

Biocomposites Composed of Epoxidized Soybean Oil Cured with Terpene-Based Acid Anhydride and Cellulose Fibers

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Received 23 July 2007; accepted 4 December 2007

DOI 10.1002/app.27866

Published online 28 January 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Epoxidized soybean oil (ESO) was cured with a terpene-based acid anhydride (TPAn) at 150°C, and the thermal and mechanical properties of the cured product were compared with ESO cured with hexahydrophthalic anhydride (HPAn), maleinated linseed oil (LOAn), or thermally latent cationic polymerization catalyst (CPI). The ESO-TPAn showed a higher glass transition temperature (67.2°C) measured by dynamic mechanical analysis than ESO-HPAn (59.0°C), ESO-LOAn (-41.0°C), and ESO-CPI (10.0°C). The storage modulus at 20°C of ESO-TPAn was higher than those of ESO-LOAn and ESO-CPI. Also, ESO-TPAn showed higher tensile strength and modulus than the other cured ESOs. Regarding the biodegradability measured by biochemical oxygen demand in an activated

sludge, ESO-TPAn possessed some biodegradability, which was lower than that of ESO-LOAn. Next, biocomposites composed of ESO-TPAn and regenerated cellulose (lyocell) fabric were prepared by compression molding method. The tensile strength of ESO-TPAn/lyocell composites increased with increasing fiber content. The tensile strength and modulus of ESO-TPAn/lyocell composite with fiber content 75 wt % were 65 MPa and 2.3 GPa, which were three times higher than those of ESO-TPAn. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1596–1602, 2008

Key words: composites; crosslinking; fibers; soybean oil; terpene

INTRODUCTION

Bio-based polymer products derived from annually renewable agricultural and biomass feedstock have become increasingly important, because raw materials derived from fossil fuels are rather limited.^{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 cost 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.^{5–7} 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.^{7,8–16} These studies show the potential for the bio-based polymeric products derived from renewable SBO. However, there are few literatures using bio-based materials as curing reagent for ESO. For example, Warth et al. reported the polyester network based on ESO and maleinated soybean oil (MASO).¹⁵ In this study, as a bio-based curing reagent for ESO, a terpene-derived acid anhydride (TPAn) was used. The TPAn is synthesized by the Diels-Alder reaction of maleic anhydride and allocimene obtained by the isomerization of α -pinene as shown in Figure 1.^{17–19}

Recently, there has been enormous interest in biocomposites composed of bio-based polymer and bio-fiber (natural fiber) as matrix material and reinforcing element from the standpoint of protection of the natural environment and saving of petroleum resources.^{2,4,20–22} Their biocomposites using sisal, abaca, pineapple leaf fibers, etc. as cellulosic natural fibers have been already studied by several groups to improve the low mechanical strength and modulus.^{23–27} Regarding the biocomposites of ESO-based materials, Warth et al. reported the biocomposites of the above mentioned ESO-MASO and biofibers such as flax and hemp.¹⁵ Also, Tran et al. reported the biocomposite composed of maleic anhydride- and epoxide-functionalized SBOs, amine-based curing

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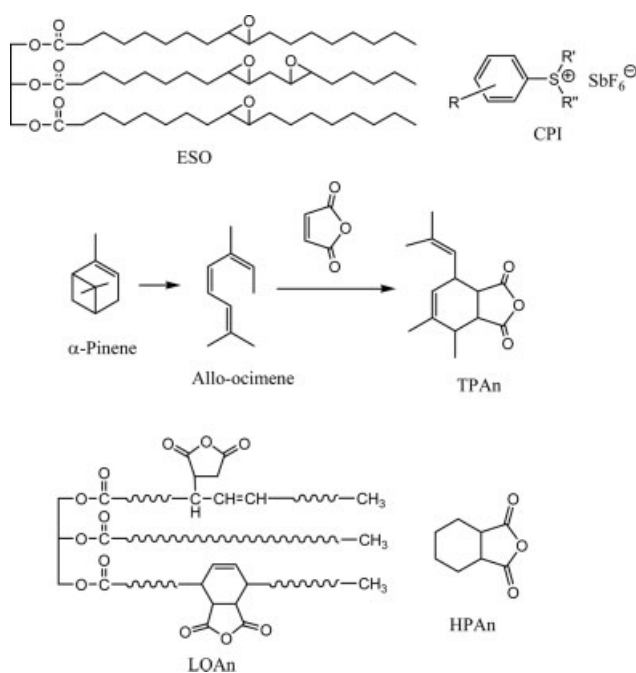


