

Preparation of SAN/Silicate Nanocomposites Using PMMA as a Compatibilizer

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Abstract: Polymer/silicate nanocomposites were prepared via two-step manufacturing process: a master batch preparation and then mixing with matrix polymer. A hybrid of PMMA and Na-MMT with exfoliated structure was first prepared by emulsion polymerization of MMA in the presence of Na-MMT. For the case that SAN24, miscible with PMMA, is used as matrix, we could prepare a nanocomposite with exfoliated structure. However, SAN31 nanocomposite shows the aggregation and/or reordering of the silicate layers due to the immiscibility between SAN31 and PMMA.

Keywords: Polymer/silicate nanocomposite, SAN, Compatibilizer, Exfoliated structure

Introduction

Polymer/silicate nanocomposites have shown remarkable enhancement of physical properties relative to conventional microcomposites [1-4]. When the silicate layers, which are the basic building unit of natural or synthetic silicates, are exfoliated in nanoscale and randomly distributed into polymer matrix, physical properties of the resultant composites are significantly enhanced.

Polymer/silicate nanocomposites can be fabricated by various methods such as in-situ polymerization of monomers [5], solution drying [6], and polymer melt intercalation [7]. Among these methods, the polymer melt intercalation where silicates are directly melt-mixed with a molten polymer has been considered as the most common and economical way for preparing polymer/silicate nanocomposites. The exfoliation of silicate layers during melt mixing depends on processing variables such as mixing time and temperature [8], the melt viscosity of matrix polymer [9], and the shear stress [8,10] applied during mixing as well as thermodynamic variables such as the interaction between polymer and silicate. Even though an organic modifier is introduced into gallery of silicate layers in order to alleviate the unfavorable interaction between polymer and silicate, it is not always possible to directly introduce polymer chains into gallery of silicate layers and then to exfoliate them during melt mixing.

Recently, Hasegawa and his coworkers [11-13] reported that polymer/silicate nanocomposites with the exfoliated structure were successfully prepared by melt mixing when the polymer compatibilization technique was applied. As a compatibilizer, they added reactive polymers containing

functional groups such as maleic anhydride to tune the interaction between hydrophobic polymers and hydrophilic silicates. Using this method they could prepare exfoliated polypropylene [11,12] or exfoliated polystyrene nanocomposites [13]. In our previous study [14], we have shown that a non-functional polymer could be also used as a compatibilizer if it is miscible with the matrix polymer. As a prerequisite, a master batch of compatibilizer and (organo)silicate with exfoliated structure should be prepared before mixing with matrix polymer. Using a master batch of poly(ϵ -caprolactone) (PCL) and organosilicate, which was prepared under controlled melt-mixing conditions, we could prepare exfoliated poly(styrene-*co*-acrylonitrile) (SAN)/(PCL/organosilicate) nanocomposite, where PCL is miscible with SAN.

In this study, we attempt to prepare an exfoliated SAN nanocomposite using the hybrid of poly(methyl methacrylate) (PMMA)/Na-montmorillonite (Na-MMT) as a master batch, where the PMMA/Na-MMT nanocomposite has an exfoliated structure. We also investigate the effect of miscibility between SAN and PMMA on the structure of the resultant nanocomposites. For the purpose, we used two different SAN copolymers with 24 and 31 wt% acrylonitrile (AN) contents. It is noted that the SAN copolymer (SAN24) with 24 wt% AN content is miscible with PMMA whereas the SAN copolymer (SAN31) with 31 wt% AN content is not miscible with PMMA.

Experimental

Materials

Two different SAN copolymers, SAN24 and SAN31, were obtained from LG Chemical Co. Ltd. Their molecular weights were 105 000 and 79 000 g/mol, respectively. Neat PMMA

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with the molecular weight of 120 000 g/mol was purchased from Sigma-Aldrich Chem. They were milled in the form of powder and dried under vacuum. Pristine Na-MMT, Kunipia-F from Kunimine, Japan, was used as received.

