/1)/WF and GPE-TA(1/1)/WF, respectively. Although tensile modulus (4.3 GPa) of PGPE-TA(1/1)/WF was much higher than that of PGPE-TA(1/1) (2.7 GPa), the tensile strength of the composite was lower than that of PGPE-TA(1/1). On the other hand, both the tensile modulus and strength of GPE-TA(1/1)/WF were much higher than those of GPE-TA(1/1) (2.4 GPa and 37 MPa). Those values increased with WF content, became maximal values (5.1 GPa and 51 MPa) at WF content 60 wt %, and were lowered at 70 wt %. In general, although the tensile modulus of polymer/plant fiber biocomposites
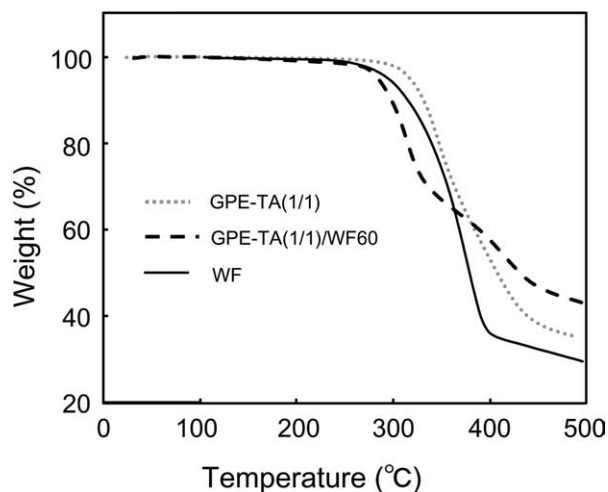
Figure 6 TGA curves of GPE-TA(1/1), WF, and GPE-TA(1/1)/WF60.

TABLE I
Tan δ Peak Temperature and 5% Weight Loss Temperature of All the Samples

| Resin	Epoxy/ hydroxyl ratio	WF content (wt%)	Tan δ peak temperature (°C)	5% Weight loss temperature (°C)
PGPE-TA	1/1	0	77	316
	1/1	50	70	295
	1/1	60	63	294
	1/1	70	60	295
GPE-TA	1/1	0	73	317
	1/1	50	59	287
	1/1	60	61	284
	1/1	70	65	287
GPE-TA	1/0.6	0	60	322
	1/0.8	0	67	321
	1/1	0	73	317
	1/1.2	0	79	312
GPE-TA	1/0.6	60	42	290
	1/0.8	60	65	293
	1/1	60	61	284
	1/1.2	60	70	289
WF	–	100	–	296
TA	–	–	–	285

is higher than the control polymer, the strength is rather lower because of a poor interfacial adhesion. It is noteworthy that the tensile strength of GPE-TA is improved by the addition of WF without any interfacial modification. This result should be attributed to the superior interfacial adhesion between GPE-TA and WF. As the reason that the tensile strength of PGPE-TA(1/1)/WF did not increase, the following factors are considered. As tensile strength of PGPE-TA(1/1) is much higher than that of GPE-TA(1/1), the interfacial adhesion strength between PGPE-TA(1/1) and WF is not higher than the strength of PGPE-TA(1/1). The structural defects because of some voids are observed as was shown in Figure 3. Also, the fact that the tensile modulus and strength of both PGPE-TA(1/1)/WF and GPE-TA(1/

1)/WF composites with WF content 70 wt % are lower than those of the composites with 60 wt % suggests that the packing of matrix resin between the WF particles is relatively insufficient for composites with 70 wt %.

Optimization of epoxy/hydroxyl ratio for GPE-TA/WF biocomposites

As the tan δ peak temperature of GPE-TA(1/1)/WF was lower than that of GPE-TA(1/1) (Fig. 5), the epoxy/hydroxyl ratio appropriate for GPE-TA/WF composites was investigated. Table I summarizes the tan δ peak temperature of GPE-TA and GPE-TA/WF60 prepared at epoxy/hydroxyl ratios from 1.0/0.6 to 1.0/1.2. In case of the control GPE-TA, the tan δ peak temperature related to glass transition temperature (T_g) increased with decreasing epoxy/hydroxyl ratio. Considering that all of the three hydroxyl groups of pyrogallol (1,2,3-trihydroxybenzene) moiety of TA are hard to react with epoxy groups of GPE, it is supposed that an actual stoichiometric epoxy/hydroxyl ratio should be lower than 1/1. Although GPE-TA(1/1.2)/WF60 exhibited the highest tan δ peak temperature among the GPE-TA/WF60 composites in a similar manner to the control resins, GPE-TA(1/0.8)/WF60 had a little higher tan δ peak temperature than GPE-TA(1/1)/WF60. In case of GPE-TA(1/0.8)/WF60, there is a possibility that the excess epoxy groups of GPE reacted with the hydroxyl groups in WF at the curing temperature of 160°C. As a result, GPE-TA(1/0.8)/WF60 had almost the same tan δ peak temperature as GPE-TA(1/0.8).

