

Interface control in polymer/clay nanocomposites

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ABSTRACT

In order to suppress a repulsive interfacial energy between hydrophilic clay and hydrophobic polymer matrix in preparing a polymer/clay nanocomposite, a third component of amphiphilic nature such as poly(ϵ -caprolactone) (PCL) was introduced into the model system of styrene-acrylonitrile copolymers (SAN)/Na-montmorillonite. Once ϵ -caprolactone was polymerized in the presence of Na-montmorillonite, the successful ring-opening polymerization of ϵ -caprolactone and the well-developed exfoliated structure of PCL/Na-montmorillonite mixture were confirmed. Thereafter, SAN was melt-mixed with PCL/Na-montmorillonite nanocomposite, which resulted in that SAN matrix and PCL fraction were completely miscible to form homogeneous mixture with retention of the exfoliated state of Na-montmorillonite, exhibiting that PCL effectively stabilizes the repulsive polymer/clay interface and contributes the improvement of mechanical properties of the nanocomposites.

Key words : nanocomposite, interface control, compatibilization, clay

INTRODUCTION

In the polymer composites, inorganic materials have been used to reinforce polymers with the advantage of the high heat durability and the high mechanical strength of inorganic materials. The interfacial incompatibility between inorganic fillers of hydrophilic nature and hydrophobic polymers exists owing to the difference in the nature of their individual intermolecular interaction and often caused failures in the inorganic/organic composites. Aiming to fabricate inorganic/organic nanocomposites generating many exciting new materials with novel properties that cannot be obtained simply by co-mixing the polymeric component with the inorganic component, the requirement for the

interface control becomes much more challenging [1-5]. For the field of polymer-clay nanocomposites, though the academic interest as well as the industrial concern on it has been rapidly expanding, it has been little known how much the critical control of interface should be given to obtain perfect nanoscale distribution of inorganic phase within the polymer matrix.

In the previous reports [6, 7], we showed that the melt intercalation of montmorillonite with styrene-acrylonitrile copolymers (SAN) could not extend to complete exfoliation due to the gluing effect of polymer. Since poly(ϵ -caprolactone) (PCL) is capable of forming a homogeneous mixture with SAN and PCL-montmorillonite mixture shows a complete exfoliation as well [8-11], PCL was introduced

to the SAN/Na-montmorillonite system for the purpose of suppression of the repulsive interfacial energy between inorganic clay and polymer matrix and thus to obtain the homogeneous distribution of silicate layers of montmorillonite with nanometer scale.

EXPERIMENTAL

Materials. SAN (AN content = 24.2 wt%, $T_g = 109\text{ }^\circ\text{C}$, $M_w = 1.4 \times 10^5\text{ g/mol}$) [25] was kindly supplied by Che-Il Industries of Korea, and used as received. ϵ -caprolactone (CL, Aldrich) was dried with NaH and distilled off with reduced pressure. Na-montmorillonite used was Kunifia-F (cation exchange capacity, CEC = 120 meq/100 g) provided by Kunimine.

Synthesis of PCL/clay nanocomposite. The PCL/Na-montmorillonite nanocomposite was synthesized by stirring 1 g of Na-montmorillonite with 15 g of CL at $170\text{ }^\circ\text{C}$ for 12 h under N_2 atmosphere. Upon cooling to room temperature, the reaction mixture solidified. In order to measure the extent of polymerization of CL and reduce the PCL content as high as possible without destruction of exfoliated state of nanocomposite, extraction of the PCL fraction was conducted by dissolution of the solidified product in THF and centrifugation at 2000 rpm for 10 min. After decanting the supernatant, the precipitant by centrifugation was collected, washed with *n*-hexane and dried *in vacuo* at room temperature. The supernatant was poured into *n*-hexane for precipitation of the extracted organic component. The resulting white solid was filtered, washed with additional *n*-hexane and dried *in vacuo* at room temperature for the characterization.

Melt blending. To obtain SAN/PCL/Na-

montmorillonite nanocomposite, melt intercalation was performed at $180\text{ }^\circ\text{C}$ and 100 rpm, using a twin-screw extruder of L/D = 6.5 and 60 cm processing zone. After vacuum drying at $110\text{ }^\circ\text{C}$ for 24 h, the mixtures were compression-molded into sheets of 10 and 1000 μm for X-ray diffraction and mechanical property measurements, respectively.