Preparation of Master Batch

A master batch of PMMA and Na-MMT (PMMA/Na-MMT) was prepared by emulsion polymerization. It was carried out in a 2-L glass reactor fitted with a reflux condenser, stirrer, sampling device, and nitrogen inlet. 10 g of Na-MMT with a cation exchange capacity of 115 meq/100 g was added to the reactor containing 1000 ml of deionized water (the ratio of Na-MMT to water is approximately 1:100). After equilibration at 50 °C, a mixture of methyl methacrylate (100 g), sodium lauryl sulfate (4 g), and tertiary-dodecyl mercaptan (0.5 g) were introduced and then the reactor was purged with nitrogen. Polymerization, initiated by 0.5 g of potassium persulfate, was carried out for 4 hrs at 50 °C with a stirring rate of 250 rpm. The resultant emulsion was freeze-dried and then washed twice with methanol and then de-ionized water. Before mixing with matrix, it was completely dried under vacuum at 80 °C.

Preparation of Nanocomposites

SAN nanocomposites were prepared by melt mixing with SAN and (PMMA/Na-MMT). SAN copolymer was melt-mixed with (PMMA/Na-MMT) in a ratio of 70/30 by weight using a Mini-Max molder (Custom Scientific Instruments, Inc.) at 200 °C for 10 min. The rotor speed was fixed at 130 rpm. For comparison, SAN/PMMA blends without Na-MMT were also prepared under the same mixing conditions. The overall scheme of preparation of nanocomposites is

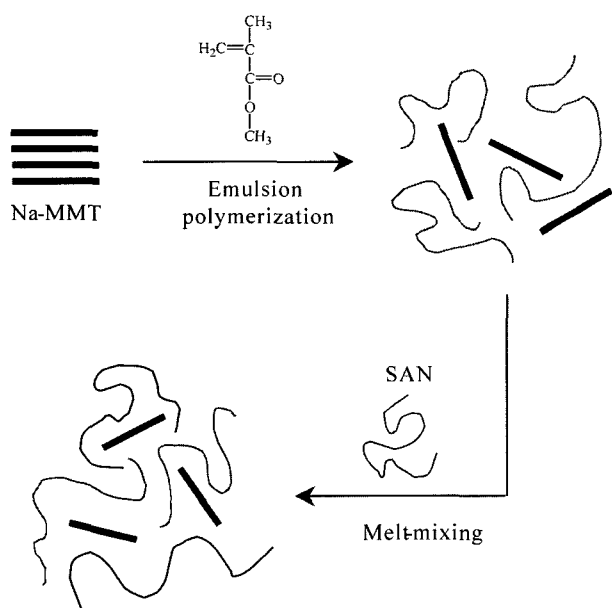


Figure 1. Schematic representation of nanocomposite preparation.

shown in Figure 1.

Characterization

The change in the basal spacing of Na-MMT was measured using an X-ray diffractometer (MAC Science, MXP 18A-HF). Ni-filtered $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation, generated at a voltage of 40 kV and current of 30 mA, was used as an X-ray source. The diffraction angle was scanned from 1.5 ° to 10 ° at a rate of 2 °/min. The structure of nanocomposites was also characterized using a JEOL-2000 FXII transmission electron microscopy (TEM), operated at an accelerating voltage of 100 kV. Sections of thickness less than 100 nm were ultramicrotomed with a diamond knife and then mounted on 200 mesh copper grids. Since silicate layers have higher electron density than polymers, they appear dark in bright-field TEM.

The miscibility between SAN and PMMA was determined using a Perkin-Elmer DSC 7 differential scanning calorimeter. Neat or blend samples were heated from 0 °C to 200 °C at a rate of 20 °C/min and then kept at the final temperature to remove thermal history applied to them. After quenching to 0 °C, they were reheated at the same heating rate. The data from second run were used for discussion.