Figure 1 Structure of the reagents used in this study.

reagents, and biofibers such as kenaf and kayocell.²⁸ On the other hand, (viscose-)rayon, cupro, and lyocell are known as cellulosic man-made fiber. Especially, lyocell is an environmentally benign man-made fiber, because lyocell is manufactured from wood pulp by cellulose dissolution in *N*-methyl morpholine *N*-oxide, which is used repeatedly by recycling.²⁹ When compared with flax, lyocell fiber has a comparable strength and longer elongation (3% vs. 11–15%). In addition, deviations in the mechanical properties as well as of the shape between different batches of lyocell fiber are lower than for natural fibers. Although lyocell fiber/biodegradable polymer composites are very interesting eco-friendly composite (green composite) from such view points, little literature is reported.^{30,31}

In this study, first the thermal, mechanical, and biodegradable properties of the ESO cured with TPAn were investigated when compared with those of the ESOs cured with maleinated linseed oil (LOAn), a thermally latent cationic polymerization catalyst (CPI), hexahydrophthalic anhydride (HPAn). Next, biocomposites composed of ESO, TPAn, and lyocell fabric were investigated to improve the mechanical properties of the ESO-TPAn.

EXPERIMENTAL

Materials

Figure 1 shows the structure of the reagents used in this study. Epoxidized soybean oil (ESO, KAPOX S-6, oxirane oxygen 6.7%) was supplied from Kao

Corporation (Tokyo, Japan). Terpene-based acid anhydride (TPAn, Epikure YH306, neutralization equivalent 117 g/eq.) was supplied from Japan Epoxy Resins (Tokyo, Japan). Figure 2 shows ¹H NMR spectrum of TPAn in CDCl₃. The assignment of the ¹H signals for the afforded structure of TPAn is as follows: δ (ppm) 5.40 (bs, 1H, H-b), 5.03 (d, 1H, H-f), 3.40 (m, 1H, H-e), 3.2–3.0 (m, 2H, H-c,d), 2.59 (m, 1H, H-a), 1.8–1.7 (m, 9H, H-h, i, j), 1.30 (m, 3H, H-g). There were some ¹H signals, which can not be assigned, probably due to the presence of isomers. Maleinated linseed oil (LOAn, HIMALEIN LN-10, acid value 45.3 mg-KOH/g, iodine value 140 g-I₂/100 g) was supplied from Itoh Oil Chemicals (Yokkaichi, Mie, Japan). Thermally latent CPI (an aromatic sulfonium hexafluoroantimonate derivative, San-Aid SI-100) was supplied by Sanshin Chemical Industry (Yanagii, Yamaguchi, Japan). HPAn was purchased from New Japan Chemical (Osaka, Japan). Tetrabutyl phosphonium bromide (TBPB) was supplied from Hokko Chemical Industry (Tokyo, Japan). Lyocell fabric (SyLPH, 300 dtex, 600 dtex, 2/2 twill, thickness: ca. 0.35 mm) was received from Unitika Textile (Tokyo, Japan).

Preparation of ESOs cured with TPAn, LOAn, HPAn, and CPI

For ESOs cured with TPAn, LOAn, and HPAn, the feed molar ratio of epoxy/dicarboxylic acid anhydride and the final curing temperature were 1/1 and 150°C when no specification regarding the ratio and temperature are added. A typical curing procedure for ESO-TPAn is as follows: ESO (10.1 g, epoxy 42.3 mmol), TPAn (9.87 g, 42.3 mmol), and TBPB (0.10 g, 0.5 phr) were mixed and stirred for 1 h at 110°C. The obtained mixture was poured on a glass plate and cured at 150°C for 24 h to give ESO cured with TPAn (ESO-TPAn) as a pale brown sheet. The ESO-LOAn and ESO-HPAn were also prepared in a similar manner with ESO-TPAn. For the ESO cured with

