

Green Nanocomposites from Renewable Resources: Plant Oil–Clay Hybrid Materials

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Worldwide potential demands for replacing petroleum-derived raw materials with renewable plant-based ones in production of valuable polymeric materials are quite significant from the social and environmental viewpoints.¹ Therefore, using inexpensive renewable resources has greatly attracted the attention of many researchers. Among them, natural oils are expected to be an ideal alternative chemical feedstock since oils, derived from both plant and animal sources, are found in abundance in the world. Triglyceride oils have been extensively used for various applications such as coatings, inks, and agrochemicals.² These oil-based polymeric materials, however, do not show properties of rigidity and strength required for structural applications by themselves. In some cases, therefore, triglyceride was a minor component in polymeric materials; this is used solely as a modifier to improve their physical properties.

Recently, there has been enormous interest in organic–inorganic nanocomposites due to their unexpected hybrid properties derived from unique combinations of each component.³ Among them, nanocomposites of organic polymers and inorganic clay minerals consisting of layered structure have been extensively studied for the past decade.^{4,5} They often exhibited improved tensile strength and moduli, reduced gas permeability, decreased thermal expansion coefficient, and enhanced thermal stability when compared with the pure polymers or conventional micro- and macrocomposites. The

enhanced properties are presumably derived from the nanoscale structure. Montmorillonite is of particular interest since it has the high aspect ratio of silicate nanolayers and the high surface area, which are suitable for reinforcement purposes. So far, a variety of polymer–montmorillonite clay nanocomposites have been prepared for thermoplastic and thermoset polymers.⁵ Recently, nanocomposites from biodegradable polyesters and clay have been greatly developed.⁶

This study deals with synthesis of *green nanocomposites* consisting of the abundant natural resources, plant oils and clay. An epoxidized triglyceride oil was subjected to intercalation into an organically modified clay, followed by an acid-catalyzed curing of the epoxy-containing triglyceride, leading to production of a new class of biodegradable nanocomposites from inexpensive renewable resources. To the best of our knowledge, this is the first example of the preparation of green clay nanocomposites from plant oil derivatives. Relevant to this study, fabrication of glass fiber-reinforced composites from epoxidized vegetable oils was reported.⁷

In this study, epoxidized soybean oil (ESO, provided by Kao Co., Japan) was mainly used as an organic monomer. The epoxide number per molecule, determined by ¹H NMR, was 3.4. The nanocomposite was synthesized by the curing of ESO using thermally latent cationic catalyst (a benzylsulfonium hexafluoroantimonate derivative, Sun Aid SI-60L, provided by Sanshin Chemical Industry Co., Japan) in the presence of octadecyl-modified montmorillonite⁸ (OMM) at 150 °C.⁹ During the thermal treatment, the cross-linking of the epoxy group took place, yielding an insoluble polymer network. Figure 1 shows wide-angle X-ray diffraction (WAXD) patterns of OMM and nanocomposites with clay contents of 5, 10, 15, and 20%. The mean interlayer spacing of the (001) plane (*d*₀₀₁) for OMM is 19 Å (2θ = 4.7°). In the case of the nanocomposite with a clay

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(8) Montmorillonite (Kunipia-F) was purchased from Kunimine Co. and OMM was synthesized according to the literature.¹³ The composition of montmorillonite is (Na, K, Ca)_{0.33}(Al_{1.67}Mg_{0.33})Si₄O₁₀(OH)₂·*n*H₂O and the introduced ratio of the octadecyl group into montmorillonite was 30%, determined by TG.

(9) The following is a typical procedure for the preparation of the nanocomposite (hybrid with a clay content of 5%). OMM (0.20 g) was dispersed in 10 mL of chloroform under gentle stirring. To this solution, ESO (2.7 g) and thermally latent catalyst (40 μL) were added; then the obtained mixture was poured into a Teflon mold (40 × 17 × 3 mm). The mixture was kept at 40 °C for 1 h to remove the solvent and subsequently heated at 150 °C for 2 h.

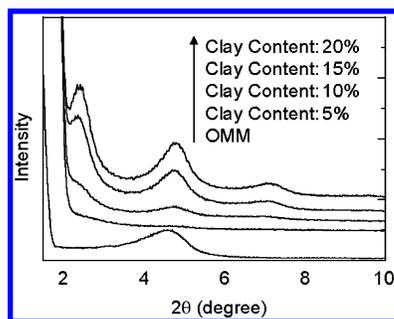


Figure 1. WAXD patterns of octadecyl-modified clay and ESO-clay nanocomposites with clay contents of 5, 10, 15, and 20%.

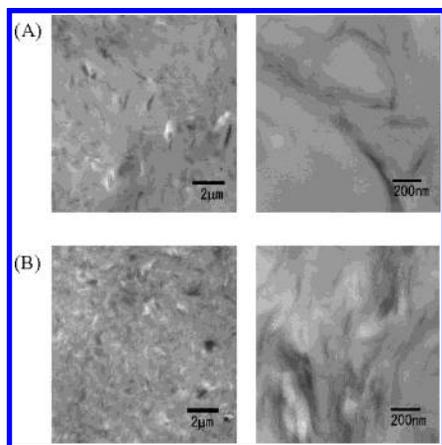


Figure 2. TEM micrographs of ESO-clay nanocomposites with clay contents of (A) 5% and (B) 15%.

content of 5%, coherent order of OMM was completely destroyed, suggesting that silicate layers of OMM may be exfoliated. In using more than 10% OMM, a new peak was observed at $2\theta = 2.4^\circ$, accompanied by the appearance of a peak at $2\theta = 4.7^\circ$. From the former data, the interlayer distance was found to be shifted to 37 Å, indicating the formation of an intercalated structure. The latter may be due to the (002) plane (d_{002}) of the silicate layers dispersed in the polymer matrix. These peaks increased as a function of the clay content.