Dynamic mechanical properties of samples were measured using a Rheometric scientific dynamic mechanical thermal analyzer (DMTA) with bending mode at the frequency of 1 Hz in the temperature range from 50 °C to 200 °C. Tensile properties of samples were measured using a Lloyd LR 10K universal tester. Cross-head speed was kept at 2 mm/min. At least five specimens for each sample were tested. Specimens have the dimension specified as ASTM D-638 type V specimen.

Results and Discussion

Figure 2(A) shows the XRD pattern of a (PMMA/Na-MMT) master batch prepared by emulsion polymerization. As can be seen in Figure 2(A), Na-MMT shows the (001) reflection peak at $2\theta = 7.3^\circ$, the characteristics of natural Na-MMT whereas the master batch of (PMMA/Na-MMT) does not show distinct reflection peak, indicating that the silicate layers of Na-MMT lose their layered geometry and dispersed in the PMMA matrix. However, a closer examination of the XRD pattern of the (PMMA/Na-MMT) reveals that a very weak and broad peak at around $2\theta = 7^\circ$ still remains. This indicates that some tactoids of several tens of silicate layers maintaining their basal spacing are dispersed within the PMMA matrix. This is also supported by TEM observation, as shown in Figure 2(B). It is concluded from Figure 2 that silicate layers are chopped into stacks of several tens of silicate layers and the stacks are randomly dispersed within the PMMA matrix. It is noteworthy that the (PMMA/Na-MMT) master batch with more completely exfoliated structure could be prepared with a smaller content of Na-MMT than

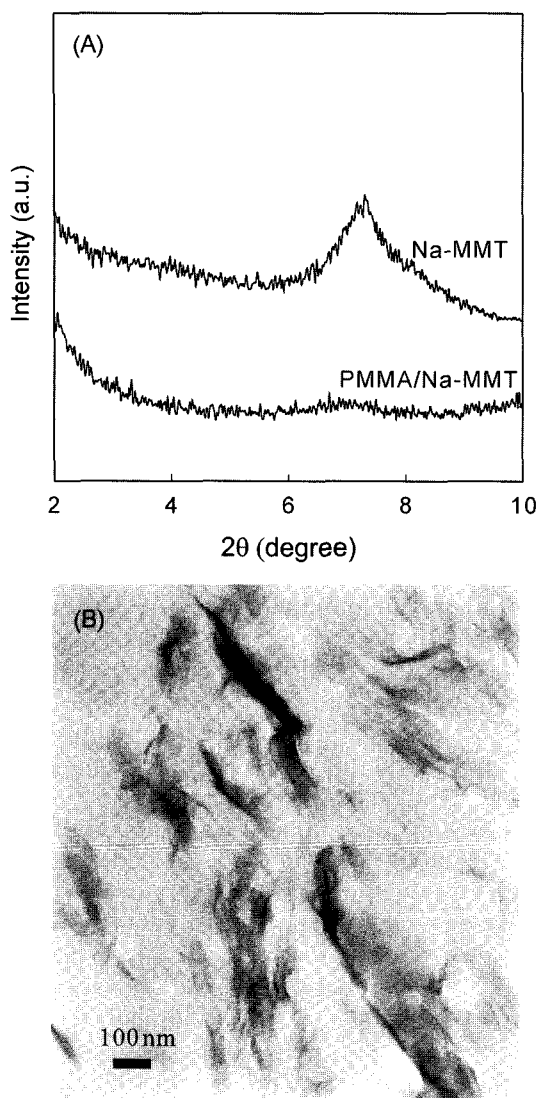


Figure 2. The structure of 90/10 PMMA/Na-MMT master batch prepared by emulsion polymerization: (A) XRD profiles and (B) TEM micrograph.

10 wt%. However, it is desirable for the content of Na-MMT in master batch to be as high as possible because the content is diluted by mixing with matrix polymer.