Table I also summarizes 5% weight loss temperature of GPE-TA and GPE-TA/WF60 prepared at epoxy/hydroxyl ratios from 1.0/0.6 to 1.0/1.2. Regarding the control GPE-TA, the 5% weight loss temperature a little decreased with decreasing epoxy/hydroxyl ratio. As TA itself has the lowest 5%
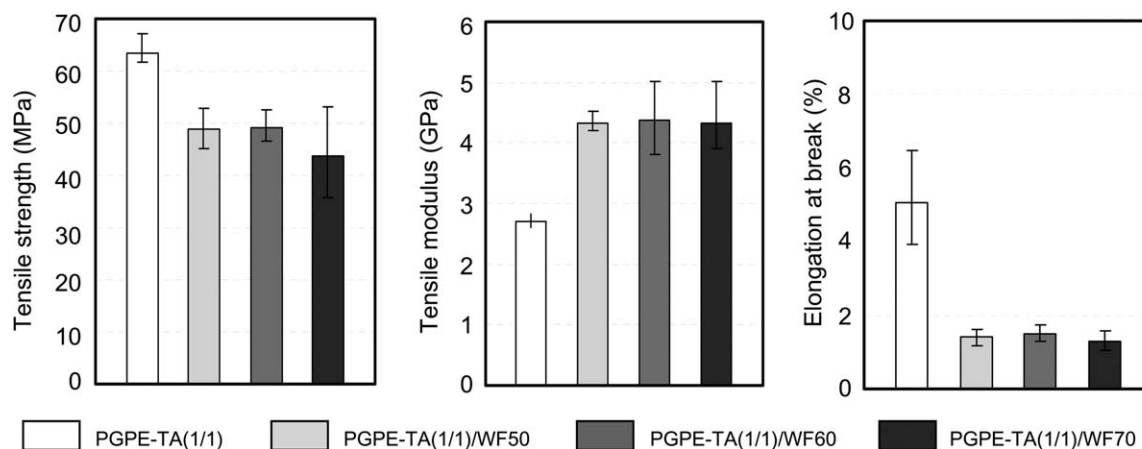
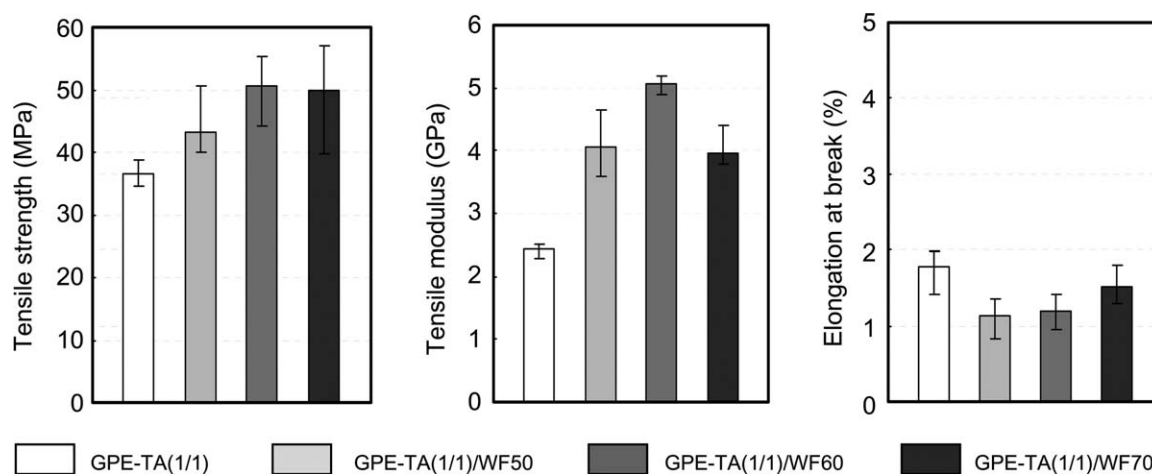**Figure 7** Tensile properties of PGPE-TA(1/1)/WF composites.

