Intercalation of Styrene–Acrylonitrile Copolymer in Layered Silicate by Emulsion Polymerization

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ABSTRACT: A well-defined styrene–acrylonitrile copolymer/montmorillonite (SAN-MMT) nanocomposite has been prepared by emulsion copolymerization of styrene and acrylonitrile in the presence of sodium ion exchanged montmorillonite (Na^+-MMT). This direct and one-step polymerization technique yielded nanocomposites intercalated with styrene-acrylonitrile copolymer without occurrence of significant delamination of MMT. The purified products by hot tetrahydrofuran extraction for up to 5 days gave evidences of copolymer intercalation. Those infrared spectra obtained from the purified products revealed the characteristic absorbances due to styrene, acrylonitrile, and MMT. Room temperature powder X-ray diffraction patterns of the purified product exhibited increased 001 d-spacing about 1.60 nm. The transmission electron microscopy micrograph of unpurified products confirmed that the 1–2-nm sized silicate layers are arranged in good order. The onset temperature of purified products are found to be moved to higher temperature, while the thermograms of differential scanning calorimetry show nothing observable transition. The modulus of elasticity of the product was increased with increasing content of MMT, whereas the stress at maximum load was decreased with the increments of MMT. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 179–188, 1999

Key words: SAN-MMT nanocomposite; emulsion copolymerization; intercalation

INTRODUCTION

The development of molecular composites in which an inorganic solids is associated with organic entities interacting at molecular level opens the way to the preparation of new materials. Undoubtedly, this type of nanoscale composites are expected to offer characteristic and potential properties that are drastically different from their bulk counterparts.[1–4]

One of the most promising synthetic approaches to obtain well-controlled dispersions of a selected organic species giving stable nanocomposite materials is intercalation of polymers in layered hosts.[5] In general, the synthesis involves either intercalation of a suitable monomer and subsequent polymerization[2–4,6–8] or polymer intercalation from solution or polymer molten state.[9–11] However, the lack of affinity between the hydrophilic silicate interlayer and hydrophobic organic monomers or polymers makes the synthetic situation difficult. This has led all those approaches so far known to use organically modified silicates or suitable compatibilizers, without exceptions. Therefore, this article reports a new and simple process of direct intercalation without using organically modified silicate or coupling agents but instead using an usual one-step emulsion technique. An emulsion system consisting of an aqueous medium can contribute to the affinity between the hydrophilic host and hydrophobic guest by the action of the emulsifier. Further-

more, the emulsion polymerization has the advantage of being able to simultaneously attain both high molecular masses and high reaction rates. Thus, it has been attempted to obtain a nanocomposite intercalated with linear chain copolymer via emulsion copolymerization in the presence of sodium ion exchanged montmorillonite (Na^+-MMT).

The work reported here deals with the creation of a hybrid nanocomposite, formed by direct intercalation of styrene-acrylonitrile copolymer (SAN) into the galleries of Na^+-MMT. Characterizations on those structures, physical properties, and internal micromorphology of the hybrid material have been performed and their results are discussed. A special attention is given to the physical picture of direct intercalation by this emulsion technique.

EXPERIMENTAL

Materials

Purified bentonite (Tae-Kwang Chem. Co, Seoul, Korea) having 70% of MMT content and 90 mEq/100 g of cation exchange capacity was used. Styrene and acrylonitrile monomers were purified by distillation under reduced pressure before use. All the water used was deionized. The other chemicals were used as supplied.

