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Synthesis of Allylester Resin Tethered to Layered Silicates by *in-situ* Polymerization and Its Nanocomposite

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Summary

Allylester resin tethered to layered silicate was synthesized by *in-situ* polymerization method and was cured by *tert*-butylperbenzoate (TBPB) directly. We ascertained the existing of carbonyl and benzyl groups which come from diallyl terephtalate in the gallery of layered silicates using the thermogravimetric analysis (TGA) and FT-IR. The residual weight and new IR peaks of the clay, which is treated by *in-situ* polymerization, imply that the hydroxy group of intercalant takes part in the polymerization of allylester resin. Also, its nanocomposite was characterized by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD patterns and TEM photographs indicate that the basal spacing (d_{001}) of the nanocomposite made by *in-situ* polymerization is larger than those of the nanocomposite made by a simple mixing.

Introduction

Recently, polymer-layered silicate nanocomposites have stimulated great interest in many researchers due to their unexpected hybrid properties derived from the unique combination of each component. Experimental work on these materials has generally shown that virtually all types and classes of polymer-layered silicate nanocomposites lead to new and improved properties when compared to their micro- and macrocomposite counterparts and the pristine polymer matrix. The unprecedented mechanical properties of polymer-layered silicate nanocomposites were first demonstrated by a group at the Toyota research center in Japan using nylon nanocomposites.[1] Since then, many polymer-layered silicate nanocomposites have been synthesized, including those with the polymers, poly(β-caprolactone),[2] polyacrylonitrile,[3] polyaniline,[4] polypyrrole,[5] polyimide,[6] polystyrene,[7-9] nylon,[10] polypropylene,[11,12] poly(ethylene oxide),[13, 14, 15] poly(p-phenylenevinylene),[16] poly(butyleneterephalate)[17] and epoxy.[18]

In order to obtain polymer-layered silicate nanocomposites, several approaches were employed: solution intercalation, *in-situ* intercalative polymerization, polymer melt intercalation, and template synthesis.[19] Among them, the melt intercalation and *in-situ* intercalative polymerization are the two most common ways of preparing polymer-layered silicate nanocomposites. Significant property enhancements are often observed for exfoliated polymer nanocomposites. However, complete and homogeneous dispersion of individual silicate layers has been achieved in a few cases only, and there are still no general applicable guidelines as to the optimum polymer-layered silicate combination. Consequently, in polymer nanocomposites, synthesis is currently a tedious trial-and-error process.

Since allylester resin has many advantages, including a range of mechanical properties, long shelf-life, dimension stability, and thermal stability, it can be widely used in applications such as optical materials, building materials, artificial marble, and wire board.[20,21] However, there is no effort to improve its properties by preparing nanocomposite.

In this work, we have focused on synthesis of allylester resin tethered to layered silicate by *in-situ* polymerization. In this step, our concept is that hydroxy group of intercalant is able to take part in the transesterification reaction that is occurred during the polymerization of allylester resin.[22-25]

Experimental

Materials

Diallyl terephthalate used in this work was obtained from Daiso, Japan. 1,3-Butanediol and Monobutyltin oxiede (MBO) were purchased from Junsei Chemical and TCI, respectively. TBPB as initiator was purchased from Aldrich. Organically modified layered silicate (OLS) utilized in this study was bis(2-hydroxy-ethyl)methyl tallow ammonium montmorillonite (Cloisite 30B, Southern Clay Products, Inc.).

