

Preparation and Properties of Biocomposites Composed of Epoxidized Soybean Oil, Tannic Acid, and Microfibrillated Cellulose

Mitsuhiro Shibata, Naozumi Teramoto, Kyohei Makino

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

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ABSTRACT: As a new biobased epoxy resin system, epoxidized soybean oil (ESO) was cured with tannic acid (TA) under various conditions. When the curing conditions were optimized for the improvement of the thermal and mechanical properties, the most balanced properties were obtained when the system was cured at 210°C for 2 h at an epoxy/hydroxyl ratio of 1.0/1.4. The tensile strength and modulus and $\tan \delta$ peak temperature measured by dynamic mechanical analysis for the ESO–TA cured under the optimized condition were 15.1 MPa, 458 MPa, and 58°C, respectively. Next, we prepared biocomposites of ESO, TA, and microfibrillated cellulose (MFC) with MFC contents from 5 to 11 wt % by mixing an ethanol solution of ESO and TA with MFC and subsequently drying and curing the compo-

sites under the optimized conditions. The ESO–TA–MFC composites showed the highest $\tan \delta$ peak temperature (61°C) and tensile strength (26.3 MPa) at an MFC content of 9 wt %. The tensile modulus of the composites increased with increasing MFC content and reached 1.33 GPa at an MFC content of 11 wt %. Scanning electron microscopy observation revealed that MFC was homogeneously distributed in the matrix for the composite with an MFC content of 9 wt %, whereas some aggregated MFC was observed in the composite with 11 wt % MFC. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 273–278, 2011

Key words: biofibers; nanocomposites; renewable resources

INTRODUCTION

Biobased polymer products derived from annually renewable agricultural and biomass feedstock have become increasingly important as sustainable and ecoefficient products that can replace products based exclusively on petroleum feedstock.^{1,2} Triglyceride plant oils represent a major class of such renewable resources. Soybean oil (SBO) is the most readily available and one of the lowest costing vegetable oils in the world. In the past decade, much effort has been dedicated to producing SBO-based polymeric materials.^{3,4} Epoxidized soybean oil (ESO) is manufactured by the epoxidation of the double bonds of the SBO triglycerides with hydrogen peroxide, either in acetic acid or in formic acid, and it is industrially available in large volumes at a reasonable cost.^{5,6} ESO is currently mainly used as a plasticizer or stabilizer to modify the properties of plastic resins, such as poly(vinyl chloride). ESO can be used as a reactive modifier or diluent of epoxy resin systems. Several researchers have investigated the curing and conversion of ESO into flexible, semiflexible, and rigid crosslinked resins with various

approaches.^{7–16} These studies have shown potential for the biobased polymeric products derived from renewable SBO. However, there have been few studies using biobased materials as curing reagents for ESO. For example, Warth et al.¹⁵ reported a polyester network based on ESO and maleinated SBO. Our groups¹⁶ reported a biobased epoxy resin system composed of ESO and terpene-derived acid anhydride, which was synthesized by the Diels–Alder reaction of maleic anhydride and allo-ocimene obtained by the isomerization of α -pinene. In this study, tannic acid (TA) was used as a biobased curing agent for ESO. Commercial TA is comprised of mixtures of gallotannins from sumac galls, Aleppo oak galls, or sumac leaves.¹⁷ The chemical formula for commercial TA is often given as $C_{76}H_{52}O_{46}$, as shown in Figure 1. However, in fact, it contains a mixture of related compounds. Its structure is based mainly on the glucose ester of gallic acid. We already reported the thermal and mechanical properties of glycerol and sorbitol poly(glycidyl ether)s cured with TA.¹⁸ Their epoxy resins were produced by the reaction of the corresponding biobased polyols and petroleum-based epichlorohydrin. Therefore, when the epoxy resins were replaced with ESO, cured products with a higher fraction of biobased carbon were expected.