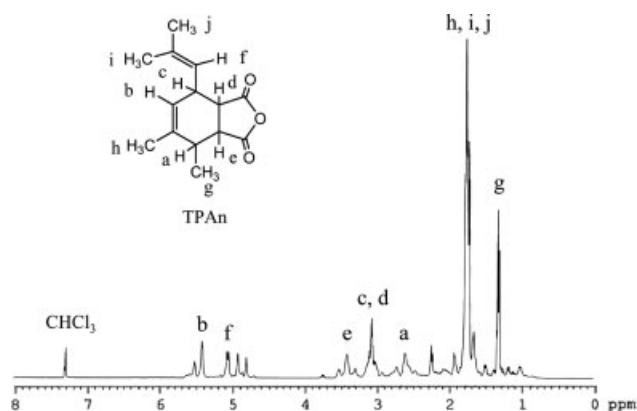


Figure 2 ¹H NMR spectrum of TPAn in CDCl₃.

TPAn, the effect of feed molar ratio of epoxy/anhydride (2/1, 1/1, and 1/2) and curing temperature (110, 130, and 150°C) were investigated.

ESO (20.0 g, epoxy 83.5 mmol) was mixed with a solution of CPI (0.20 g, 1 phr) in acetone (1 mL), and stirred for 1 h at 40°C. The obtained mixture was poured on a glass plate and cured at 60°C for 1 h to give ESO cured with CPI (ESO-CPI) as a pale brown sheet.

Preparation of ESO-TPAn/lyocell composites

ESO (15.2 g, epoxy 63.5 mmol), TPAn (14.8 g, 63.5 mmol), and TBPB (0.15 g, 0.5 phr) were mixed and stirred for 1 h at 110°C. In the mixture was impregnated a lyocell fabric (3.74 g, 100 mm × 120 mm × 0.35 mm), and pre-polymerized at 150°C for 1 h. The obtained prepreg was press-molded at 150°C for 1 h at a pressure of 3 MPa, and then post-cured at 150°C for 24 h in an electric oven to give ESO-TPAn/lyocell composite (7.53 g, 49.7 wt%). By changing weight ratio of ESO-TPAn and lyocell fabric, ESO-TPAn/lyocell composites with fiber content 25 and 75 wt% were also prepared in a similar manner. The thickness of the composite specimens with fiber content 25, 50, and 75 wt% was about 1.1, 0.6, and 0.4 mm, respectively. A mini test press (Toyo Seiki, Tokyo, Japan) was used to prepare all the composites.

Measurements

Proton nuclear magnetic resonance (¹H NMR) spectrum was recorded on a Bruker (Madison, WI) AV-400 (400 MHz) using CDCl₃ as a solvent. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu (Kyoto, Japan) FTIR 8100 by the KBr-pellet or attenuated total reflectance method. The differential scanning calorimetry (DSC) was performed on a Perkin-Elmer (Yokohama, Japan) DSC Pyris 1 DSC in a nitrogen atmosphere. An empty aluminum pan was used as reference. All the samples (ca. 10 mg) were heated to 150°C at a heating rate of 20°C/min, held at that temperature for 3 min, and then cooled to -150°C at a cooling rate of 100°C/min. After that, the second heating scans were monitored between -150 and 150°C at a heating rate of 20°C/min for determining glass transition temperature (T_g). Dynamic mechanical analysis (DMA) of rectangular specimen (30 × 5 × 2 mm³) was performed on a rheograph solid (Toyo Seiki, Tokyo, Japan) with a chuck distance of 20 mm. The DMA measurement was monitored from -100 to 100°C at a heating rate of 2°C/min and a frequency of 10 Hz. Tensile test of rectangular specimen (80 × 5 mm) was performed using an autograph AG-I (Shimadzu, Kyoto, Japan) equipped with a load cell of 5 kN capacity at 20°C. The thickness of the specimen was adjusted to 2.0 mm by filing with sandpaper for the cured ESOs, and was varied from 0.4 to 1.1 mm