Figure 2 shows transmission electron microscopy (TEM) images of the nanocomposites with clay contents of 5 and 15% in which irregular dispersions of the silicate layers were found. Some particles of the silicate layer maintained their original ordering, whereas some were exfoliated. The stacked silicate layers were observed randomly in the polymer matrix. In the nanocomposite with a clay content of 5%, the aggregation thickness slightly decreased, as compared with that of 15%.

Storage modulus (E'), loss modulus (E''), and dissipation factor ($\tan \delta$) of the nanocomposite with a clay content of 10% as a function of temperature are shown in Figure 3. The glass transition temperature (T_g) of the nanocomposite was observed at 2 °C. The smooth trace of $\tan \delta$ means the homogeneous structure of the present nanocomposite. In the region of high temperature, E' was almost constant, suggesting that the epoxy group of ESO scarcely remained unreacted in the measured sample. Above the T_g , E' of the nanocomposite increased as a function of the clay content (see Supporting Information), which is due to mechanical rein-

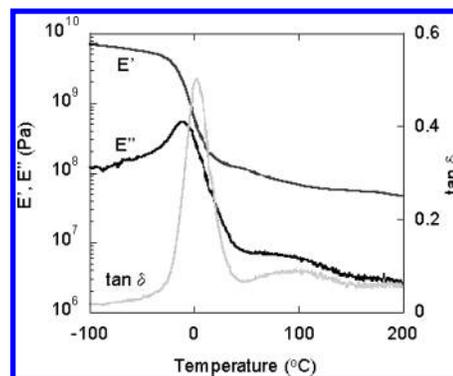


Figure 3. Dynamic viscoelasticity of ESO-clay nanocomposite with a clay content of 10%.

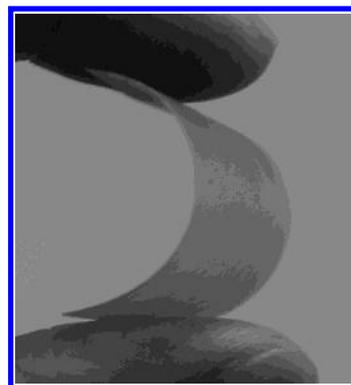


Figure 4. Photograph of ESO-clay nanocomposite showing high flexibility.

forcement by clay particles.¹⁰ T_g of the nanocomposite also increased from -2 to 4 °C with increasing clay content from 5% to 15% (see Supporting Information), which may be due to a decrease in mobility of the cross-linked polymer chain by silicate layers. This behavior is characteristic of the present ESO-clay nanocomposite; an increase in T_g was not often observed in the nanocomposite formation of polymers with clay.¹¹

Thermal stability of the present nanocomposite was evaluated by thermogravimetry (TG) under nitrogen. In the nanocomposite with a clay content of 5%, the temperature at 5 wt % loss was 278 °C (see Supporting Information), suggesting relatively high thermal stability. It is to be noted that a flexible nanocomposite film with good mechanical strength was formed by using the organophilic clay as an inorganic component (Figure 4). On the other hand, only a very soft film was obtained without the clay, which does not seem suitable for structural applications. This characteristic property may be derived from a decrease in cross-linking density of the ESO polymer by dispersion of silicate layers and from reinforcement with clay particles.

Similarly, an epoxidized linseed oil (ELO)-clay nanocomposite was synthesized. The WAXD pattern of this nanocomposite was very similar to that of the ESO-

(10) Under the reaction conditions to produce the present nanocomposite, a cured film solely from ESO for measurement of dynamic viscoelasticity was not obtained.

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clay hybrid. In the dynamic viscoelasticity measurement, E' of the ELO–clay nanocomposite was larger than that of the ESO–clay in the temperature range from 50 to 200 °C. This is probably due to the higher content of the reactive epoxy group in ELO with the epoxide number of 5.5, resulting in the higher cross-linking density of the ELO polymer.

In conclusion, *green nanocomposites* have been developed by an acid-catalyzed curing of epoxidized plant oils in the presence of organophilic clay. The nanocomposite with the homogeneous structure of organic and inorganic components was obtained, in which silicate layers of the clay were intercalated and randomly distributed in the polymer matrix. The reinforcement effect by the addition of the clay was confirmed by dynamic viscoelasticity analysis. Furthermore, the nanocomposite exhibited flexible property. We preliminarily found good biodegradability of the cured polymer from ESO;¹² thus, the present nanocomposites are highly expected to be a new class of biodegradable plastics and coating materials from inexpensive renewable resources, con-

tributing to global sustainability. Further investigations on green nanocomposites from plant oils are underway in our laboratory.

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Supporting Information Available: Figures showing the effect of clay content of ESO–clay nanocomposite on storage modulus, relationships between clay content and T_g of nanocomposite, and TG trace of ESO–clay nanocomposite with a clay content of 5% (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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