Comparison of Characteristics of SAN–MMT Nanocomposites Prepared by Emulsion and Solution Polymerization

MYUNG HWAN NOH, DONG CHOO LEE[1]

[1] Department of Polymer Science and Engineering, Inha University, Inchon 402-751, South Korea

ABSTRACT: Nonextractable styrene–acrylonitrile copolymer–montmollironite (SAN–MMT) nanocomposites were prepared by two different intercalation process: (1) a usual one-step emulsion copolymerization in the presence of the Na^+–MMT; and (2) a solution copolymerization with MMT modified by dimethyl dihydrogenated tallow ammonium. For comparative purposes, the copolymerization conditions (such as comonomer feed ratio and the polymerization temperature and times) were set up to be the same. The X-ray diffraction pattern demonstrated that the net increase of basal spacing of the purified emulsion products (0.76 nm) far exceeded that of composite (0.39 nm) prepared by solution method. The average molecular masses recovered from the composite extracts revealed $M_w = 53 \times 10^4$ for emulsion products, while the composite made by solution yielded $M_w = 4.8 \times 10^4$ g/mol. Likewise, the hybrid from the emulsion polymerization exhibited higher stress at maximum load over the solution products. The dispersibility of MMT particles in the polymer matrix was investigated by using optical microscopy (OM) and scanning electron microscopy (SEM) for those unextracted samples. It was found that almost complete hybrids were obtained when the styrene (ST)–acrylonitryl (AN) comonomer was emulsion polymerized in the presence of Na^+–MMT, yielding both better miscibility and intercalation capability. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2811–2819, 1999

Key words: SAN–montmorillonite, emulsion copolymerization; intercalation; nanocomposite

INTRODUCTION

The development of compounds in which an inorganic solid is associated with organic entities interacting at molecular level (nanocomposite) opens the way to the preparation of new materials with predetermined characteristics. Therefore, various intercalation processes—the grafting of organic groups onto the surface of inorganic surface or the entrapment of molecules in inorganic matrices by sol-gel methods—constitute examples of experimental procedures used to obtain well-controlled dispersions of a selected organic species giving stable nanocomposite materials.

In our recent works on a PMMA– and a epoxy–MMT hybrid composite,[1,2] it was confirmed that a simple one-step emulsion polymerization could offer a new approach to the synthesis of a nanocomposite. The structural characterization for those composites provided evidence that the overwhelming number of fractions of the silicate layers were intercalated with polymers without significant delamination, giving the uniform dispersion of polymer

in the clay layers and enhancing the modulus of elasticity and thermal stability.

On the other hand, various attempts have been made so far to incorporate the organic polymers with clays, depending on their physical, chemical, and mechanical interactions.[3] In particular, a technique of grafting polymers on the clay surfaces by using various organophilic clays has recently attracted a lot of attention.[4–7] Mainly, this technique involved the intercalation of a suitable organic onium salt by cation exchange reaction to the surface of clay interlayer to grant organophilicity, with the subsequent polymerization of the impregnated monomers in the interlayers of the clay.

This article demonstrates the experimental results of comparisons that have been made on characteristics between the styrene–acrylonitrile copolymer–montmollironite nanoscale composites prepared by an emulsion technique (ESAN–MMT) and those of composites obtained from the solution polymerization by employing organophilic clay (SSAN–MMT). As such, it provides a vital starting point for the proper selection of composite preparation methods, not only for the production of an effective and stable nanocomposite but also for the settlement of toxicological and environmental problems.

EXPERIMENTAL

Materials

Cloisite NA^+, supplied by Southern Clay Products Inc., is a Na^+-exchanged MMT, with a cation exchange capacity of 98 meq/100 g. The Cloisite 6A, supplied by the same company, is a organophilic MMT being modified by dimethyl dihydrogenated tallow ammonium and 140 meq/100 g of modifier concentration. The particle size of Cloisite Na^+ in aqueous phase by dynamic light-scattering measurement was found as 1.5 μm but was reduced to 0.5μm after 1 h of sonication, while the measurement of particle size of Cloisite 6A in cyclohexanone was unfeasible due to the sedimentation of the clay particles. Monomers were purified by distillation under reduced pressure before use. Other organic materials were purified by common methods.