according to the fiber content for ESO/TPAn/lyocell composites. Span length was 50 mm and the testing speed was 10 mm/min. Five composite specimens were tested for each set of samples, and the mean values and the standard deviation (σ) were calculated. Biodegradability of the cured neat resins was evaluated by measuring biochemical oxygen demand (BOD) under an aerobic condition in an activated sludge. To phosphate buffer (pH 7.4, 200 mL) containing 0.25 mM CaCl₂, 0.09 mM MgSO₄, 0.09 mM NH₄Cl, and 0.9 μ M FeCl₃ were added 3.13 mL of activated sludge containing 50 mg suspended part, which was obtained from sewerage facilities of Chiba Institute of Technology, and 20 mg of pulverized sample. The suspension was steadily stirred with a magnetic stir bar. BOD was measured at 25°C by using BOD tester 200F (Taitec, Koshigaya, Japan). Carbon dioxide was absorbed into a 50% sodium hydroxide aqueous concentrate in a cup equipped within the glass bottle. Volume of the consumed oxygen was directly measured using a scaled cylinder. The morphology of the composites was observed by scanning electron microscopy (SEM), using a JSM-840 machine (Japan Electron, Tokyo, Japan). The samples for the observation of matrix/fiber interface were prepared by fracturing the composites after immersion in liquid nitrogen for about 5 min. The surface of the sample was sputter coated with gold to provide enhanced conductivity.

RESULTS AND DISCUSSION

Investigation of curing condition of ESO and TPAn

The T_g of the ESO cured with TPAn at various feed molar ratios of epoxy/anhydride (2/1, 1/1, and 1/2) and curing temperatures (110, 130, 150°C) was measured by means of DSC to optimize the curing condition (Table I). The strict comparison of T_g values was carried out at the following section by means of DMA. When the curing temperature is changed at stoichiometric molar ratio of epoxy/dicarboxylic anhydride 1/1, the T_g of ESO-TPAn increased with increasing curing temperature. However, the T_g 's cured at 130°C and 150°C are not so different, suggesting the curing temperature of 150°C is almost full curing condition. The curing over 150°C resulted in a deep coloration of the materials due to some decomposition. Next, when the molar ratio of epoxy/anhydride was changed at curing temperature of 150°C, the ESO-TPAn cured at 1/1 had the highest T_g , suggesting that a relatively high crosslinking density is obtained due to the reaction of equimolar amounts of epoxy and dicarboxylic acid anhydride. The T_g of ESO-TPAn(1/2) was considerably higher than that of ESO-TPAn(2/1), while still lower than that of the 1/1 sample. In the following investiga-

TABLE I
 T_g Measured by DSC for the ESOs Cured with TPAn at Various Curing Conditions

Sample	Epoxy/ anhydride molar ratio	Curing temperature (°C)	T_g [DSC] (°C)
ESO-TPAn (110°C)	1.0/1.0	110	25.6
ESO-TPAn (130°C)	1.0/1.0	130	45.7
ESO-TPAn	1.0/1.0	150	48.4
ESO-TPAn (1/2)	1.0/2.0	150	39.6
ESO-TPAn (2/1)	2.0/1.0	150	-4.3

tion, the molar ratio of epoxy/anhydride and curing temperature in the epoxy-anhydride curing system were fixed at 1/1 and 150°C, respectively.

Characterization of the cured ESOs

Figure 3 shows the FTIR spectra of the ESOs cured with TPAn, LOAn, and HPAn at the feed molar ratio of epoxy/anhydride 1/1 (ESO-TPAn, ESO-LOAn, and ESO-HPAn) and the ESO cured with CPI (ESO-CPI). It is obvious that the epoxy ring absorption at 810 cm^{-1} observed for ESO is almost disappeared, and that the absorptions of dicarboxylic acid anhydride group at 1880–1850 and 1800–1780 cm^{-1} of TPAn, HPAn, and LOAn are disappeared and new absorption of C=O stretching of ester group at 1730 cm^{-1} appears for ESO-TPAn, ESO-LOAn, and ESO-HPAn. These results suggest that ester bonds are formed by the reaction of epoxy and dicarboxylic acid anhydride, as is shown in Figure 4. On the other hand, the epoxy ring absorption peak is little remaining for ESO-CPI, suggesting that a complete

