High-performance Nanofiber-reinforeced Composite from All Bio-based Materials

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An all bio-based polymer composite consisting of poly(L-lactic acid) nanofibers and network polymers of epoxidized soybean oil has been developed. The mechanical properties improved as compared with those of each solo material, and the composite showed relatively good transparency.

Recently, there has been great interest in bio-based polymeric materials, since usage of bioresources as starting substrate of polymeric materials halts greenhouse warming and contributes to global sustainability without depletion of scarce fossil resources.[1] Poly(L-lactic acid) (PLLA) is a commercially available bio-based biodegradable polyester derived from inexpensive renewable resources such as corn and sugar beets.[2] At present, Nature Works produces PLLA by combination of bio and chemical processes using corn as a raw material. PLLA offers great promise in a wide range of commodity applications.

Natural oils are expected as an ideal alternative chemical feedstock, since oils, derived from both plant and animal sources, are found in abundance in the world.[3] They are mainly used in oleochemical industry for various applications. Inexpensive triglyceride plant oils have been used for production of valuable resins.[4] However, these oil polymer-based materials do not show enough properties of rigidity and strength required for structural applications by themselves; oils have been used as a toughening agent to produce interpenetrating networks.[5] Recently, we have developed plant oil-based polymeric nanocomposites by using epoxidized plant oils as a main monomer.[6]

Electrospinning is a convenient and straightforward process to fabricate nonwoven mats of ultrafine fibrous polymers.[7] The diameter of the electrospun fibers is often in the submicron range; in contrast, conventional polymer fibers are in the range of more than micron size in diameter. The small fiber diameter and nonwoven morphology give rise to large specific surface area, which is advantageous in filter and biomedical applications.[8] Very recently, we have fabricated nanofibrous nonwoven mats of gelatin/PLLA composites and applied them to scaffold of tissue engineering.[9]

This study deals with development of a nanofiber-reinforced, oil polymer-based composite. Development of composite materials using nanofibers and oil-polymers has advantages as follows: (a) Large specific surface area of nanofibers increases interaction between fibers and oil-polymers, resulting in effective improvements of the mechanical properties of the oil-polymers. (b) Lowering light scattering at the interface between fibers and oil-polymers by decrease in the diameter of the fibers leads to better transparency. (c) The material design of the present polymer composite derived from all bio-based raw materials will contribute to carbon cycle of materials globally.

In this study, the composite was prepared by the curing of epoxidized soybean oil (ESO) with a thermally latent acid catalyst in the presence of PLLA nanofiber mat,[10] which was fabricated by the electrospinning using 1,1,1,3,3,3-hexafluoro-2-isopropanol (HFIP) as a solvent.[11] Figure 1 shows a SEM image of the nanofiber mat. The diameter of the PLLA nanofiber was 600 ± 200 nm. The weight ratio of the ESO polymer and the PLLA nanofiber in the composite was 69:31.

Figure 2 shows strain–stress curves of the ESO polymer, the PLLA nanofiber mat, and the resulting composite. The tensile modulus and strength as well as the elongation at break of the composite were much superior to those of the ESO polymer. The tensile strength of the composite compares with that of polyethylene or soft-type poly(vinyl chloride). These results indicate the enormous improvement of the mechanical properties of the oil network polymer by the reinforcement with the nanoscaled fiber.

Dynamic viscoelasticity analysis was carried out as a function of temperature. Figure 3 shows traces of storage modulus (E') of the ESO polymer and the composite. In both traces, E' suddenly decreased around −25 °C, which is ascribed to the glass-transition temperature of the ESO polymer. Additionally, two large decreases of E' were observed in the composite; these are due to the glass-transition temperature (T_g) and melting point of PLLA around 57 and 166 °C, respectively, suggesting the phase separation of the ESO polymer and the PLLA nanofiber in the composite. It is to be noted that the E' value greatly increased to larger than 10^8 Pa in the rubbery region of the ESO polymer (below T_g of PLLA). These data strongly suggest

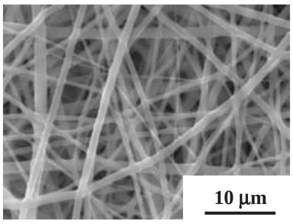

Figure 1. A SEM image of PLLA nanofiber mat.