Preparation of Hybrid

(1) Emulsion Polymerization. In a 2-L four-necked round bottom flask were placed 600 mL of deionized water, 1.5 g of sodium lauryl sulfate, and 7.6 g of Na^+–MMT. This mixture was stirred at 60°C for 1 h while maintaining sonication. Then 150 g of comonomer (the feed ratio of styrene–acrylonitryl was 7/3 in wt %) and 1.56 g of potassium per sulfate were introduced, and its copolymerization in an emulsion state was allowed to proceed with vigorous agitation for 8 h at 82°C. The reaction mixture was then cooled to room temperature, 10 wt % of aluminum sulfate water solution was added. Products thus obtained were separated by filtration and washed with water several times, and then dried at 70°C under reduced pressure for 48 h. A part of the product was exposed to the soxhlet extraction by tetrahydrofuran (THF) for more than 5 days until no weight loss was detected.

(2) Solution Radical Polymerization. In a four-necked flask, 7.6 g of organophilic clay was suspended in 600 mL of cyclohexanone with vigorous stirring, keeping sonication at 60°C for 1 h. To this reaction mixture, 150 g of comonomer constituted with the same feed ratio as that of the emulsion polymerization and 1.56 g of AIBN were added. This mixture was allowed to react while maintaining vigorous stirring at 82°C for 8 h, and the reaction was terminated by pouring the reaction mixture into a large quantity of *n*-hexane. The products were separated, washed with *n*-hexane several times, and dried under reduced pressure at 70°C for 2 days. A part of the products was purified by hot extraction with THF for more than 5 days.

Measurements and Characterization

Polymer loading for both the purified and the unpurified composite was determined by thermogravimetric analysis (TGA), using a Du Pont 9900 analyzer. A 20-mg sample was then heated to 600°C at a heating rate of 20°C/min in a nitrogen atmosphere. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet spectrophotometer in the wave number range 4,000 ∼ 400 cm^{-1}, and the KBr method was used. X-ray diffraction (XRD) patterns for those powdery samples were obtained from a Philips PW X-ray crystallographic unit mounted with a Guiniar focusing camera. The CuKα radiation source was operated at 40 kV and 20 mA. Patterns were recorded by monitoring those diffractions that appeared in the 2 θ range 2° ∼ 30°C. Thermal char-

acterizations for both the purified and unpurified product were carried out by differential scanning calorimetry (DSC, Du Pont 2100 differential scanning calorimeter) and TGA. DSC measurement was carried out by heating 10 mg of the sample to 160°C at a heating rate of 10°C/min in a nitrogen atmosphere, and the second set of scanning data was accepted. The molecular masses and the molecular mass distribution behaviors of the polymers, having been recovered from the composite extracts, were determined by size exclusion chromatography (SEC). A Waters Model 201 equipped with a U6K injector, an M6000A solvent delivery system, and three linear columns packed with μ-styragel were used. The fractured surface of the composite was imaged by using a scanning electron microscope (SEM, JSM-840A, JEOL), operated with a high-tension voltage of 20 kV. Likewise, an optical microscope, the OPTIPHOT2-POL polarizing microscope, was used to observe the dispersibility of the MMT in SAN matrix of the unpurified composites. Tensile testing of un-extracted products was carried out by employing an Instron (Hounsfield Co. H 25KS). An average value of five specimens was accepted.