Figure 8 Tensile properties of GPE-TA(1/1)/WF composites.

weight loss temperature (285°C), the presence of unreacted TA moiety in the GPE-TA with a higher TA content caused a decrease of the 5% weight loss temperature. In case of the composites with WF content 60 wt %, GPE-TA(1/0.8)/WF60 exhibited the highest 5% weight loss temperature among the GPE-TA/WF composites.

Figure 9 shows the tensile properties of GPE-TA/WF60 composites prepared at various epoxy/hydroxyl ratios. The GPE-TA(1.0/0.8)/WF60 showed the highest tensile modulus (5.22 GPa), strength (54.9 MPa) and elongation at break (1.35%), indicating that the best ratio of epoxy/hydroxyl is about 1.0/0.8. In case of polypropylene (PP)/WF composites, it is known that the preparation of the PP/WF composite with WF content higher than 50 wt % is not easy, and that the addition of maleic anhydride-grafted polypropylene (MAH-PP) improves the tensile properties. The tensile modulus and strength of PP/MAH-PP/WF (45/5/50) composite are reported to be 4.55 GPa and 40.4 MPa, respectively.[25] It is also known that that tensile modulus and strength

of high-density polyethylene (HDPE)/WF (35/65) composite are 2.6 GPa and 15.6 MPa, and those of HDPE/poly(ethylene-*co*-butyl acrylate-*co*-maleic anhydride)/WF (32.5/2.5/65) are 2.5 GPa and 18.6 MPa, respectively.[26] The GPE-TA/WF composites in which neither modifier nor compatibilizer is added have higher tensile modulus and strength than these petroleum-based plastics/WF composites.

CONCLUSIONS

The GPE-TA/WF and PGPE-TA/WF biocomposites with WF content 50–70 wt % were prepared by compression molding and their thermal and mechanical properties were investigated. The storage moduli in the rubbery state at more than 80°C for PGPE-TA(1/1)/WF and GPE-TA/WF(1/1)/WF were much higher than those of PGPE-TA(1/1) and GPE/TA(1/1), respectively. The tensile moduli of PGPE-TA(1/1)/WF and GPE-TA/WF(1/1)/WF were improved by the addition of WF. Although tensile strength of GPE-TA(1/1)/WF was improved that of PGPE-
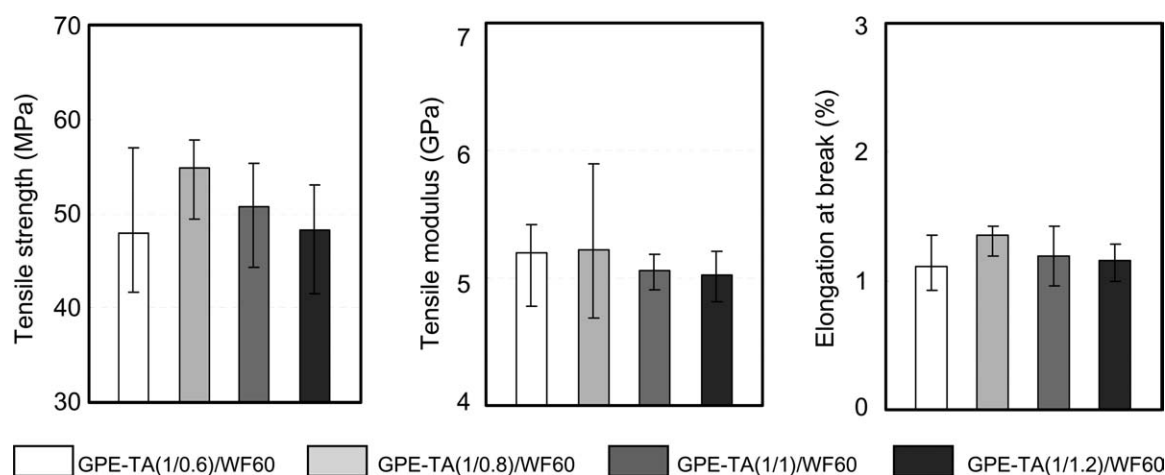

Figure 9 Tensile properties of GPE-TA/WF60 composites prepared at various epoxy/hydroxyl ratios.

