New Bio-based Polymeric Materials from Plant Oils

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Introduction

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. Using such plant-based raw materials contributes to global sustainability without depletion of scarce resources. This study deals with development of new bio-based composite materials from epoxidized plant oils.

Plant Oil-Clay Nanocomposites

Recently, nanocomposites between organic polymers and inorganic compounds have attracted considerable interests since they often show unexpected hybrid properties synergistically derived from the two components.

In this study, epoxidized soybean oil (ESO) was mainly used as an organic monomer. The nanocomposite was synthesized by the curing of ESO using thermally-latent cationic catalyst in the presence of octadecyl-modified montmorillonite (OMM) at 150 °C.[1,2] Figure 1 shows wide X-ray diffraction patterns of OMM and nanocomposites with the clay content of 5, 10, 15, and 20 weight %. The mean interlayer spacing of the (001) plane for OMM is 19 Å (2θ=4.7°). In case of the nanocomposite, the interlayer distance was 37 Å (2θ=2.4°), suggesting the formation of an intercalated structure. This peak increased as a function of the clay content.

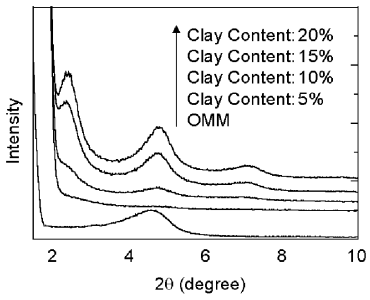

Figure 1. WAXD patterns of ESO-clay nanocomposites with different content of OMM.

TEM micrograph of the nanocomposite with the clay content of 5 % is shown in Figure 2, which clearly indicates that the stacks of OMM layers forming clay crystallines were dispersed in the polymer matrix. The resulting nanocomposite showed good flexible property.

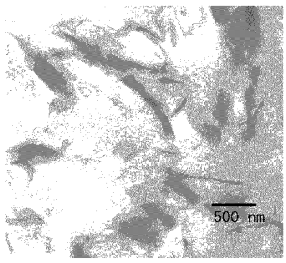

Figure 2. TEM microphoto of ESO-clay nanocomposite with clay content of 5%.

Storage modulus (E'), loss modulus (E"), and dissipation factor (tan δ) of the nanocomposite with the clay content of 10 % as a function of temperature are shown in Figure 3. The glass transition temperature (Tg) of the nanocomposite was observed at 2 °C. The smooth trace of tan δ means the homogeneous structure of the present nanocomposites. In the region of high temperature, E' was almost constant, suggesting that the epoxy group scarcely remained unreacted in the measured sample. Above Tg, E' of the nanocomposite increased as a function of the clay content, which is due to mechanical reinforcement by clay particles.

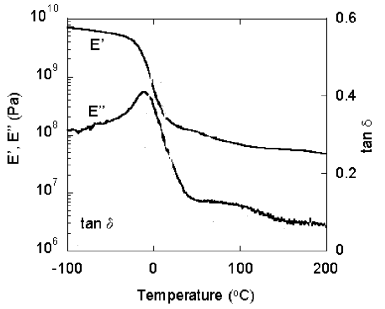

Figure 3. Dynamic viscoelasticity of ESO-clay nanocomposite with clay content of 10 %.

Plant Oil-Silica Nanocomposites

Organic-inorganic hybrid coatings (ceramers) involving sol-gel process have been developed. In this study, the acid-catalyzed curing of ESO and 3-glycidyloxypropyltrimethoxysilane (**1**) was carried out at 140 °C to produce a new class of biodegradable nanocomposites.[3] In this curing, the epoxy group of both monomers was reacted to give an organic crosslinked polymer, and the trimethoxysilyl group was hydrolyzed by the same catalyst, yielding an inorganic component.

Dynamic viscoelasticity analysis showed that Tg of the ESO-silica nanocomposite with content of **1** = 20 % was 19 °C, which was larger than that obtained by the curing of ESO without **1** (6 °C). The homogeneous nanostructure of the composite was confirmed by the smooth tan δ trace. Constant storage modulus above Tg indicates that the curing completely took place under the present reaction conditions.

Biodegradability of the ESO-silica nanocomposite with content of **1** = 20 % was evaluated by BOD measurement in an activated sludge. The degradation gradually took place and the biodegradability reached 50% after 50 days, indicating the good biodegradability of the present nanocomposite.

The coating of the ESO-silica nanocomposites was prepared using a film applicator with slit thickness of 50 μm on a glass plate. Universal hardness increased as a function of the content of **1** and the pencil scratch hardness reached 2H in the sample with the content of **1** = 20 %, indicating that the present nanocomposite film showed high hardness enough for practical use.

Plant Oil-Aliphatic Polyester Composites

The curing of ESO in the presence of poly(caprolactone) (PCL) produced the composite material with semi-IPN structure; the DSC and dynamic viscoelasticity analyses showed the good miscibility between the ESO polymer and poly(caprolactone). The tensile modulus and stress as well as the elongation at break of the composite were much superior to those of the ESO polymer.

Conclusion

Novel bio-based composite materials from plant oils have been developed. The curing of ESO in the presence of OMM produced an organic-inorganic hybrid with homogeneous structure. The reaction of ESO and **1** gave nanocomposite coatings with high hardness. The ESO-PCL composite showed good mechanical properties.

Natural oils are found in abundance in all over the world, making them an ideal alternative chemical feedstock. Therefore, the present study is highly significant as fundamental research for production of a new class of bio-based polymers from renewable oils, contributing sustainable development in the new century.

References

[1] Uyama, H.; Kuwabara, M.; Tsujimoto, T.; Nakano, M.; Usuki, A.; Kobayashi, S. *Chem. Mater.* **2003**, *15*, 2492.
[2] Uyama, H.; Kuwabara, M.; Tsujimoto, T.; Nakano, M.; Usuki, A.; Kobayashi, S. Macromol. Biosci. **2004**, *4*, 354.
[3] Tsujimoto, T.; Uyama, H.; Kobayashi, S. *Macromol. Rapid Commun.* **2003**, *24*, 711.