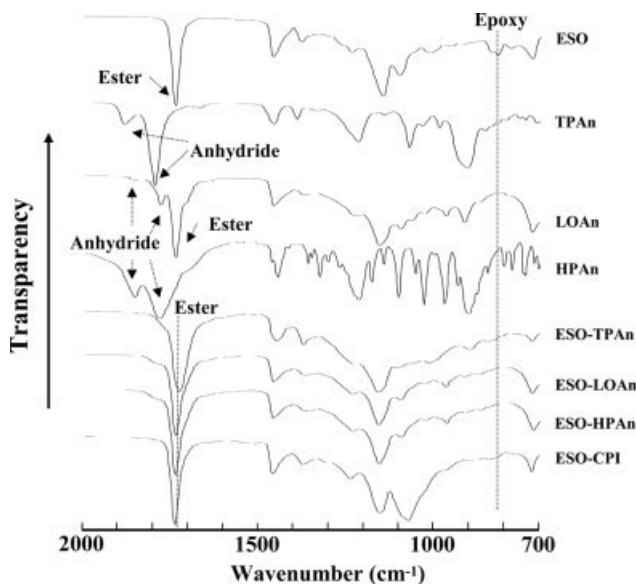


Figure 3 FTIR spectra of ESO, TPAn, LOAn, HPAn, ESO-TPAn, ESO-LOAn, ESO-HPAn, and ESO-CPI.

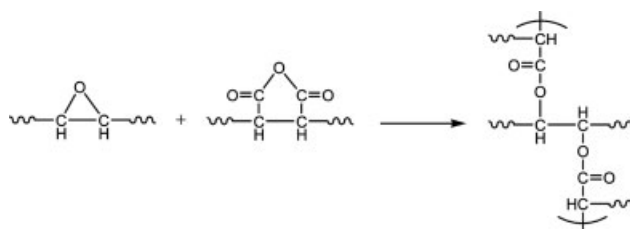


Figure 4 Curing reaction of epoxy and dicarboxylic acid anhydride.

conversion of the epoxy ring-opening homopolymerization is difficult probably due to steric hindrance.

Thermal and tensile properties of the cured ESOs

Figure 5 shows DMA charts of ESO-TPAn, ESO-LOAn, ESO-HPAn, and ESO-CPI. The $\tan \delta$ peak temperatures in the DMA charts corresponding to

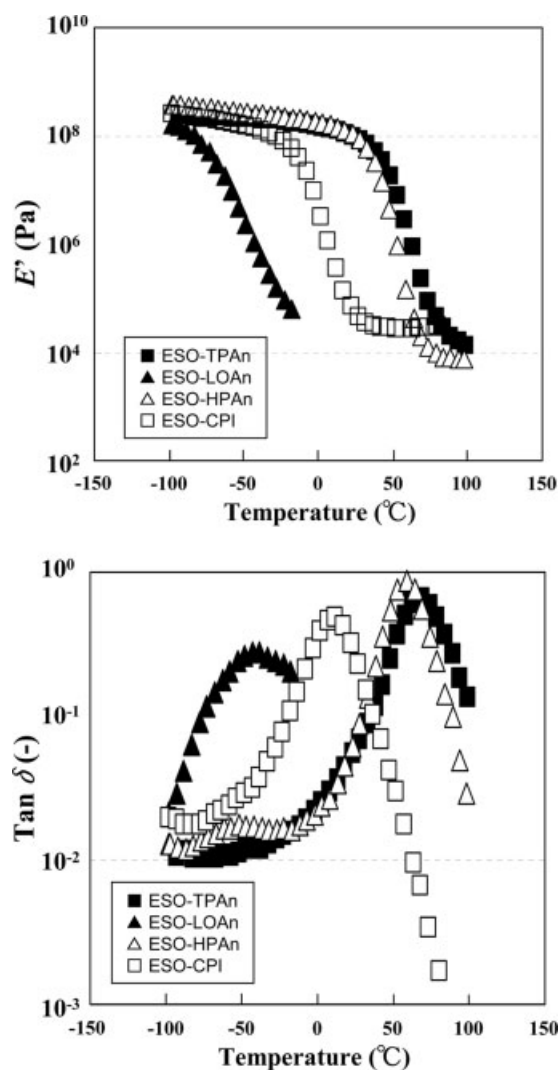


Figure 5 Dynamic viscoelastic curves of ESO-TPAn, ESO-LOAn, ESO-HPAn, and ESO-CPI.