Emulsion Copolymerization

A 2 L four-neck flask fitted with mechanical stirrer, thermometer, dropping funnel, and condenser was charged with 1200 mL of aqueous dispersions containing 12.5–100 g of Na^+-MMT. Being sonicated for 30 min at 60°C, 250 mL of styrene/acrylonitrile (7/3) and 40 mL of sodium lauryl sulfate aqueous solution (20 wt %) were added with keeping gentle stirring. The temperature was then raised to 80°C and the initiator, potassium persulfate (0.5~2 g), dissolved in 20 mL of water was introduced to the reactor slowly, which started the copolymerization. The stirring rate was controlled to keep 600 rev/min. After 5 h of reaction, the copolymerization was terminated by addition of 700 mL of aluminum sulfate solution (10 wt %). The coagulated products being separated were subjected to a series of intensive washing by performing four cycles of centrifugations and redispersions into water. The products were dried under reduced pressure at 60°C and

pulverized. The major part of the product was then exposed to hot tetrahydrofuran (THF) extraction for up to 5 days.

Characterization and Measurements

The amount of polymer loading was estimated by measuring the weight loss of the nanocomposite, thermogravimetrically. DuPont 9900 thermogravimetric analyzer (TGA) was used. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Spectrophotometer by the KBr method at the wave number range of 4000–400 cm^{-1}. The room temperature powder X-ray diffraction (XRD) patterns for both the pure MMT and hybrid composites were obtained from the Philips PW-1847 X-ray crystallographic unit mounted with a Guinian focusing camera. The CuKα radiation source was operated at 40 kv and 20 mA. Patterns were recorded by monitoring those diffractions appeared in the 2θ range from 2° to 30°. Thermal characterizations of the composites were carried out by using differential scanning calorimetry (DSC; Perkin–Elmer DSC 7) and TGA. DSC measurements were performed by heating 10 mg of each sample up to 160°C at the heating rate of 10°C/min under the nitrogen atmosphere. The second scanning data were accepted. TGA measurements were carried out by heating 20 mg of each sample up to 600°C at the heating rate of 20°C/min under the nitrogen atmosphere. The morphological aspects of the hybrid materials have been examined by using transmission electron microscopy (TEM) in order to determine the internal micromorphology. A JEOL-200 CX TEM, with an acceleration voltage of 200 kV, was used. The fractured surfaces of the composite were observed by the scanning electron microscopy, JSM-840A, JEOL which was operated with a high-tension voltage of 20 kV. The state of MMT dispersion of the unpurified composite in the SAN copolymer matrix was examined by optical microscopy. The OPTIPHOT2-POL Polarizing microscope was used. Measurements of average molecular masses and polydispersity indices of the copolymers extracted and recovered from those composites were carried out by size exclusion chromatography. The Waters Model 201 equipped with the U6K injector, M 6000A solvent delivery system, and three linear columns packed with μ-styragel was used. The copolymer composition of the polymer intercalated was determined by elemental analysis. The Heraeus CHN-O-RAPID elemental analyzer was

Table I   Input Ratios of Comonomer to MMT and Contents of SAN in Nanocomposites

Sample	Input Ratio of Comonomer[a]/MMT[b] (g/g)	SAN Content in Product (wt %) A[c]	SAN Content in Product (wt %) B[d]
CSAN[e]5	[a]100/5	92.5	38.5
CSAN10	100/10	88.8	35.6
CSAN20	100/20	79.2	36.4
CSAN30	100/30	74.1	28.9
CSAN40	100/40	69.4	27.4

[a] The ratio of styrene-acrylonitrile comonomer is 70 : 30 in weight.
[b] MMT.
[c] Products not purified by extraction.
[d] Products purified by hot tetrahydrofuran extraction for 5 days.
[e] SAN-MMT nanocomposite not purified by extraction.

employed. The stress–strain behavior of the unpurified composite was observed by tensile testing. An Instron (Hounsfield Co. H 25KS) was used. The results of 5 specimens were averaged.

RESULTS AND DISCUSSION

Structural and Molecular Characterization

The SAN-MMT nanocomposites were prepared by a synthetic procedure similar to that initially developed by Lee et al.,[8] for PMMA-clay hybrid composite. In its most basic form it involves dispersion of sonicated Na^+ exchanged MMT in a heterogeneous monomer/water system, followed by emulsion polymerization. Table I lists the input ratios of comonomer to MMT of the series of SAN-MMTs prepared in this manner.