TA(1/1)/WF was rather lower than PGPE-TA(1/1). The GPE-TA(1/1)/WF60 exhibited the highest tensile strength (51 MPa) and modulus (5.1 GPa). FE-SEM analysis of the fractured surface of GPE-TA(1/1)/WF composites revealed that WF is tightly incorporated into the cross-linked epoxy resins. When the epoxy/hydroxyl molar ratio for GPE-TA/WF60 was varied, the composite prepared at 1.0/0.8 showed the highest tensile modulus and strength (5.2 GPa and 55 MPa).

Consequently, the GPE-TA/WF biocomposite with WF content over 50 wt % is easily prepared without using any solvent and compatibilizer, and exhibited superior mechanical properties to PP/WF and HDPE/WF composites. These all bio-based composites are expected to be environmentally benign materials for the replacement of petroleum-based plastics/WF composites.

References

1. Saheb, D. N.; Jog, J. P. Adv Polym Technol 1999, 18, 351.
2. Bledzki, A. K.; Gassan, J. Prog Polym Sci 1999, 24, 221.
3. Mohanty, A. K.; Misra, M.; Hinrichsen, G. Macromol Mater Eng 2000, 276, 1.
4. Mohanty, A. K.; Misra, M.; Drzal, L. T. J Polym Environ 2002, 10, 19.
5. Yu, L.; Dean, K.; Li, L. Prog Polym Sci 2006, 31, 576.
6. Yu, L.; Petinakis, S.; Dean, K.; Bilyk, A.; Wu, D. Macromol Symp 2007, 249, 535.
7. Shibata, M.; Ozawa, K.; Teramoto, N.; Yosomiya, R.; Takeishi, H. Macromol Mater Eng 2003, 288, 35.
8. Oksman, K.; Skrifvars, M. S.; Eli, J. F. Compos Sci Technol 2003, 63, 1317.
9. Plackett, D. J Polym Environ 2004, 12, 131.
10. Teramoto, N.; Urata, K.; Ozawa, K.; Shibata, M. Polym Degrad Stab 2004, 86, 401.
11. Mathew, A. P.; Oksman, K.; Sain, M. J Appl Polym Sci 2005, 97, 2014.
12. Seriwzawa, S.; Inoue, K.; Iji, M. J Appl Polym Sci 2006, 100, 618.
13. Lee, S. H.; Wang, S. Compos Part A 2006, 37, 80.
14. Gamstedt, E. K.; Bogren, K. M.; Neagu, R. C.; Akerho, L. M. M.; Lindstrom, M. J Thermoplast Compos Mater 2006, 19, 613.
15. Shibata, M. In Biodegradable Polymer Blends and Composites from Renewable Resources; Yu, L., Ed.; Wiley: Hoboken, 2009; Chapter 12.
16. Mohanty, A. K.; Khan, M. A.; Hinrichsen, G. Compos Sci Technol 2000, 60, 1115.
17. Shibata, M.; Takachiyo, K.; Ozawa, K.; Yosomiya, R.; Takeishi, H. J Appl Polym Sci 2002, 85, 129.
18. Zini, E.; Focarete, M. L.; Noda, I.; Scandola, M. Compos Sci Technol 2007, 67, 2085.
19. Coats, E. R.; Loge, F. J.; Wolcott, M. P.; Englund, K.; Mcdonald, A. G. Bioresour Technol 2008, 99, 2680.
20. Mohanty, A. K.; Wibowo, A.; Misra, M.; Drzal, L. T. Compos Part A 2004, 35, 363.
21. Choi, J. S.; Lim, S. T.; Choi, H. J.; Hong, S. M.; Mohanty, A. K.; Drzal, L. T.; Misra, M.; Wibowo, A. C. Macromol Symp 2005, 224, 297.
22. Shibata, M.; Nakai, K. J Polym Sci Part B 2010, 48, 425.
23. Yang, H. S.; Kim, D. J.; Kim, H. J. Bioresour Technol 2003, 86, 117.
24. Ye, X. P.; Julson, J.; Kuo, M.; Womac, A.; Myers, D. Bioresour Technol 2007, 98, 1077.
25. Nygard, P.; Tanem, B. S.; Karlsen, T.; Brachet, P.; Leinsvang, B. Compos Sci Technol 2008, 68, 3418.
26. Panthapulakkal, S.; Sain, M. Compos Part A 2007, 38, 1445.