In recent years, microfibrillated cellulose (MFC), with the diameters in the range 10–100 nm, which is

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

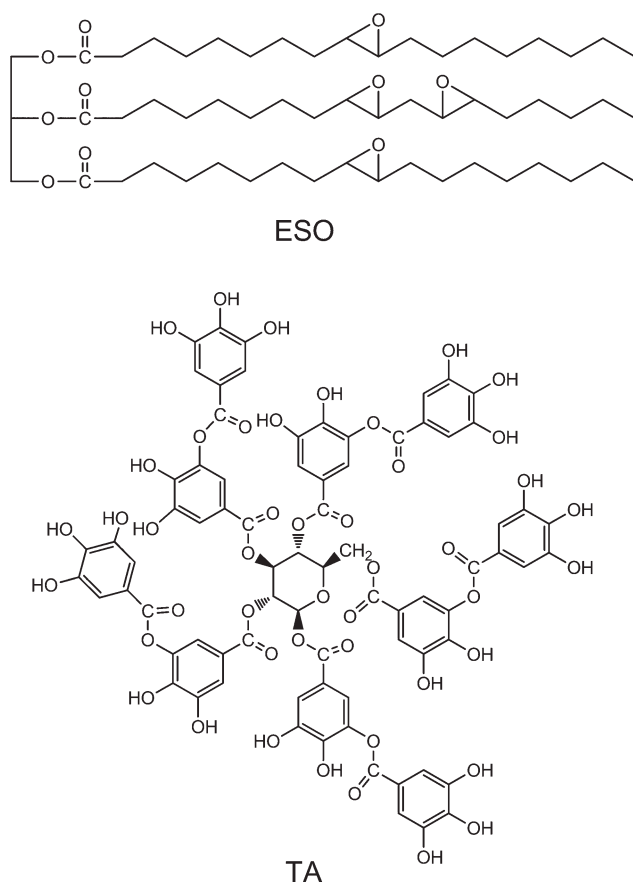


Figure 1 Main components of the reagents used in this study.

obtained through a simple mechanical process that includes refining and high-pressure homogenization, has received significant research attention as a reinforcing fiber of polymers.^{19–28} Drzal and coworkers²⁵ reported that the mechanical properties of composites of MFC and bisphenol F-type epoxy resin cured with a polyether amine were improved by the silane coupling treatment of the MFC. It is important in the preparation of superior polymer–MFC composites to devise a surface treatment method of MFC. In this study, the reinforcement of an ESO–TA-based epoxy resin system with MFC was investigated. It was expected that MFC would be dispersed in the matrix polymer without special surface modification by the use of TA as a hydrophilic hardener.

EXPERIMENTAL

Materials

Figure 1 shows the structures of the main components of the reagents used in this study. ESO (KAPOX S-6, oxirane oxygen = 6.7%) was supplied from Kao Corp. (Tokyo, Japan). TA was supplied from Kanto Chemical Co., Inc. (Tokyo, Japan). MFC (trade name Celish KY-100G) was supplied by Dai-icel Chemical Industries, Ltd. (Tokyo, Japan). This

product had a 10 wt % solid content in a water suspension. MFC was disintegrated into nanometer to submicrometer wide fibers forming a network, as was obvious from scanning electron microscopy (SEM) images reported previously.^{24,29}

Curing reaction of ESO with TA

A mixture of 20.00 g of ESO (epoxy, 83.78 mmol), 5.70 g of TA (hydroxyl, 83.8 mmol), and 28 g of ethanol was stirred for 20 min at 75°C. The resulting homogeneous solution was poured onto a polytetrafluoroethylene plate and degassed in a vacuum desiccator at room temperature for 24 h. The obtained mixture was dried at 80°C for 24 h and cured at 210°C for 2 h in an electric oven to give ESO cured with TA in an epoxy/hydroxyl ratio of 1.0/1.0 (ESO–TA1.0) as a brown sheet. For ESO–TA1.0, the curing temperature was changed over the range from 150 to 230°C. Also, the curing time at 210°C was changed over the range from 1 to 5 h. ESOs cured with TA in epoxy/hydroxyl ratios of 1.0/0.6, 1.0/0.8, 1/1.2, and 1.0/1.4 (ESO–TA0.6, ESO–TA0.8, ESO–TA1.2, and ESO–TA1.4, respectively) were also prepared at under the postcuring conditions at 210°C for 2 h in a similar manner to that used for ESO–TA1.0.