In order to determine the polymer contents loaded in the layers of silicate layers and the structural characteristics of the intercalated products, those composites dried were extracted with boiling tetrahydrofuran for 5 days. Figure 1 shows the variations of the copolymer content in the composites with the extraction times. It can clearly be seen from the figure that a considerable amounts of the unextractable copolymers are still remained, even after 120 h of extraction. These residual polymers can be regarded as the copolymer intercalated in the galleries of MMT. Figure 1 also demonstrates that the most of the non-

Figure 1   SAN copolymer content variations of nanocomposites with increasing times of extraction.

bonded organic materials can be eliminated from the composite by 48 h of extraction.

The determination of copolymer content in the composite, being either extracted or unextracted, is carried out by TGA. The thermograms obtained are illustrated in Figures 2 and 3, and those thermograms allow estimation of the values of polymer contents which are summarized in Table I. As evident from the table, the unpurified products exhibit large which in turn leads to form quite different comonomer composition in the micelle from the input comonomer ratios.

The IR spectra of the representative composites are illustrated in Figure 4 along with those of pure SAN and MMT. It can clearly be seen that the spectra of the composites, especially the extracted product (ESAN), exhibit the presence of characteristic absorptions due both to the organic and inorganic groups. The absorption bands at 3630, 1050, and those between $600-400$ cm^{-1} can

Figure 2   TGA thermograms of unextracted nanocomposites and pure SAN copolymer.

Figure 3 TGA thermograms of extracted nanocomposites and pure SAN copolymer.

be associated respectively with —OH stretching of the lattice water, Si—O stretching, and Al—O stretching. Absorptions, on the other hand, at 3070, 3030 cm^{-1} aromatic C—H) stretching, 2960, 2930 cm^{-1} (aliphatic C—H stretching), and 2226 cm^{-1} (—C≡N stretching), respectively, are the consequences of the SAN copolymer. However, no evidence of new absorption bands can be found and this implies that the fixation of the copolymer at the interlayer of MMT is mainly due

Figure 4 IR spectra of MMT, nanocomposites, and pure SAN copolymer.

Figure 5 Room temperature powder XRD patterns of extracted nanocomposites and MMT.

to the strong secondary valence forces acting between the Na$^+$ ion and —C≡N group.

An another strong evidence of the intercalation can be obtained from the X-ray diffraction patterns (XRD) of those purified composites. Figure 5 shows the room temperature powder XRD patterns obtained from the purified composites and pristine MMT. Undoubtedly, the overall patterns of the composites are essentially the same with that of the pure MMT except for the positions of 001 reflections. This is a strong indication that the overwhelming fraction of the composite retains the crystalline structure of MMT. Moreover, the peak positions of 001 d-spacing of those composites are transferred to 2θ angles lower than that of the pristine MMT. The interlamellar distances calculated from the positions of 001 reflections are listed in Table II along with the data of copolymer loading quantities. It turns out that the basal spacing of the composite is enlarged with the decreasing amounts of MMT added, and the average value found is close to 1.60 nm. This value is comparable with 1.57 nm for the system of PMMA-MMT,[8] larger than 1.51 nm for nylon 6-clay hybrid,[13] but smaller than 1.77 nm for polyether-Na-MMT hybrid.[15] The value of 1.60 nm also provides an estimation on the chain con-

Table II Polymer Loading Behaviors and Variations of Basal Spacing of Nanocomposites

| Sample | Organic Loading | | Basal Spacing (nm) |
	Before Extraction (SAN/MMT[a])	After Extraction (SAN/MMT)	
MMT[a]	0/100	0/100	0.96
CSAN5	92.5/7.5	38.4/61.6	1.87
CSAN10	88.8/11.2	35.6/64.4	1.63
CSAN20	79.2/20.8	36.4/63.6	1.54
CSAN30	74.1/25.9	28.9/71.1	1.49
CSAN40	69.4/30.6	27.4/72.6	1.42

[a] Montmorillonite.

formation of the copolymer intercalated, that is, the copolymer chains run parallel to the interlayers with fully extended double layers of zig-zag conformation. Furthermore, the intensive reflections of the composites compared to that of the pristine MMT at $2\theta = 4°-8°$ range also indicate that the composite may constituted with alternating layers of polymer and MMT.[14] Accordingly, the X-ray analysis leads to a conclusion that a copolymer also can be intercalated into the interlayers of Na^+-MMT by a simple emulsion technique without accompanying a significant delamination of clay layers.