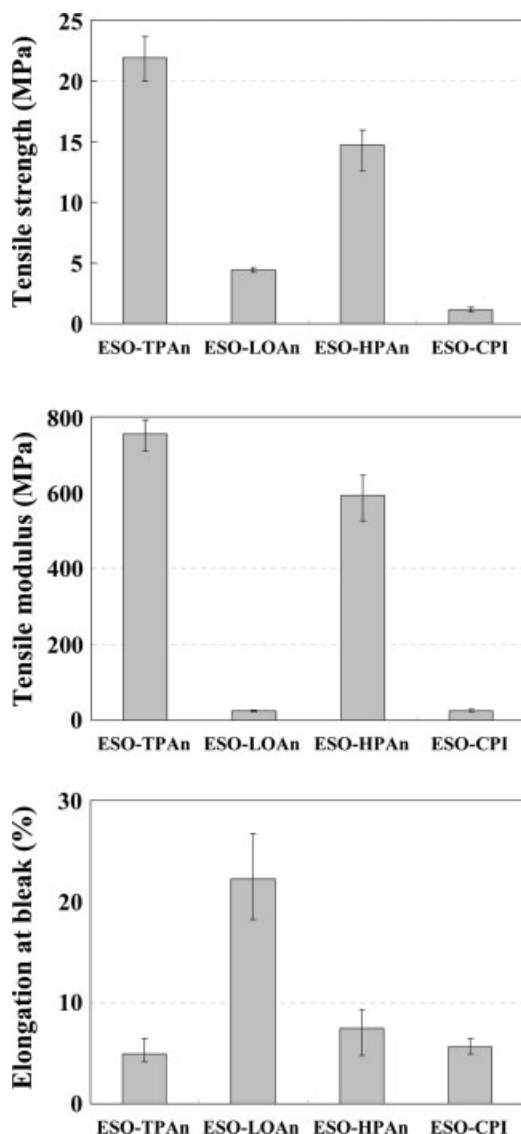


Figure 6 Tensile properties of ESO-TPAn, ESO-LOAn, ESO-HPAn, and ESO-CPI.

T_g 's for ESO-TPAn, ESO-HPAn, ESO-CPI, and ESO-LOAn were 67.2, 59.0, 10.0, and -41.0°C , respectively. The T_g of ESO-CPI was a reasonable value when compared with the reported value (6°C).¹¹ Also, T_g (DMA) of the ESO cured with MASO at the molar ratio of epoxy/anhydride 1/1 is reported to be 16°C .¹⁵ The higher T_g of ESO-TPAn and ESO-HPAn than ESO-LOAn and ESO-MASO is attributed to the fact that the anhydride content of TPAn and HPAn is much higher than LOAn. Because LOAn has a flexible linseed oil moiety as shown in Figure 1, the cured ESO-LOAn was a soft material at room temperature. What ESO-TPAn showed a higher T_g than ESO-HPAn should be related to the fact that the cyclohexene moiety of TPAn is substituted by a bulky isobutenyl group and two methyl groups. The storage modulus (E') at 20°C of ESO-TPAn was much higher than those of ESO-LOAn and ESO-CPI.

The E' of ESO-TPAn dropped at a little higher temperature region than that of ESO-HPAn.

Figure 6 shows the comparison of tensile properties at 20°C for ESO-TPAn, ESO-LOAn, ESO-HPAn, and ESO-CPI. The ESO-TPAn and ESO-HPAn had higher tensile strength and modulus than ESO-LOAn and ESO-CPI, because the former products are in glassy state, while the latter in rubbery state at 20°C . The reported tensile strength and modulus of the ESO-MASO are 3.7 and 15 MPa, which were comparable of those of ESO-LOAn (4.4 and 24 MPa).¹⁵ The ESO-TPAn showed a little higher tensile modulus and strength than ESO-HPAn. The ESO-LOAn showed much higher elongation at break, due to the effect of flexible linseed oil moiety of LOAn. What the elongation of ESO-CPI was as low as that of ESO-TPAn should be related to the fact that the distance between crosslinking points formed by the homopolymerization of the epoxy ring for ESO-CPI is very short, and the intermolecular interaction is relatively weak because of the formation of ether linkage.