RESULTS AND DISCUSSION

Polymer-Loading Behavior

As is well known, in the solution radical polymerization technique, the intercalation or grafting of the polymers to the clay interlayers depends largely on the swelling degree of the organophilic clay promoted by the solvent. Hence, the role of the solvent is to improve the solvation of the interlayer organic cations and the inclusion of monomers between the layers of clay that can be maximized by the solvent. In addition, it must be a good solvent for the monomer and the resulting polymer in order to facilitate movement of the monomer molecules between the clay layers prior to the start of the polymerization. Taking these effects into account, a cyclohexanone was used as the polymerization solvent because it can improve the swelling and penetration of the monomers in the clay interlayers due to the strong attractive forces acting on both the interlayer organic cations and the monomers to be introduced.[3,8,9] However, the vital disadvantages of solution polymerization are the ease of chain transfer to solvent and its removal from the product.

Table I   The Input Ratio and Copolymer Contents in the Composites

Sample Code	Input Ratio of Monomer/Clay (g/g)	Polymer Content in Product (wt %)	
		Before Extraction	After Extraction
ESAN 5	95/5	86.8	39.8
SSAN 5	95/5	82.5	33.3

Table I compares the contents of polymer loading for those composites prepared by both the emulsion and solution polymerization. The value of polymer content revealed by either purified or unpurified SSAN-5 is seemingly comparable with that of ESAN-5, but one cannot simply assign the value of SSAN-5 as the true value of polymer loading because the weight loss on ignition of organophilic clay employed is 47%, which means the clay contains a large quantity of organic modifier. Thus, the real values of polymer loading estimated on the basis of the above weight losses are 70.9 and 17.7 wt % for those products before and after extraction, respectively. This low value of polymer loading, especially for the extracted SSAN-5, is mainly a consequence of both the lower swellability of the solvent compared to water and a higher rate of polymer conversion of emulsion polymerization, together with the loss of interlayer space due to the occupation of a bulky organic modifier.

The lower swellability is considered to be partly responsible for the imperfect dispersion of the Cloisite 6A in the given solvent, even if it has been sonicated. However, the reason for not employing a dispersing agent is to equalize the polymerization conditions with that of the emulsion polymerization and to reduce side reactions, such as chain transfer or termination.

Average Molecular Masses and Their Polydispersity Indices of Loaded Polymers

The results of SEC measurements for the polymers recovered from the extracts of both composites are given in Table II. The table shows that the M_w of RESAN is 11 times larger than that of the RSSAN product. This low value of M_w marked by the solution product is considered to be due not only to the large mass amounts of initiator but also to the shortage of polymerization time. These

Table II Average Molecular Masses and Polydispersity Index of SAN Obtained from the Composite Extracts

Sample Code[a]	$\bar{M}_n \times 10^{-4}$ (g/mol)	$\bar{M}_u \times 10^{-4}$ (g/mol)	$\bar{M}_u/\bar{M}_n$
RESAN 5	18.5	53.0	2.9
RSSAN 5	2.8	4.8	1.7

[a] RSAN, polymer recovered from composite extracts.

unreasonable reaction conditions are intended, as described previously, to make the two polymerization systems identical and to compare their final results. The reasons for low M_w are partly responsible for the chain transfer effect to the solvent, although no quantitative analysis has been conducted, and the unreacted monomers or oligomers remained in the polymerization system due to the increased viscosity of the reaction medium as the polymerization proceeded. This behavior indicates that the solution polymerization in the presence of cyclohexanone is unlikely to be applicable to the high polymeric SAN intercalation.

On the other hand, a large value of polydispersity index (PDI) for the emulsion product can be found in the figures in Table II. As is well known,[10] emulsion polymerization usually results in molecular mass broadening, possibly due to its greater disproportion rather than the coupling reaction at the termination step. On the contrary, the acrylonitryl (CN) content in SAN copolymer was found to be 33.1% for the product obtained from the solution technique, while the emulsion product had a 25.5% content. This result is possibly attributed to the grater solubility of CN in water and hence leads to the decrease of CN content in the monomer containing micelles in emulsion polymerization.