Preparation of the composite of ESO–TA1.4 with MFC

To prevent the phase separation of ESO due to the water contained in MFC, the water contained in MFC was substituted with ethanol by the following procedure: after a mixture of wet MFC (14.7 g, solid MFC = 1.47 g) and ethanol (28 g) was shaken, the suspension was centrifuged at 3500 rpm for 5 min, and then, the supernatant ethanol was decanted off. After five repetitions of this procedure, ethanol (28 g) was added to the final ethanol–wet MFC, and the mixture was stirred to give an ethanol suspension of MFC. The mixture of ESO (epoxy, 20.00 g, 83.78 mmol) and TA (hydroxyl, 7.97 g, 117.2 mmol) was stirred for 10 min at room temperature. To the solution was added a whole amount of the obtained ethanol suspension of MFC, and the mixture was mechanically stirred for 15 min at 75°C. The obtained suspension was degassed in a vacuum desiccator at room temperature for 24 h and then dried at 80°C for 24 h in an electric oven. The resulting compound was compression-molded at 210°C and 5 MPa for 2 h to give a composite of ESO–TA1.4 and MFC with a fiber content of 5.0 wt % (ESO–TA1.4–MFC5) as a brown sheet. Composites of ESO–TA1.4 and MFC with fiber contents of 7, 9, and 11 wt % (ESO–TA1.4–MF7, ESO–TA1.4–MF9, and ESO–

TABLE I
Optimization of the Curing Temperature and Time for ESO-TA with an Epoxy/Hydroxyl Ratio of 1.0/1.0

Curing temperature (°C)	Curing time (h)	Tan δ peak temperature (°C)	Tensile strength (MPa) $\pm \sigma$	Tensile modulus (MPa) $\pm \sigma$
150	2	46	4.4 \pm 0.2	54 \pm 7
170	2	52	9.8 \pm 1.1	265 \pm 24
190	2	53	11.4 \pm 0.6	335 \pm 3
210	2	57	12.7 \pm 0.6	409 \pm 12
230	2	50	9.2 \pm 0.4	234 \pm 28
210	1	55	8.9 \pm 0.4	257 \pm 10
	2	57	12.7 \pm 0.6	409 \pm 12
	3	55	12.0 \pm 0.7	390 \pm 33
	4	51	11.5 \pm 0.7	309 \pm 20
	5	51	11.2 \pm 1.0	318 \pm 49

TA1.4-MF11) were also prepared in a similar manner to that used for ESO-TA1.4-MFC5.

Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu FTIR 8100 instrument (Kyoto, Japan) by the attenuated total reflectance method. Thermomechanical analysis (TMA) was conducted on a MAC Science (Yokohama, Tokyo, Japan) TMA 2000S instrument at a heating rate of 10°C/min under a nitrogen atmosphere. The 5% weight loss temperature was measured on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 20°C/min under a nitrogen atmosphere. Dynamic mechanical analysis (DMA) of the rectangular films (length = 40 mm, width = 5 mm, thickness = 1.5 mm) was performed on a Rheograph Solid (Toyo Seiki Co., Ltd., Tokyo, Japan) with a chuck distance of 20 mm, a frequency of 1 Hz, and a heating rate of 2°C/min. Tensile testing of the rectangular plate (length = 40 mm, width = 5 mm, thickness = 1.5 mm) was performed at 25°C with an Autograph AG-I (Shimadzu). The span length and testing speed were 25 and 10 mm, respectively. Five specimens were tested for each set of samples, and the mean values and the standard deviation (σ) were calculated. The morphology of the composites was observed by field emission scanning electron microscopy (FE-SEM) with a Hitachi S-4700 machine (Hitachi High-Technologies Corp., Tokyo, 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