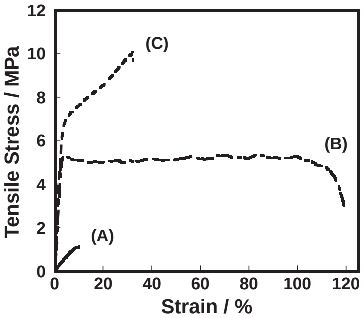

Figure 2. Strain–stress curves of (A) the ESO polymer, (B) the PLLA nanofiber mat, and (C) the ESO polymer–PLLA nanofiber composite.

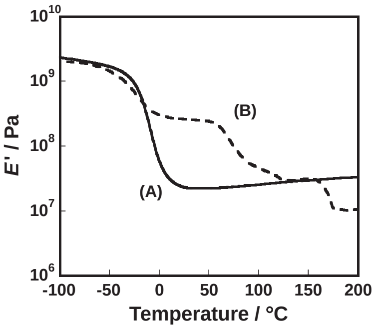

Figure 3. Dynamic viscoelasticity of (A) the ESO polymer, and (B) the ESO polymer–PLLA nanofiber composite.

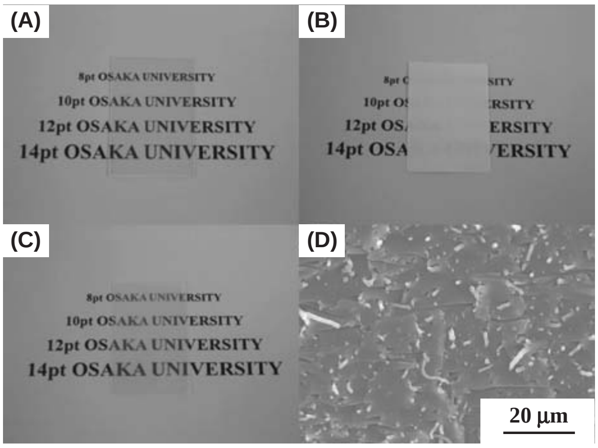

Figure 4. Photos of surface appearance of (A) the ESO polymer, (B) the PLLA nanofiber mat, and (C) the ESO polymer–PLLA nanofiber composite, and (D) cross section of the composite observed by SEM.

the large reinforcement effect by the PLLA nanofiber.

The photographs of the ESO polymer, the PLLA nanofiber mat, and the ESO polymer–PLLA nanofiber composite are shown in Figure 4. The transparency of the ESO polymer was very high because of its amorphous nature. Whereas the PLLA nanofiber mat was not transparent, the composite showed relatively good transparency. Figure 4D shows a SEM image of the cross section of the composite. It was shown that the PLLA nanofibers are well dispersed in the ESO polymer network. Taking account of that the difference in the refractive indices of PLLA and the ESO polymer is much smaller than that of PLLA and air, the high transparency of the composite is probably attributed to the good dispersion of the PLLA nanofiber in the oil-polymer matrix and the small light scattering at the surface of the fiber/ESO polymer interface.[12] Although the transmittance of the present composite is not high enough for practical applications, better transparency may be attained by using nanofibers with smaller diameters.

In conclusion, the high-performance composite of bio-based polymers derived from soybean and corn was fabricated by the curing of ESO in the presence of the PLLA nanofiber mat. The nanoscaled structural control greatly improved the mechanical properties of the oil network polymer, and the composite showed relatively good transparency. These characteristics are useful for various applications of bio-based commodity products. Furthermore, this study provides the material design of compounding bio-based polymers for development of high-performance nanomaterials, significantly contributing to global sustainability. Further investigations on development of bio-based polymer composites are under way in our laboratory.

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10 The PLLA mat (0.08 g) was impregnated with 3.96 g of ESO containing 0.04 g of a thermally latent catalyst (a benzylsulfonium hexafluoroantimonate derivative, SAN-AID SI-60L, Sanshin Chemical Industry Co.) under reduced pressure. The mixture was placed between Teflon sheets and subjected to hot pressing at 55 °C for 10 h, subsequently heating at 100 °C for 30 min. The weight ratio of the ESO polymer and PLLA fiber in the composite was calculated from the feed weight of the PLLA mat and the weight of the resulting composite.

11 A HFIP solution of PLLA (9 wt %) was placed in a 10-mL glass syringe with a 25-gauge needle, which was connected to a high-voltage generator. The glass syringe was horizontally mounted in a syring pump. The flow rate of the delivery system and the distance between the needle tip and the drum collector were fixed as 3 mL/h and 20 cm, respectively. A grounded rotating metal drum served as a counter electrode. A voltage of 17 kV was applied to the solution, and the jet emerging from the solution was collected on the drum.

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