It is expected that the miscibility between the matrix polymer and the PMMA is necessary to prepare the exfoliated nanocomposites. The miscibility between blend pair can be easily identified by measuring the glass transition temperature (T_g) of blend, i.e., a miscible polymer blend exhibits a composition dependent single T_g . Figure 3(A) shows DSC thermograms for SAN24, (PMMA/Na-MMT), and 70/30 SAN24/(PMMA/Na-MMT) nanocomposite. Instead of two T_g 's of the SAN and PMMA, a new and single T_g at 111 °C is observed for the SAN24/(PMMA/Na-MMT) nanocomposite, indicating that SAN24 is miscible with (PMMA/Na-MMT)

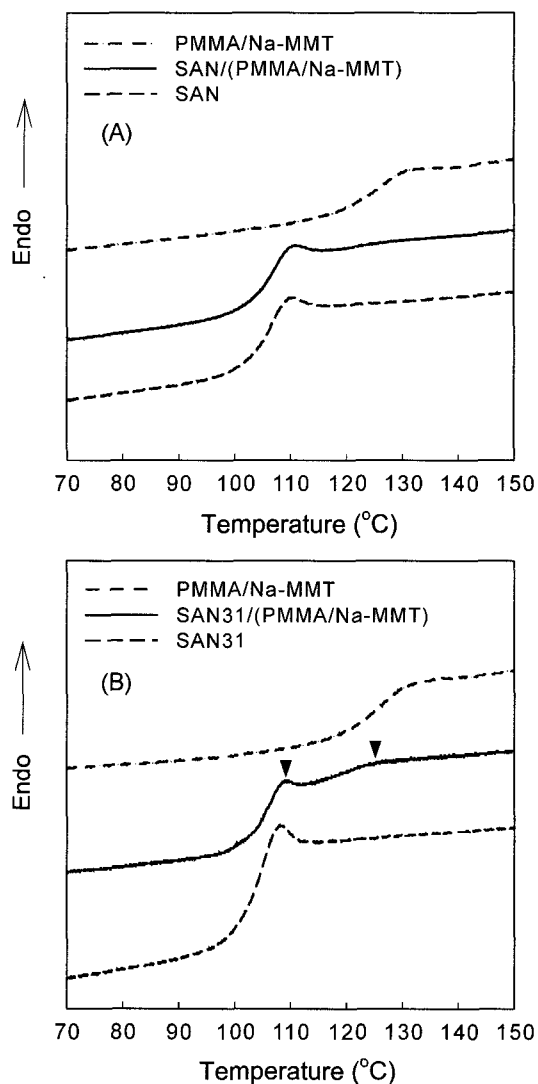


Figure 3. DSC thermograms of (A) SAN24 and (B) SAN31 nanocomposites. In nanocomposites, the content of (PMMA/Na-MMT) master batch was fixed at 30 wt%.

under the mixing conditions applied in this study.

SAN31 with higher AN content shows different miscibility with (PMMA/Na-MMT). Although the T_g 's of the components in the blend slightly changed compared to neat ones, two distinct ones are observed as shown in Figure 3(B), indicating that SAN31 is not miscible with (PMMA/Na-MMT). The effect of AN content on the miscibility between SAN and PMMA has been well investigated [15]: PMMA is miscible with SAN only in the range from 9 up to 26.5 wt% of AN in SAN, which is consistent with this study.

Figure 4 shows XRD profiles of the SAN nanocomposites with different AN content. Since the content of (PMMA/Na-MMT) in the blend is fixed at 30 wt%, the content of Na-MMT in the nanocomposites becomes 3 wt%. The (001) reflection peak of Na-MMT in (PMMA/Na-MMT) disappears when