Optimization of the curing conditions of ESO-TA

The chemical formula for commercial TA is often given as C₇₆H₅₂O₄₆ (Fig. 1). However, in fact, it con-

tains a mixture of related compounds. Also, it is supposed that all of the three hydroxyl groups of the pyrogallol (1,2,3-trihydroxybenzene) moiety of TA are hard to react with the epoxy groups of ESO. Therefore, the curing temperature, curing time, and epoxy/hydroxyl ratio of the ESO-TA systems were optimized. The curing temperature and time were changed over the range of 150–230°C and 1–5 h, respectively. The epoxy/hydroxyl ratio was changed over the range from 1/0.6 to 1/1.4 on the basis of the oxirane oxygen content (6.7 wt %) of ESO and the hydroxyl value (68 g/equiv) of TA, as calculated from the structure shown in Figure 1. Because the FTIR absorption peak at 840 cm⁻¹, characteristic of the epoxy ring, which was observed for ESO, disappeared even for the cured material with an epoxy/hydroxyl ratio of 1/0.6, we could not evaluate the optimized ratio by means of FTIR spectroscopy. We believe that some homopolymerization of ESO occurred for the epoxy-rich mixture by a catalytic action of TA. Table I summarizes the tan δ peak temperature corresponding to the glass-transition temperature (T_g) measured by DMA and the tensile strength and modulus for the ESO-TA with an epoxy/hydroxyl ratio of 1.0/1.0 cured at 150–230°C for 2 h or cured at 210°C for 1–5 h. When the curing time was 2 h, the maximal tan δ peak temperature (57°C), tensile strength (12.7 MPa), and tensile modulus (409 MPa) were obtained at 210°C. When the curing temperature was 210°C, curing for 2 h showed the highest tan δ peak temperature and tensile strength and modulus. These results indicate that the control of curing temperature and time was very important for the biobased epoxy curing system containing aliphatic and sugar-based moieties with relatively low heat resistance. Consequently, conditions of 210°C and 2 h were selected for the curing of ESO-TA. Table II summarizes the results of DMA and tensile testing for the ESO-TA with an epoxy/hydroxyl ratio of 1.0/0.6–1.0/1.4 cured at 210°C for 2 h. The tan δ peak temperature measured by DMA increased with decreasing epoxy/hydroxyl ratio

TABLE II
Optimization of Epoxy/Hydroxyl Ratio for the ESO-TA Cured at 210°C for 2 h

Epoxy/OH	Tan δ peak temperature (°C)	Tensile strength (MPa) $\pm \sigma$	Tensile modulus (MPa) $\pm \sigma$
1.0/0.6	28	1.5 \pm 0.1	28 \pm 2
1.0/0.8	46	6.0 \pm 0.8	116 \pm 18
1.0/1.0	57	12.7 \pm 0.6	409 \pm 12
1.0/1.2	58	12.7 \pm 0.4	450 \pm 28
1.0/1.4	58	15.1 \pm 0.8	458 \pm 31

over the range from 1.0/0.6 to 1.0/1.2 and leveled off at a ratio of 1.0/1.4. The tensile strength and modulus increased with decreasing epoxy/hydroxyl