Synthesis and curing of allyester resin containing OLS

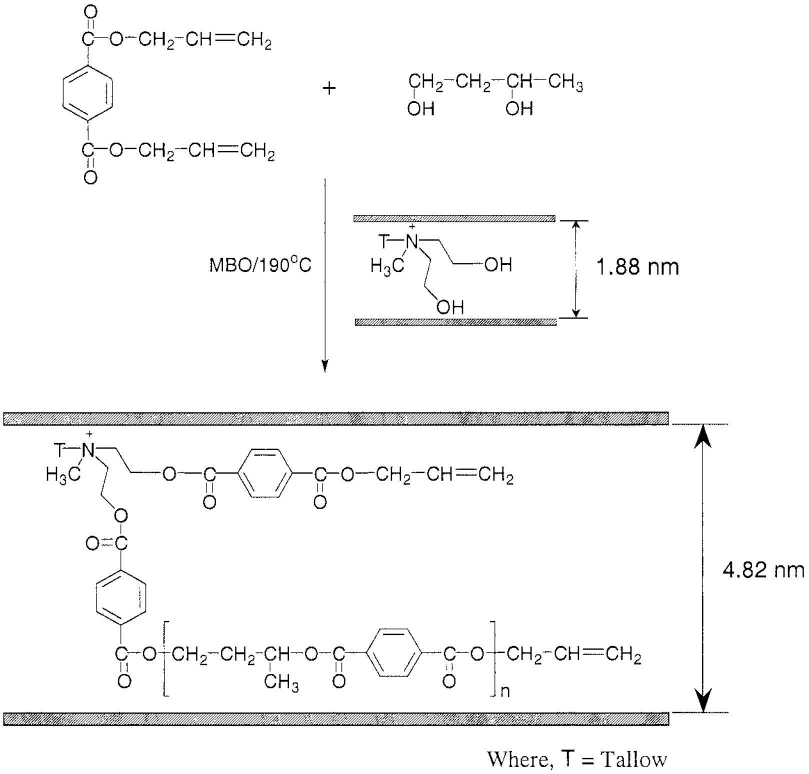
Diallyl terephthalate (76.35 g; 0.310 mol) and 1,3-Butanediol (33.25 g; 0.375 mol) were poured into a three-neck round flask equipped with a dean-stark trap and than Cloisite 30B (7.64 g) was gradually added. The mixture was stirred in a round flask at 60 °C for 4 hours in order to swell the OLS. Catalyst (MBO) (0.076 g) was added and the mixture was stirred at 190 °C for 5 hours under nitrogen atmosphere. After the end of reaction, the unreacted diol and remained allylalcohol were removed under vacuum. In order to make cured allylester nanocomposite, allylester resin and TBPB (3 phr) were mixed and stirred homogeneously at room temperature. The mixture was poured into a vial and cured for 10 hours at 90 °C and for 12 hours at 140 °C (post-curing) in the convection oven. Finally the cured nanocomposite was allowed to cool to room temperature.

Characterization and measurements

FT-IR spectra were recorded on a Nicolet Magna-550 FT-IR spectrometer. The X-ray diffraction patterns of the samples were determined by a wide angle X-ray diffractometer (MAC Science Co., Ltd.; M18XHF^{22}-SRA) using CuKα radiation under 100 kV, 50 mA. Ultrathin sections of nanocomposite with a thickness of approximately 50 nm were prepared with an ultramicrotome (Leica Reichert; Ultracut S/FC S) equipped with a diamond knife. The nanocomposite structure was observed using a transmission electron microscopy (JEOL; JEM-1200EXII) at an acceleration voltage of 120 kV. TGA was performed with a Mettler Toledo model TG 50 thermal analysis system. The TGA scans were recorded at 20 °C/min under a nitrogen atmosphere from room temperature to 600 °C. All samples were dried in a vacuum oven for 3 days at 60 °C.

Results and Discussion

Our initial approach to a general preparation of dispersed silicate nanocomposites focuses on the synthesis of an allylester prepolymer, which is tethered to the surface of layered silicates (Scheme 1). Our hope is that, as the transesterification reaction inside the galleries progresses, the silicate layers will be pushed gradually apart, leading to intercalated or exfoliated nanocomposite. In order to confirm whether the transesterification reaction occurs on the surface of OLS, we separated only the pure OLS portion from allylester resin, which was made by *in-situ* polymerization with clay using soxhlet extraction apparatus by chloroform as solvent.



Scheme 1. Synthetic sequence for the preparation of allylester resin tethered with layered silicate

Figure 1 shows the FT-IR spectrum of Closite 30B, extracted OLS, and allylester resin without clay. As shown in Figure 1 (B), the new bands at 1720 (–C=O stretching), 1276 (aromatic ring stretching), and 730 cm^{-1} (out-of-plane C-H bending in the aromatic ring) were observed in the spectrum of the extracted OLS. We suspect that these new peaks may indicate formation of allylester group in the intercalant. Additional evidence for transesterification reaction on the surface of clay is provided by the weight loss in the TG thermograms of the extracted OLS and Closite 30B as illustrated in Figure 2. As shown in Figure 2, there was no difference of degradation curve shape for both. However, we observed that the degradation of extracted OLS commences at a higher temperature than that of the Closite 30B. The degradation temperature at 95% weight loss for Closite 30B is 243 °C whereas that of extracted OLS is 270 °C. These results are believed to be due to having a rigid aromatic ring in intercalant. In addition, the silicate content of extracted OLS was found to be 72.6 wt.-% and that of Closite 30B was 82.3 wt.-% at 500 °C, respectively. This weight difference (ca. 9.7 wt.-%) occurred by increasing the intercalant weight due to transesterification with diallyl monomers. From the FTIR and TG data, we assert that the transesterification reaction occurred on the surface of Closite 30B successfully during the polymerization of allylester resin.

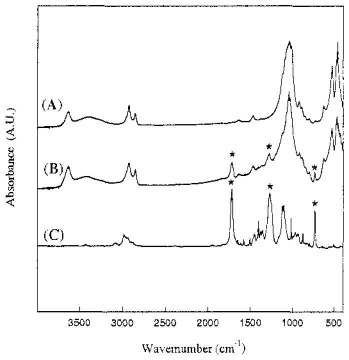


Figure 1. FT-IR spectrum of (A) Closite 30B; (B) extracted OLS; (C) pure allylester resin.