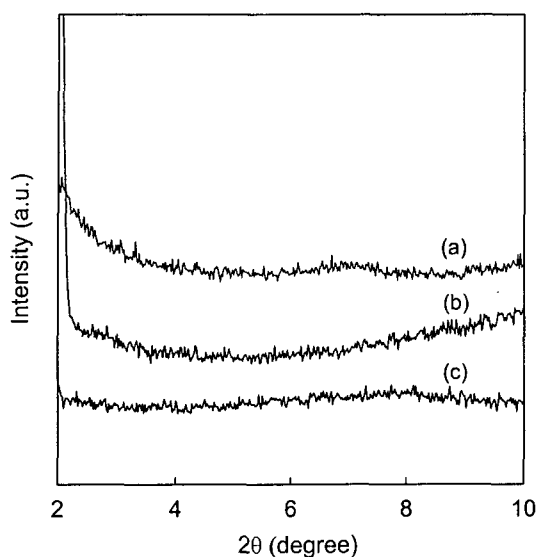


Figure 4. XRD profiles of (a) PMMA/Na-MMT master batch, (b) 70/30 SAN24/(PMMA/Na-MMT) nanocomposite, and (c) 70/30 SAN31/(PMMA/Na-MMT) nanocomposite.

SAN24 is used as matrix, but does not for the matrix of SAN31. This indicates that the resultant SAN nanocomposite has more exfoliated structure than (PMMA/Na-MMT) when SAN is miscible with the PMMA compatibilizer. Unlike the SAN24 nanocomposite, the SAN31 nanocomposite still shows a weak and broad peak of (001) reflection, indicating that the degree of exfoliation of SAN31 nanocomposite remains nearly unchanged. The exfoliated structure for SAN24

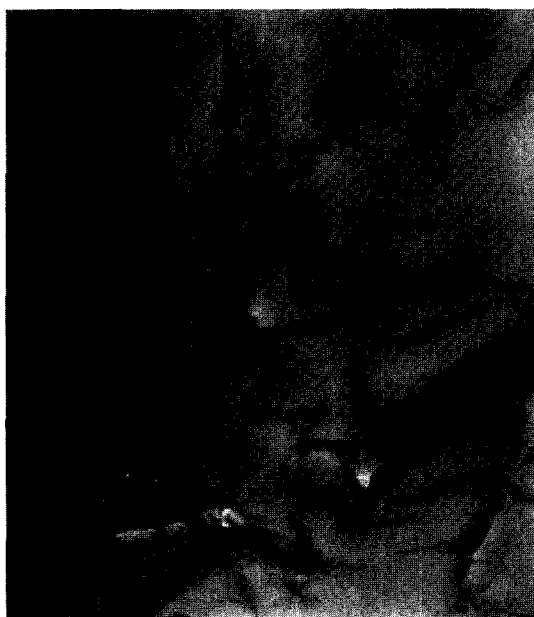


Figure 5. TEM micrograph of 70/30 SAN24/(PMMA/Na-MMT) nanocomposite.

nanocomposite is also supported by TEM micrograph of Figure 5. This may be explained by considering the interaction between matrix polymer (SAN24) and compatibilizer (PMMA). In other words, PMMA chains already intercalated in (PMMA/Na-MMT) may attract SAN24 copolymer chains, resulting in more polymer chains in intergallery of Na-MMT. Consequently, some tactoids of silicate layers are more finely chopped to give better exfoliated structure. From these results, it is clear that the miscibility between matrix and compatibilizer in master batch plays a critical role in preparing exfoliated nanocomposite.

Dynamic storage modulus (E') of 70/30 SAN24/(PMMA/Na-MMT) nanocomposite is plotted against temperature in Figure 6. For comparison, E' of silicate-free SAN24/PMMA blends are also presented in the same figure. Na-MMT-