Thermal Characterization

TGA thermograms of those purified composites and of pure SAN copolymer are shown in Figure 3. As evident from the figure, the onset of copolymer decomposition in the nanocomposite is found to moved to higher temperature, indicating the enhancement of thermal stability of composites. This enhancement of thermal stability can be regarded as an additional evidence of the interactions between organic polymer and MMT. It is also noticeable that the composites are showing nearly the same decomposition temperature at around 430°C regardless of their polymer loading. This means that the thermal insulation effect of MMT dose not depend much on the contents of intercalated copolymer.

DSC traces of both the unpurified and purified composites are shown in Figures 6 and 7, respectively, together with the thermogram of pure SAN copolymer. The pure SAN copolymer containing about 19 wt % of acrylonitrile exhibits an endotherm approximately at 107°C, and those compos-

Figure 6 DSC thermograms of pure SAN copolymer and nanocomposites not extracted.

ites demonstrate an increasing trend of their T_gs with the amounts of MMT added. The appearance of T_gs obtained from those unpurified products, as

Figure 7 DSC thermograms of nanocomposites extracted.

Figure 8 Instron data of nanocomposites and SAN copolymer.

is demonstrated in Figure 6, is considered to be arisen due mainly to the copolymers adsorbed on the outer surfaces of MMT, and the increasing trend of T_g with the amounts of MMT is undoubtedly the consequence of the increased thermal insulation effect of MMT. On the contrary, the DSC thermograms of the extracted composites do not show any traces of clear thermal transitions. The disappearance of glass transitions indicates the absence of a discrete polymer phase, and again demonstrates that those two dimensional polymer chains being confined in the interlayer are not free from the molecular motion similar to that of native copolymers.

Stress–Strain Behavior of Composite

Tensile properties of unpurified composites against the ratios of clay/copolymer (g/g) are shown in Figure 8. Owing to their powdery texture, the composite containing less than 70 wt % of SAN copolymer was not able to prepare tensile test specimen. Clearly, the figure shows that the modulus of elasticity of composite has been enhanced with the increment of MMT content, whereas the stress at maximum load is decreased. The enhancement of the modulus is ascribed to the high resistance exerted by the MMT against

the plastic deformation of SAN copolymer. Additionally, the stretching resistance of the oriented backbone bonds of copolymer chain in the gallery has also been contributed to the enhancement of the modulus. On the contrary, the stress at maximum load shows a decreasing trend with increasing quantity of MMT. This result is considered to be responsible for the relatively weak particle–polymer bonding, and in particular, at the high concentration of MMT, the ductile failure is evident because the strain at maximum load has been marked only 5%.

Morphologies of Intercalated Composite

The morphological aspects of the composite materials have been examined by using TEM in order to observe the dispersion state of the intercalated silicate layers. Figure 9 shows the TEM micrograph of unpurified CSAN-5 composite, which demonstrates the 1–2 nm sized silicate layers are arranged in good order and are dispersed homogeneously in the copolymer matrix. This result confirms that the composite prepared is nanoscaled material and no delamination of the MMT layers are taking place during the intercalation reaction.

50nm

Figure 9 TEM micrograph of nanocomposite (CSAN5).