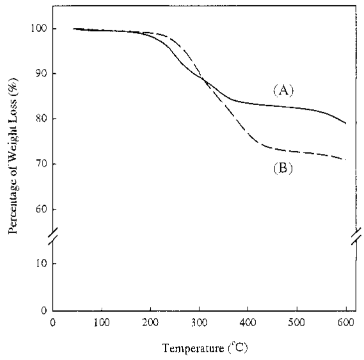


Figure 2. TG thermogram of (A) Closite 30B; Extracted OLS.

The X-ray diffraction patterns for the low 2θ values, where the basal reflection of the interlayer *d* spacing appears, are shown in Figure 3 for two nanocomposite samples formed under different preparation method (i.e., one is made by *in-situ* polymerization method and the other is made by simple mixing with allylester resin and Closite 30B). There is a definite intercalated structure, for all the different methods that we tried, manifesting itself through an interlayer *d*-spacing increase of about 2~3 nm compared to that of the Cloisite 30B (2θ = 4.73 ° ; 1.88 nm). However, allylester-clay nanocomposite made by *in-situ* polymerization has increased the extent of intercalation, as the XRD data show that the shoulder at ca. 2.34 ° (3.77 nm; Figure 3(A)) was shifted to 1.83 °(4.82 nm; Figure 3(B)). Transmission electron microscopy (TEM) was performed to examine morphology development of nanocomposite.

Figure 4 (A) is the TEM micrograph of the nanocomposite prepared by simple mixing with Closite 30B clay. The dark lines are the clay layers perpendicular to the sample surface. Large clay aggregates (tactoids) are visible, although the inter layer spacing is expanded. On the other hand, the nanocomposite prepared by *in-site* polymerization shows a better clay dispersion. (Figure 4 (B)) while the individual clay layer is visible, small aggregates can still be observed.

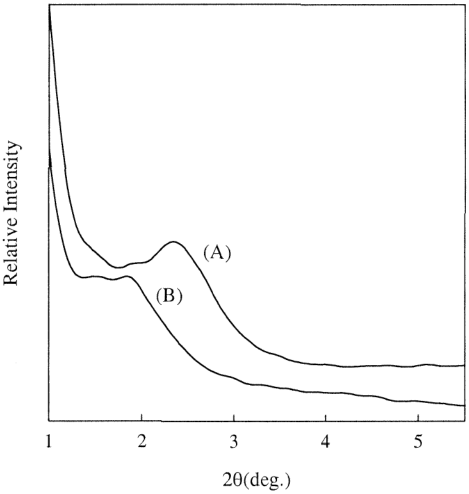


Figure 3. XRD patterns of allylester-clay nanocomposites prepared by different methods: (A) Simple mixing (B) *in-situ* polymerization.

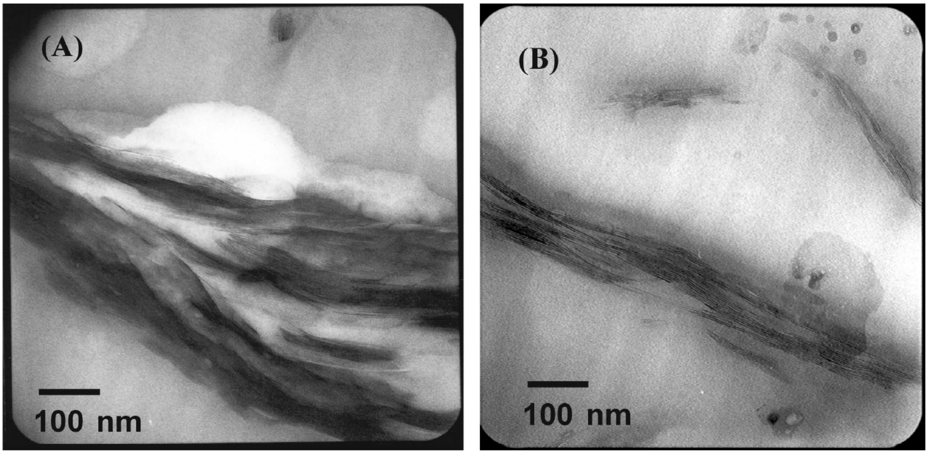


Figure 4. TEM photographs of allylester-clay nanocomposites prepared by different methods: (A) Simple mixing (B) *in-situ* polymerization.

Conclusions

We have compared *in-situ* polymerization method with simple mixing method to synthesize allylester-clay nanocomposite. We have ascertained that hydroxy group of intercalant takes part in transesterification reaction during *in-situ* polymerization of allylester resin. Also, the using *in-situ* polymerization leads to better clay layers separation and a more disordered intercalated allylester-clay nanocomposite. This is a result of the favorable transesterification reaction of the clay surface with diallyl terephthalate monomer.

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