Structural Characterization

Figure 1 demonstrates the IR spectra obtained from purified and unpurified composites, along with those of MMTs and pure SAN copolymers. In Figure 1(a), both the unpurified (ESAN-5) and purified composite (PESAN-5) by emulsion technique exhibit characteristic frequencies of aromatic C—H stretching at 3,070 and 3,030 cm^{-1}, aliphatic C—H stretching at 2,920 cm^{-1}, and —C≡N stretching at 2,226 cm^{-1}, which corre-

spond to those bands of functional groups contained in SAN copolymer. The C—H bending of the aromatic group in the fingerprint part at 750 cm^{-1} is also a proof of intercalation.

Concurrently, an observation of those spectra shown in Figure 1(b), particularly the spectrum of PSSAN-5, gives a strong evidence that the SAN copolymer has been intercalated or grafted in the interlayer of organophilic clay. The strong absorption bands of the C—H stretching of the aliphatic
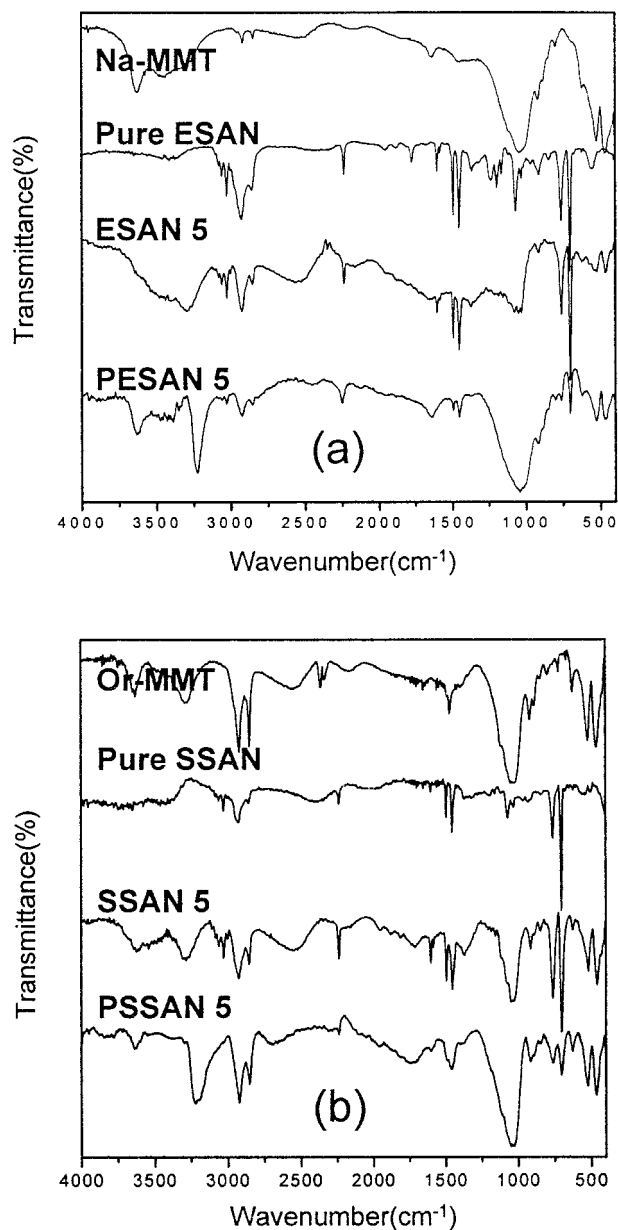
Figure 1 IR spectra of composites synthesized by (a) emulsion- and (b) solution polymerization.
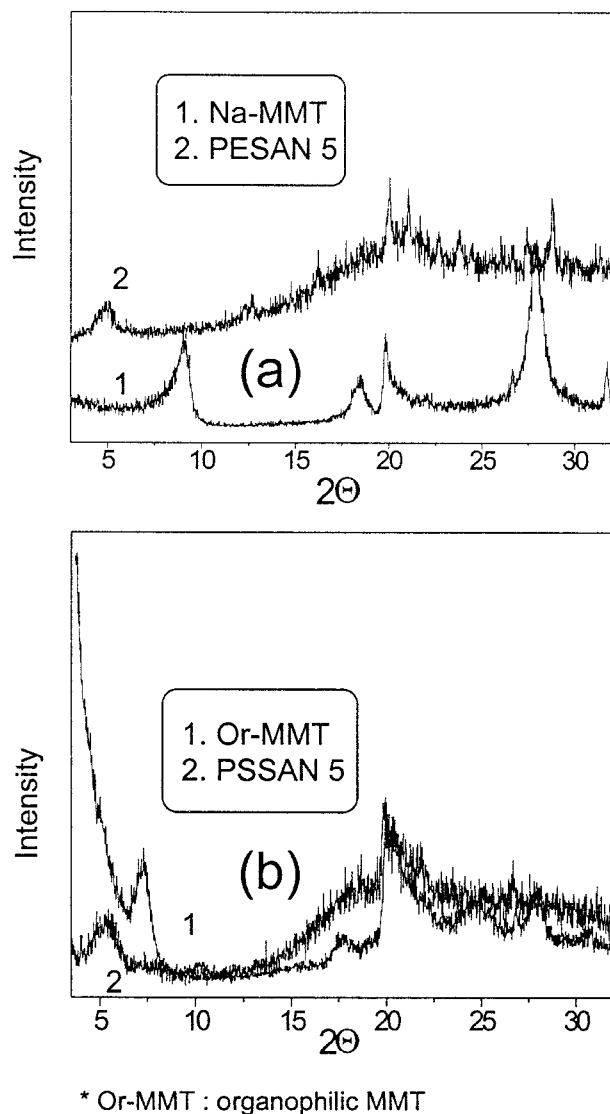
Figure 2   XRD patterns of MMT and purified composites.