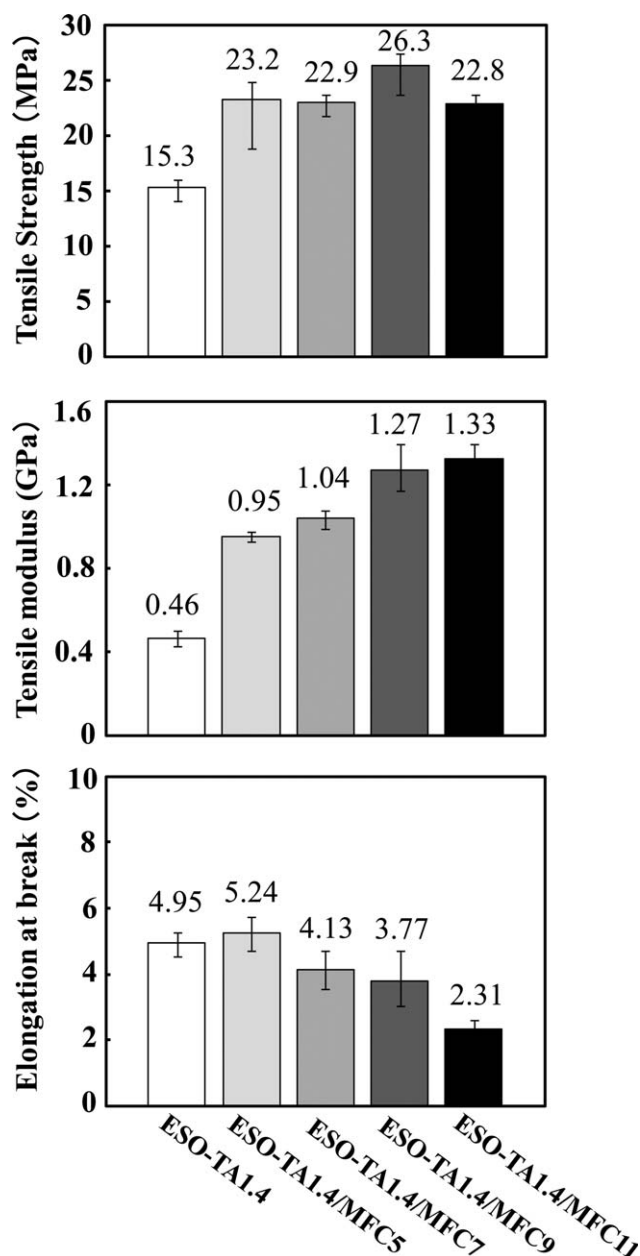
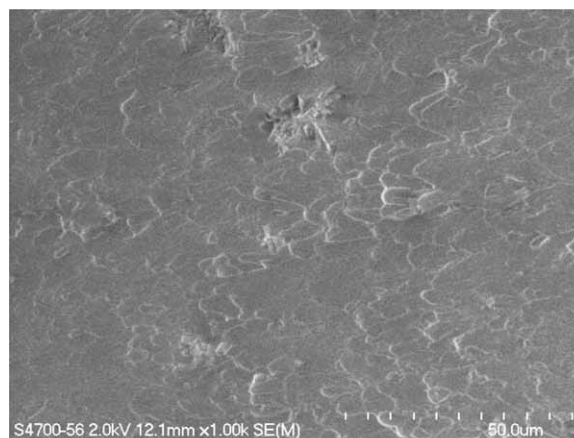
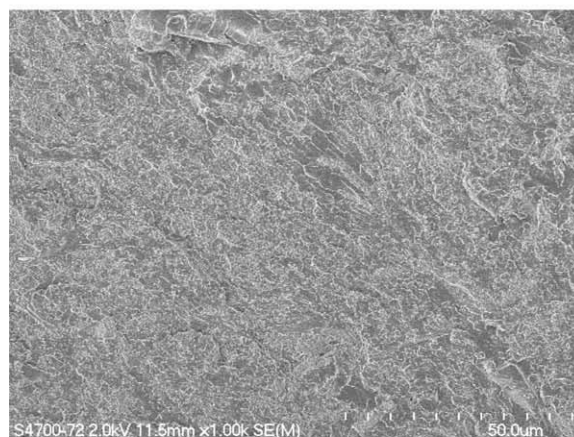


Figure 2 Tensile properties of ESO-TA1.4-MFC composites.

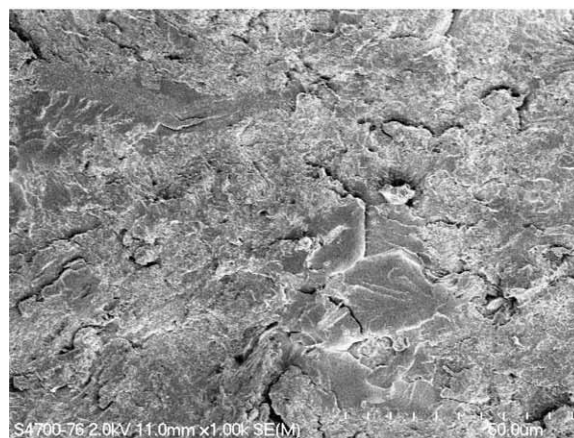
ratio, and the highest values were obtained at a ratio of 1.0/1.4, although there was little difference in the tensile moduli between ESO-TA1.2 and ESO-TA1.4. The tan δ peak temperature, tensile strength, and