Biodegradability of the cured ESOs

Figure 7 shows the biodegradability of the cured ESOs measured by BOD in an activated sludge. The biodegradation gradually took place for all the cured ESO samples. The biodegradability of ESO-LOAn reached higher than 20% after 1 month, which was much higher than those of ESO-TPAn, ESO-HPAn, and ESO-CPI ($\sim 10\%$). The high biodegradability of ESO-LOAn is related to the facts that both ESO and LOAn are natural plant oil-based materials, and that the hydrolysable ester bond is formed by the crosslinking reaction, and that the cured material with a low crosslinking density is in rubbery state at 25°C .

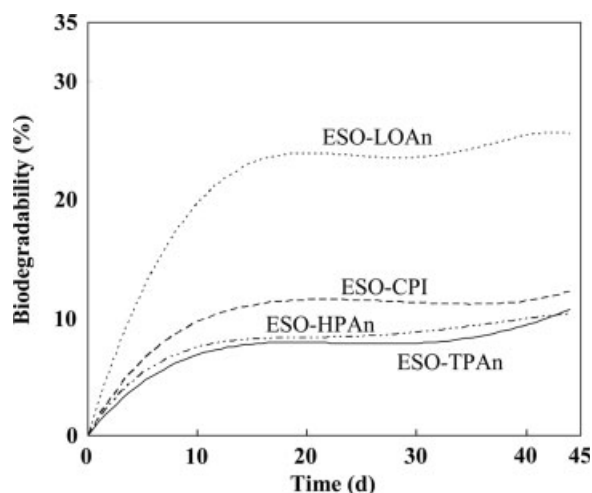


Figure 7 Biodegradability measured by BOD in an activated sludge of ESO-TPAn, ESO-LOAn, ESO-HPAn, and ESO-CPI.

Although ESO-CPI is in rubbery state at 25°C, alkyl-ene ether bond, which is resistant to hydrolysis is formed.

Morphology and tensile properties of ESO-TPAn/lyocell composites

Figure 8 shows the SEM photographs of the fractured surface of ESO-TPAn/lyocell composite with fiber content 50 wt %. It is obvious that the ESO/TPAn resin is fully impregnated between the lyocell fibers. The interfacial delamination between the resin phase and fibers was not appeared.

Figure 9 shows the tensile properties of the ESO-TPAn/lyocell composites. Tensile strength of the ESO-TPAn/lyocell composites increased with increasing fiber content, suggesting that the interfacial adhesiveness between ESO-TPAn and lyocell is good. Tensile moduli also increased with fiber content until 50 wt %. The tensile strength and modulus of ESO-TPAn/lyocell composite with lyocell content 75 wt % were 65 MPa and 2.3 GPa, which were three times higher than those of ESO-TPAn. The effect of fiber content on elongation at break of the composites was little, judging from a large error bar in case of fiber content 0 and 25 wt %. It is reported that the tensile strength, modulus, and elongation at break changed from 3.7 MPa, 15 MPa, 46% without fiber to 6.0 MPa, 33 MPa, 33% with fiber content 5 wt %, and 7.7 MPa, 95 MPa, 19% with fiber content 15% for the composites of ESO/MASO and short hemp fibers of about 2 mm length.¹⁵ In case of the composites used lyocell fabrics, it is noteworthy that significantly higher strength and modulus are attained when compared with the short hemp fiber compo-