part of the organic modifier at 2,920 and 2,850 cm^{-1} from the organophilic MMT and PSSAN-5, even though they are partly overlapped with those of aliphatic C—H stretchings of SAN copolymer, imply that polymers inserted are bound strongly with organic modifier, and hence the polymer is grafted on the interlayer surface.

The results obtained so far by IR spectrum analysis lead to the conclusion that SAN copolymers can be incorporated with MMT interlayer, whether modified with organic ammonium salt or not. However, the case of solution polymerization using organophilic MMT yielded grafted products but a low degree of polymer content, which can be

estimated qualitatively from the intensities of characteristic bands of SAN copolymer.

Figure 2 compares the changes of d(001) basal spacing of the purified composites obtained by emulsion [Fig. 1(a)] and solution [Fig. 2(b)] techniques, and the interlayer distances estimated from the figures are summarized in Table III. A trend is immediately obvious from the XRD data showing that the interlayer distance of emulsion product has expanded as much as 0.76 nm, while the solution product containing organic modifier shows only 0.39 nm expansion. The 0.76 nm expansion of PESAN-5 seems eminently plausible and consistent with the data known so far, which has been obtained from the poly(ether)–Na–MMT $(0.81 nm)^{11}$, and exceeds that of the nylon 6–clay composite $(0.6 nm).^{12}$ This is an indication that the polymer–Na–MMT hybrid nanocomposite by emulsion polymerization has potential for practical applications. On the contrary, as evident from the Table III, the gallery expansion of the solution product is only 0.39 nm. If the existence of organic modifier is taken into account, the expansion of basal spacing is reduced to about 0.2 nm. This low degree of gallery expansion is, in the main, a consequence of the poor swelling power of cyclohexanone and its low conversion to polymer, as long as the polymerization conditions are controlled in order to be identical with those of emulsion polymerization. Thus, the composite prepared by the solution polymerization studied was found to be far behind in its degree of polymer loading and average molecular mass than in the case of composite by emulsion technique. When considering that the driving force for the polymer intercalation by solution method is the entropy gained by desorption of solvent molecules due to the gain in translational freedom of many desorbed molecules from the clay galleries, the be-