ESO-TA1.4



ESO-TA1.4/MFC9



ESO-TA1.4/MFC11

50 μm

Figure 3 FE-SEM images of the fractured surface of ESO-TA1.4, ESO-TA1.4-MFC9, and ESO-TA1.4-MFC11.

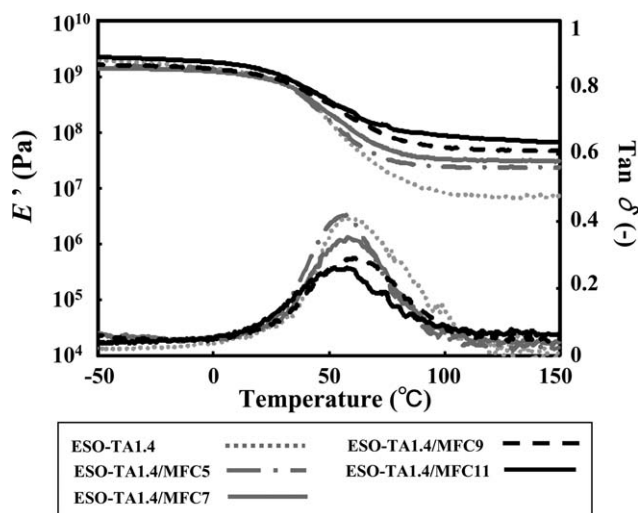


Figure 4 Temperature dependency of E' and $\tan \delta$ for the ESO-TA1.4-MFC composites.

tensile modulus (58°C, 15.1 MPa, and 458 MPa, respectively) of ESO-TA1.4 were comparable to those of the ESO cured with the petroleum-based popular acid anhydride hardener, hexahydrophthalic anhydride (with values of 59°C, 14.7 MPa, and 593 MPa, respectively).¹⁶ When the epoxy/hydroxyl ratio was lower than 1.0/1.4, the ESO-TA mixture became so viscous that we could not prepare a void-free cured sample. Consequently, conditions with a curing temperature of 210°C, a curing time of 2 h, and an epoxy/hydroxyl ratio of 1.0/1.4 were selected for the curing of ESO-TA.

Properties of ESO-TA1.4/MFC

When the commercial MFC containing 90% water was directly added to a 50% ethanol solution of ESO and TA, some ESO-rich component was phase-separated, and a homogeneous cured material was not obtained. When the mixture was cured after freeze drying, a relatively homogeneous ESO-TA-MFC composite with an MFC content of 5 wt % was obtained. However, the composite had a much lower

$\tan \delta$ peak temperature (42°C) and tensile strength (4.0 MPa) than the control ESO-TA1.4 (58°C and 15.1 MPa, respectively). Therefore, the water in the MFC aqueous suspension was substituted with ethanol, and the obtained ethanol suspension of MFC was added to a mixture of ESO and TA, as is described in the Experimental section. By this method, a homogeneous composite with a higher performance than the control cured resin was obtained.

Figure 2 shows the relationship between the tensile properties and fiber content for ESO-TA1.4-MFC composites. The tensile modulus of the composites increased with increasing fiber content and reached 1.33 GPa at an MFC content of 11 wt %. On the other hand, the elongation at break decreased with increasing MFC content. With regard to the tensile strength, although all of the ESO-TA1.4-MFC composites had a higher value than the control ESO-TA1.4, a clear relationship between the tensile strength and MFC content was not elucidated. As a result, the highest tensile strength (26.3 MPa) was obtained when the MFC content was 9 wt %.