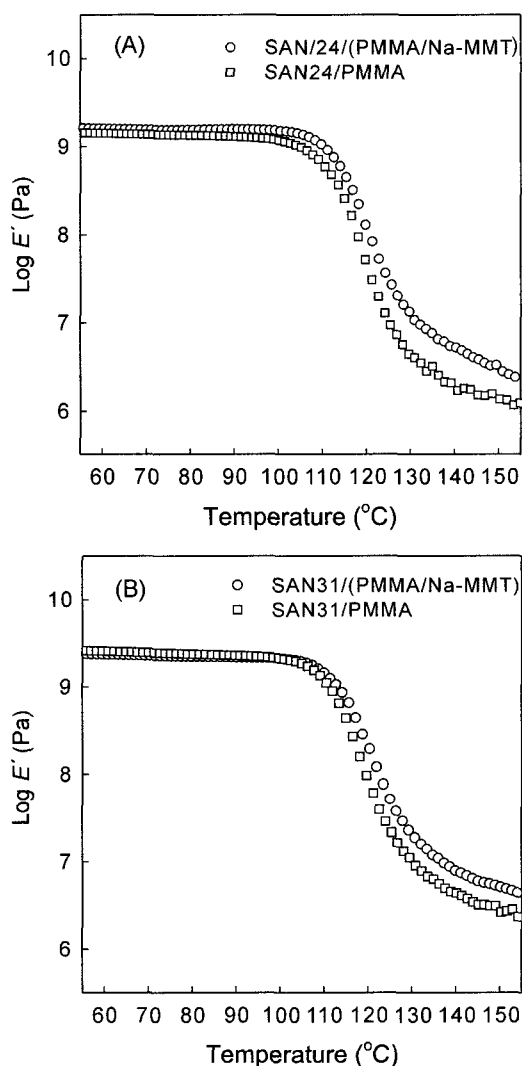


Figure 6. Dynamic storage moduli of (A) SAN24 and (B) SAN31 nanocomposites containing (PMMA/Na-MMT) master batch. Results from silicate-free SAN24/PMMA and SAN31/PMMA blends are also shown for comparison.

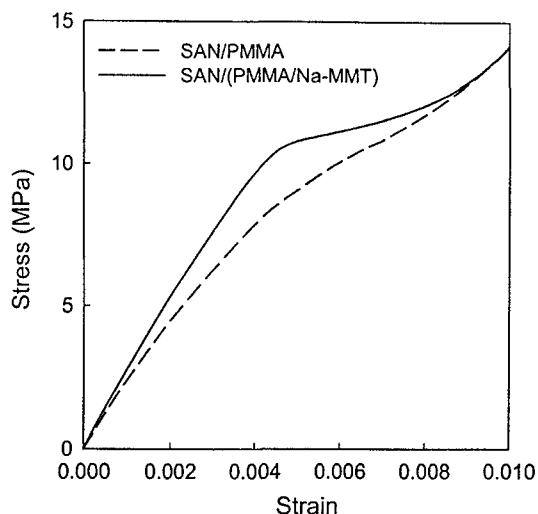


Figure 7. Comparison of stress-strain curve of SAN24 nanocomposite with that of silicate-free SAN24/PMMA blend.

containing SAN24 nanocomposite has the higher E' than SAN24/PMMA blend over the entire temperature range examined. The increase in E' results from reinforcement of silicate layers exfoliated in nano-scale. It is also realized from comparison of Figure 6(A) with 6(B) that the increase of modulus due to nanocomposite at rubbery state is larger for SAN24 than for SAN31. The reinforcement of Na-MMT is also clearly seen in tensile properties, as shown in Figure 7.

Conclusions

We prepared polymer/silicate nanocomposites via two-step manufacturing process. In the first step, a hybrid of PMMA and Na-MMT with exfoliated structure was prepared as a master batch using emulsion polymerization. It was then melt-mixed with SANs with different AN content at the second step. For the case that SAN24, miscible with PMMA, is used as matrix, the nanocomposite shows an exfoliated structure. Unlike the SAN24 nanocomposite, SAN31 nanocomposite shows the (001) reflection peak of Na-MMT due to immiscibility between SAN31 and PMMA. It is concluded that the miscibility between matrix polymer

and compatibilizer plays a critical role in preparing exfoliated nanocomposite.

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