Table III   XRD Data of MMT and Purified Composites

Sample Code	Interlayer Distance (nm)	Δd (nm)[a]
Na-MMT	0.96	—
Or-MMT	1.25	—
PESAN 5	1.72	0.76
PSSAN 5	1.64	0.39

[a] Variation of interlayer distance of the montmorillonite induced by organic loading.
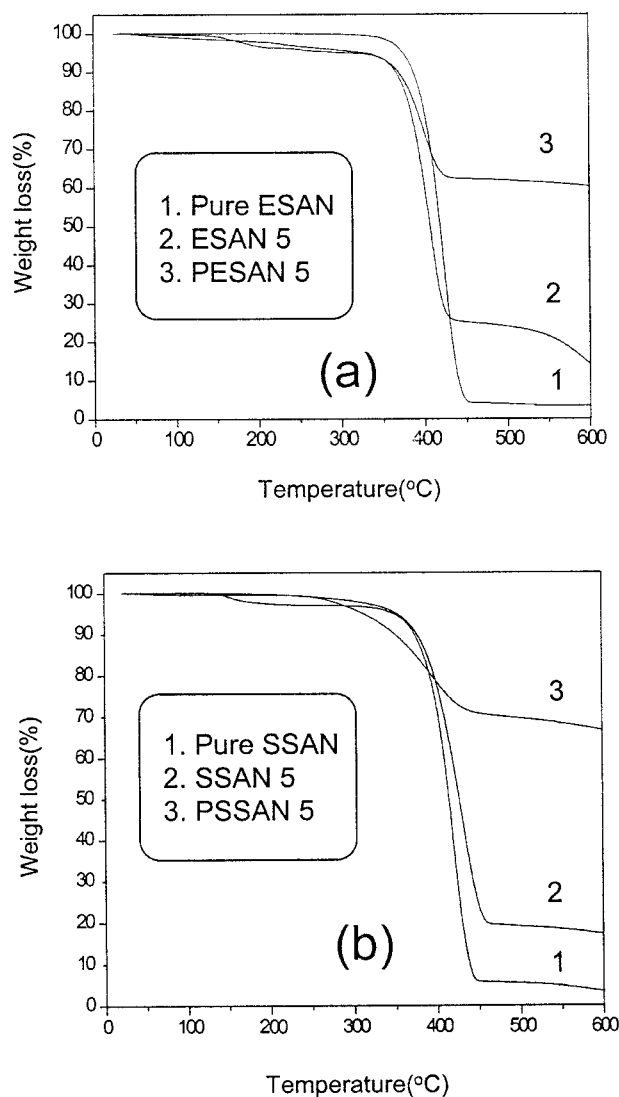
Figure 3 TGA thermograms of pure SAN, composites, and extracted composites.

havior that showed poor intercalation in this study can be explained by the less entropy gain by the desorbed cyclohexanone because of the strong polar interaction between the solvent and positively charged onium moieties.

Thermal Characterization

The TGA thermograms of pure SAN and of those unextracted and purified composites shown in Figure 3(a,b) compare the onset temperatures of thermal decomposition. The pure SAN and the unextracted composites prepared by both methods exhibit nearly the same behavior of thermal

decomposition, regardless of their preparation methods, but the purified composite by emulsion clearly shows an enhanced temperature of decomposition at around 340°C, while the purified PSSAN-5 marks 272°C. This is because, among other reasons, the difference in the molecular masses of those polymers being intercalated. As has been shown in Table II, the M_n value of RSSAN-5 is only 2.8×10^4 g/mol, which is an indication that the composite contains polymers mainly of low molecular masses.