Figure 3 shows FE-SEM images of the fractured surfaces of the ESO-TA1.4, ESO-TA1.4-MFC9, and ESO-TA1.4-MFC11 biocomposites. The surface of ESO-TA1.4 was very smooth, except for the fractured pattern. On the other hand, the surface of ESO-TA1.4-MFC9 was very rough; this suggested that MFC was homogeneously dispersed in the matrix polymer. However, the surface of ESO-TA1.4-MFC11 was heterogeneous and several microcracks were observed; this suggested that some aggregation of MFC occurred and that the space between the aggregated fibrils was not fully filled out with the epoxy resin because of the high volume fraction of MFC. The difference in the morphology was responsible for the fact that the tensile strength of ESO-TA1.4-MFC11 was lower than that of ESO-TA1.4-MFC9.

Figure 4 shows the temperature dependence of the storage modulus (E') and $\tan \delta$ for the ESO-TA1.4-MFC composites. E' at the rubbery plateau region over 100°C increased with MFC content; this suggested that a good dispersion of MFC in the matrix

TABLE III
Properties of ESO-TA1.4 and ESO-TA1.4-MFC with Various MFC Contents

Sample abbreviation	5 wt % loss temperature (°C)	Tan δ peak temperature (°C)	T_g from TMA (°C)	CTE (10^{-5} K^{-1})	
				α_1^a	α_2^b
ESO-TA1.4	345.4	58	47.7	9.74	20.46
ESO-TA1.4-MFC5	329.5	58	48.6	10.98	24.54
ESO-TA1.4-MFC7	329.1	59	51.1	12.37	27.79
ESO-TA1.4-MFC9	324.9	61	56.7	14.28	27.06
ESO-TA1.4-MFC11	318.5	57	56.4	16.10	27.79

^a CTE between $T_g - 20$ (°C) and $T_g - 10$ (°C).

^b CTE between $T_g + 10$ (°C) and $T_g + 20$ (°C).

was attained. The $\tan \delta$ peak temperature corresponding to T_g increased a little with MFC contents over the range from 5 to 9 wt % (see also Table III); this indicated that there was some interaction between MFC and crosslinked ESO-TA. However, the $\tan \delta$ peak temperature of ESO-TA1.4-MFC11 was rather lower than that of ESO-TA1.4-MFC9. This result was attributed to the heterogeneous morphology of the former composite.

Table III summarizes the results of the TMA and TGA measurements of the ESO-TA1.4-MFC composites. T_g measured by TMA exhibited a similar tendency to the $\tan \delta$ peak temperature measured by DMA. The coefficients of thermal expansion (CTEs) below T_g and above T_g somewhat increased with MFC content. Because crystalline cellulose had a much lower CTE than ESO-TA1.4,³⁰ we believe that microbubbles or voids were contaminated into the composites. Although the 5 wt % loss temperature measured by TGA for ESO-TA1.4-MFC decreased with increasing MFC content, their values were higher than that of dried MFC (315.1°C).

CONCLUSIONS

As the result of the optimization of the curing conditions, ESO-TA with an epoxy/hydroxyl ratio of 1.0/1.4, which was cured at 210°C for 2 h, had the most balanced thermal and mechanical properties. The ESO-TA1.4 cured under the optimized conditions exhibited $\tan \delta$ peak temperature, tensile strength, and modulus values comparable to the ESO cured with tetrahydrophthalic anhydride. Direct mixing and the ethanol suspension method were compared as the preparation methods of the biocomposite of ESO-TA and MFC. Consequently, the biocomposite prepared by the ethanol suspension method gave better thermal and tensile properties. The tensile modulus of the composites increased with increasing MFC content and reached 1.33 GPa at an MFC content of 11 wt %; this was 2.9 times higher than that of ESO-TA1.4. The ESO-TA1.4-MFC9 composites showed the highest $\tan \delta$ peak temperature (61°C) and tensile strength (26.3 MPa), which was 72% higher than that of ESO-TA1.4. The SEM observation revealed that MFC was homogeneously distributed in the matrix for the composite with an MFC content of 9 wt %, whereas some aggregated MFC was observed for the composite with 11 wt % MFC.

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