Characterization. In order to confirm the polymerization of ϵ -caprolactone with Na-montmorillonite, DSC, $^1\text{H-NMR}$ and GPC experiments were conducted for the PCL fraction recovered from the PCL/Na-montmorillonite composite. The DSC measurement was performed on Perkin-Elmer DSC7 at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ from $-80\text{ }^\circ\text{C}$ to $250\text{ }^\circ\text{C}$ to measure glass transition temperature (T_g) and melting temperature (T_m). The $^1\text{H-NMR}$ experiment was conducted on Bruker AMX-500 spectrometer at room temperature using deuterated CHCl_3 as solvent. Molecular weight was measured at $25.0 \pm 0.1\text{ }^\circ\text{C}$ on GPC (Waters 600) using CHCl_3 as solvent/eluent. The results were calibrated with polystyrene standards. In addition, a thermogravimetry (TG) analysis on a TA model 2010 was conducted at a rate of $5\text{ }^\circ\text{C}/\text{min}$ to monitor the degradation behavior of organic components and to measure the content of inorganics in the polymer/clay mixture.

The change of gallery height of Na-montmorillonite was elucidated on a wide-angle x-ray spectroscopy (MacScience MXP18) with reflection mode. X-ray generator was run at 18 kW and the target was Cu standard ($\lambda = 1.5405\text{ \AA}$). Scanning was performed from 0 to 10 degree with a rate of 1 degree/min. For correction of scattering angle,

a pure silicone standard was used. The basal spacing of the layered silicates, d_{100} was calculated using the Bragg's law, $\lambda = 2d\sin\theta$ from the position of the (100) plane peak in XRD spectrum. Transmission electron micrographs were taken from 100 to 120 nm thick, cryo-microtomed section using JEOL JEM-2000FX TEM with accelerating voltage of 100 kV.

Tensile strength was determined with a dumbbell-shaped specimens under uniaxial tensile mode. From extrudate vacuum-dried at 110 °C for 24hr, a dumbbell-shaped specimen was compression-molded at 210 °C for 10 min and conditioned at 90 °C for 12 hr before testing. A specimen was tested on an Instron 4201 universal testing machine of crosshead speed of 5 mm/min at ambient temperature. We repeated tensile measurement on ten specimens to ensure accuracy.

RESULTS AND DISCUSSION

Recently, polymerization of CL confined within galleries of layered silicates has been studied [11-14], in which it was reported that intercalated or exfoliated structure of clay nanocomposites were obtained depending on the species of cation on the silicate surface.

$^1\text{H-NMR}$ analyses verified the polymerization of CL monomer in the nanocomposites. All the chemical shifts are assigned and clearly demonstrated conversion from CL to PCL. Complete conversion of CL to polymer was concluded because residual CL was not detected in the NMR spectra of any of the composites. Additional evidence of CL polymerization in the presence of clay was obtained from the investigation of thermal

behavior, in which the specimen collected after polymerization showed typical DSC thermogram of PCL of T_g around -52 °C and sharp T_m at 69 °C with no peaks associated with CL monomer, representing complete conversion of CL to polymer. In GPC measurements for the PCL fraction extracted from the nanocomposite, the weight-averaged (M_w) and the number-averaged molecular weight (M_n) were 11,000 and 8,000, respectively. At the previous studies for the polymerization of CL in the presence of clay, high dependence of the PCL molecular weight on the reaction environments such as temperature, catalyst, etc has been reported. Even though the molecular weight of PCL in this study obtained is not high, the role of compatibilizer does not extremely require high molecular weight and thus, additional endeavor to obtain PCL of higher molecular weight was not given.

In ascertaining intercalation behavior of silicate layers, XRD measurements presented that the characteristic (001) peak of pristine Na-montmorillonite at 6.45 degree of 2θ completely disappeared after polymerization of CL, implying effective delamination of silicate layers of montmorillonite and thus, expecting its well dispersion within the PCL matrix. Finally, TGA was used to obtain the content of montmorillonite in the nanocomposite, showing that the inorganic content in the PCL/Na-montmorillonite nanocomposite after solvent washing was 67.5 wt%, which was used in melt blending with SAN.

For the comparison with melt-mixtures of SAN/Na-montmorillonite of inorganic content of

5 wt%, SAN with the pre-made PCL/Na-montmorillonite nanocomposite was melt-blended with a composition of 5 wt% inorganic content. As observed in Figure 1, the melt-prepared SAN/Na-montmorillonite composite shows a strong peak in XRD spectrum representing the ordered structure with d_{100} of about 1.85 nm and TEM image featuring well-stacked structure of silicate layers of Na-montmorillonite, implying that the diffusion of SAN molecules into the gallery of silicate layers was highly suppressed even under high shear force. On the other hand, the mixture of SAN with the PCL/Na-montmorillonite nanocomposite does not produce any significant peak in the XRD spectrum below 10 degree of 2θ , implying that the delaminated silicate layers of montmorillonite is successfully preserved during melt blending with SAN. Supporting the fact for the SAN/PCL/Na-montmorillonite nanocomposite, it was very hard to detect stacked structure of silicate layers except irregularly dispersion of dissociated silicate layers on TEM image.