The SEM images of the fractured surfaces of the composites prepared by emulsion (a) (CSAN-5) and solution polymerization technique by employing organophillic MMT (b) (SSAN-5), are shown in Figure 10 and are compared. The fractured surface of (a) shows not only the smooth surface due to the finely dispersed MMT particles but also no traces of MMT particles. Conversely, from the fractured surface of (b), voids and some deformation parts can be found, which may result the coarseness of fractured surface. This is probably the consequence of the irregular dispersion of micron sized MMT particles.

Figure 11 illustrates the optical micrographs of unpurified CSAN-5 composite. The nonpolarized micrograph shows a well dispersed morphological phase of the fine MMT particles having average diameter of about 0.5 μm in the copolymer matrix. This effect is tentatively ascribed to the enhanced miscibility due to the increased surface area of those fine MMT particles which are incorporated with the copolymer residing at both the inside layer and outer surfaces.

Possible Physical Picture of Direct Intercalation

Figure 12 compares the XRD patterns taken from the sonicated and untreated Na$^+$-MMT in pure water for 1 h. The figure shows that the peak

ⓐ SAN-MMT by Emulsion Polymerization

ⓑ SAN-MMT by Solution Polymerization

Figure 10 SEM micrographs of fractured surfaces of nanocomposites.

position reflecting the dimension of 001 basal spacing is nearly the same. This means that the sonication is unable to change the interlayer distance of MMT. However, the measurements of the particle sizes of those sonicated and untreated samples by the dynamic light scattering method confirmed the decreased average size of the sonicated product as 0.5 μm in diameter from 1.5 μm in the range of clay/water ratio 0.013/0.104. This is an indication that the sonication can disentangle the aggregated particles, and hence increase the surface area of the MMT. The figure also reveals that the crystal structure of the sonicated

Figure 11 Nonpolarized optical micrograph of CSAN5 unextracted.

Table III   Average Molecular Masses and Polydispersity Indices of SAN Copolymer Recovered from Extracted Composite and Pure SAN by GPC

Sample	$\bar{M}_n \times 10^{-4}$ (g/mol)	$\bar{M}_u \times 10^{-4}$ (g/mol)	$\bar{M}_u/\bar{M}_n$
Pure SAN	1.3	2.7	2.1
ERSAN[a]5	1.7	4.6	2.7
ERSAN10	1.4	5.2	3.7
ERSAN20	1.7	6.3	3.7
ERSAN30	2.7	7.7	2.8
ERSAN40	2.5	6.5	2.6

[a] Polymer recovered from composite extracts.

MMT is quite similar to that of quantity of copolymer loading, particularly in case where the samples containing low amounts of MMT are involved. This is the consequence of the adsorption of the excess copolymers on the outer surfaces of MMT particles. Besides, it is also noteworthy that the extracted products reveal about 33 wt % of copolymer content in average, which is a strong evidence of intercalation.

The molecular masses and polydispersity of SAN copolymers recovered from the composite extracts are compared in Table III with that of the pure SAN which has been synthesized with exclusion of clay but using smaller quantity of emulsifying agent than the case of composite preparations. Trends are obvious from the table that the molecular masses of the copolymers obtained from the composite are found not only higher than that of pure SAN, but also proportional to the amounts of MMT added. This molecular mass increasing behavior can be ascribed to the higher concentration of surfactants. The surfactant concentration has been kept at values higher than the critical micelle concentration to avoid the formation of coagulation during the emulsion polymerization. The increasing trend of molecular mass is in line with the following eq. (1) in that the polymer size increases with the emulsifier concentration, under the assumption that there is no termination to occur by chain transfer.[12]

$$X_n = Nk_p[M]/R_i \qquad (1)$$

where X_n is the number average degree of polymerization, N is the concentration of micelles plus particles at a steady state, and R_i is the rate of initiation.[12] The higher concentration of emulsifier can raise the numbers of monomer containing micelles, and hence leads to the higher degree of polymerization. On the other hand, the Table III shows the comparable values of polydispersity indices with that of the pure SAN, suggesting the negligible effect of MMT particles on the molecular mass distribution. All those molecular mass data appeared in Table III are of direct relevance that the presence of MMT dose not affect greatly on the average molecular mass, and hence it seems reasonable that the molecular mass of polymer being intercalated, though not decisive, may be equivalent to those values listed in Table III.