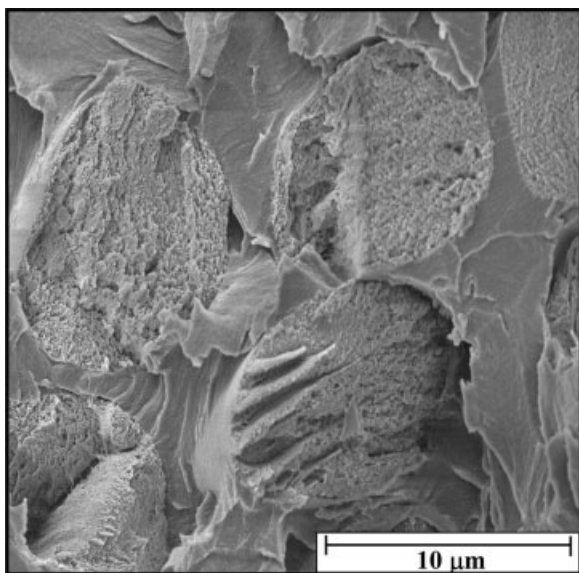


Figure 8 SEM photographs of the fractured surface of ESO-TPAn/lyocell composite with fiber content 50 wt %.

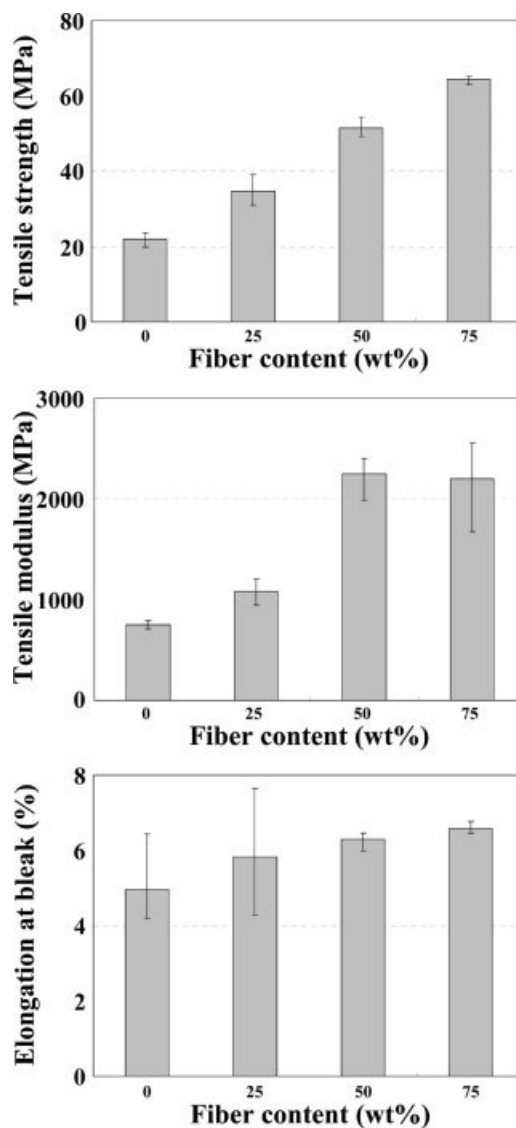


Figure 9 Tensile properties of ESO-TPAn/lyocell composites as a function of fiber content.

sites because the lyocell content can be increased to about 75%. What the elongation of the ESO/TPAn/lyocell composites did not decrease at least with an increase of fiber content should be related to the fact that lyocell fiber has a longer elongation than the other natural lignocellulosic fibers and that the incorporated fibers are fabrics.

CONCLUSION

Thermal and mechanical properties of ESO cured with TPAn were compared with those of ESO-HPAn, ESO-LOAn, and ESO-CPI. The ESO-TPAn showed higher T_g 's measured by DMA than ESO-HPAn, ESO-LOAn and ESO-CPI. The storage modulus at 20°C of ESO-TPAn was higher than those of ESO-LOAn and ESO-CPI. The ESO-TPAn showed the higher tensile strength and modulus than the

other cured ESOs. Also, ESO-TPAn possessed some biodegradability, which was lower than that of ESO-LOAn. The tensile strength of ESO-TPAn/lyocell biocomposites increased with increasing fiber content. The tensile strength and modulus of ESO-TPAn/lyocell composite with lyocell content 75 wt % were 65 MPa and 2.3 GPa, which were three times higher than those of ESO-TPAn. The biocomposites of ESO-TPAn and lyocell are expected to be used as structural materials, which can be completely incinerated or can be biodegraded.

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