To confirm the miscibility in organic phase between SAN and PCL components, a DSC study was conducted for the melt-blended specimens of following compositions; SAN: PCL/Na-montmorillonite = 92.6:7.6, 85.2:14.8 and 77.8:22.2 in wt% (then the respective inorganic contents were 5, 10 and 15 wt%). Single T_g behavior at the midpoint of T_g 's of SAN and PCL and complete disappearance of PCL crystalline phase were observed for all the composition tested, expressing that the organic phase of perfect miscibility is established in our nanocomposite. Combining the results of XRD, TEM and thermal behavior it can be concluded

that the homogeneous distribution of delaminated silicate layers of Na-montmorillonite in the repulsive SAN matrix was accomplished by compatibilization of PCL molecules.

Referring to the previous reports concerning exfoliated structure of clay nanocomposites, the mechanical properties tend to dramatically increase even with very small amount of clay. To verify the dissociation of layered nanoplatelets of Na-montmorillonite and its distribution on the polymer matrix with nanoscale, which were expected based on the XRD measurement, mechanical properties were critically investigated. Figure 2 depicts the stress-strain curves of the uniaxially tensioned specimens of neat SAN, SAN/Na-montmorillonite and SAN/PCL/Na-montmorillonite. As expected, SAN/Na-montmorillonite specimen showed typical brittle failure without yielding like neat SAN. Note that modulus of the mixture increased beyond that of neat SAN by the presence of inorganic phase and tensile strength and toughness were lowered than those of neat SAN, attributed to the weak interface of the mixture. On the other hand, stress-strain curve of SAN/PCL/Na-montmorillonite showed that the tensile strength as well as the modulus effectively increased. Even though the amount of strength increase of the obtained nanocomposite is not so large due to the presence of PCL component of not-high molecular weight and poor mechanical properties, the simultaneous increase in tensile strength and modulus for the PCL-containing SAN/Na-montmorillonite nanocomposite over those of neat SAN is strongly supporting

evidence that the homogeneous distribution of reinforcing components was well established.

Consequently, it can be concluded that the limited intercalation of Na-montmorillonite with SAN copolymer and its poor distribution in the polymer matrix can be modified to the exfoliated state through the introduction of PCL, and that the final morphology, i.e. degree of distribution of Na-montmorillonite, and the corresponding material properties can be effectively controlled with the presence of PCL and its amount on the interface between organic and inorganic phases.

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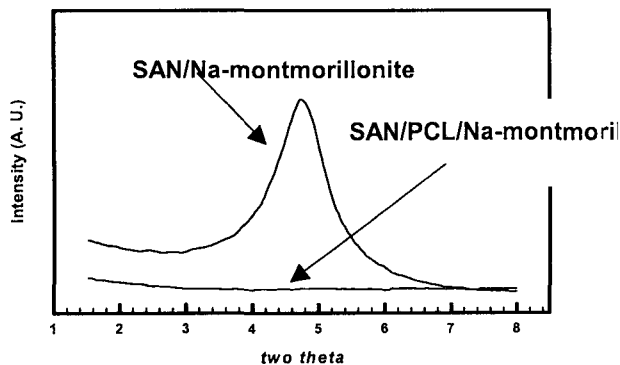


Figure 1. XRD spectra and transmission electron microphotographs of the SAN/Na-montmorillonite composite and the SAN/PCL/Na-montmorillonite nanocomposite. Note the complete disappearance of (100) peak of Na-montmorillonite, implying retention of exfoliation state of PCL/Na-montmorillonite nanocomposite when blended with SAN.

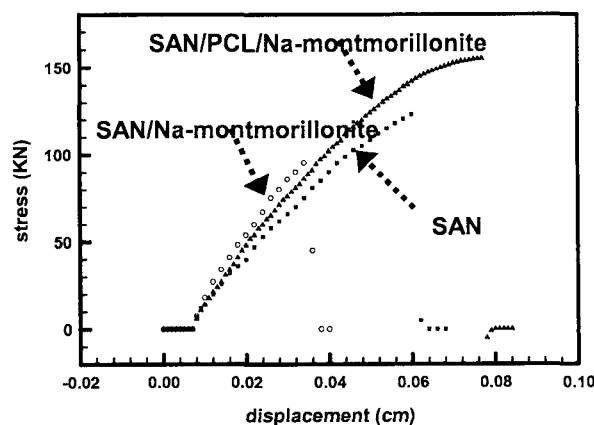


Figure 2. Stress-strain curves obtained from SAN24, SAN24/Na-montmorillonite and SAN24/PCL/Na-montmorillonite nanocomposite