Table IV shows the comonomer composition variations of the intercalated copolymer in the purified composite, together with the data ob-

Figure 12 Room temperature powder XRD patterns of (a) untreated MMT and (b) sonicated MMT in pure water for 1 h.

Table IV   Comonomer Composition Variations of Intercalated Copolymer in Composite Extracted

Sample	Input Ratio (g/g) MMT/SM[a]/AN[b]	Comonomer Ratio of Product (wt %) MMT/SM/AN	SM/AN
Pure SAN	0/70/30	0/81.3/18.7	81.3/18.7
ESAN[c]5	5/70/30	61.6/33.7/4.7	87.8/12.2
ESAN10	10/70/30	64.4/31.7/4.0	88.9/11.1
ESAN20	20/70/30	63.7/32.0/4.4	88.0/12.0
ESAN30	30/70/30	71.1/26.6/2.4	91.8/8.2
ESAN40	40/70/30	72.6/24.8/2.6	90.6/9.4

[a] Styrene.
[b] Acrylonitrile.
[c] SAN-MMT nanocomposite purified by extraction.

tained from the pure SAN copolymer. As evident from the table, all the acrylonitrile contents of the copolymer intercalated are found to be lower than those of input quantity. These relatively low values of the acrylonitrile contents are, in the main, a consequence of the solubility difference between comonomers to water. The solubility of acrylonitrile in water at room temperature is 118 g/L, whereas the styrene marks only 0.07 g/L, the untreated sample, which implies that the exfoliation of the MMT by sonication in an aqueous medium can not be readily occurred.

On the other hand, according to a recent experimental work on the swelling characteristics of clay in the aqueous system[16] the swelling distance of the interlayer can be estimated as follows:

$$d = \{\varepsilon/100\}(t + R_{ion}) + R_{ion} \quad \text{(in m)} \quad (2)$$

where d is the half distance between the two layers, ε is the volumetric strain (%), t is the thickness of the MMT mineral layer, and the R_{ion} is the nonhydrated radius of typical ions existed in the MMT interlayer. Fitting those parameters of known values[8,16] to eq. (2) yields $2d = 35$ nm when the MMT is assumed to be fully expanded. Thus, the monomer containing micells (sized usually 2–10 nm[12] can be introduced directly into the interlayer of MMT by the hydrophilic interaction between the interlayer Na^+ and the micells, and are subsequently polymerized without any occurrence of delamination, while the large-sized monomer droplets (10^3–10^4 nm) are simply copolymerized on the outer surfaces of MMT. Consequently, it is reasonable to suggest that the inter-calation by emulsion polymerization dose not happens under the mechanism of "destruction-reconstruction" but direct intercalation without structural destruction.

CONCLUSIONS

SAN copolymer intercalated MMT nanocomposites were prepared successfully by a simple emulsion copolymerization technique. The XRD patterns of the composite purified by hot extraction with tetrahydrofuran show 001 basal spacing enlargement as much as 1.60 nm, without accompanying exfoliation of clay layers. Thermal characterization by TGA for those purified composites gives evidence of enhanced onset temperature of thermal decomposition, while the DSC thermogram dose not exhibit any traces of thermal transition which is due to the restricted molecular motion of the confined polymer chains. TEM micrograph obtained from the samples not purified reveals orderly arrangement of 1–2 nm sized silicate layers in the copolymer matrix. Scanning electron microscopy and optical micrographs also support the homogeneous dispersions of MMT particles in the SAN copolymer matrix.

For this novel method for the preparation of nanocomposite by emulsion technique, the direct intercalation mechanism without accompanying delamination is proposed on the basis of the interlayer distance of clay derived experimentally from the swelling characteristics of clay in water.

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