Glass-transition temperatures(T_gs) of the different composite materials, either purified or un-
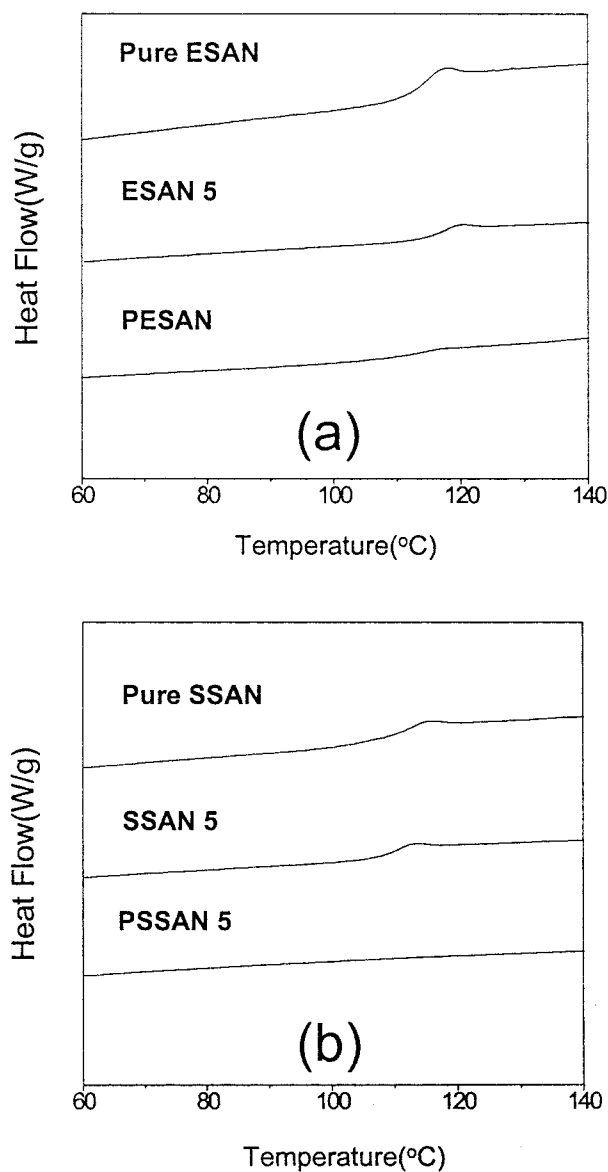
Figure 4 DSC thermograms of pure SAN, composites, and extracted composites.

Table IV Tensile Properties of Different Composites

Sample Code	Stress at Max Load (MPa)	Strain at Max Load (%)	Young's Modulus (GPa)
ESAN 5	42.7	2.75	1.62
SSAN 5	22.3	2.30	1.51

extracted, and the free SAN copolymer that has been recovered from the composite extracts have been determined by DSC measurements and compared, as illustrated in Figure 4(a) (emulsion) and Figure 4(b) (solution). As evident from those figures [Fig. 4(a,b)], both purified composites, PESAN-5 and PSSAN-5, demonstrated no detectable traces of thermal transition, which can be considered as a direct consequence of lower mobility of polymer chains owing to the chain confinement in the galleries of MMT. The unextracted ESAN-5 in Figure 4(a) exhibits T_g = 115°C, which is comparable or slightly higher than that of free polymer, while the unpurified SSAN-5 and pure SSAN in Figure 4(b) show lower T_gs at 110° and 111°C, respectively. Thus, a direct comparison of T_gs between ESAN-5 and SSAN-5 makes it clear that the composite made by the emulsion method demonstrates a higher T_g. Undoubtedly, the higher value of T_g for the emulsion product, even though the —C—N content is low, might stem from the decrease in free volume with the increasing molecular mass, which was originated by the increasing number of connected mers in the system and hence the decreased number of end groups.[13]

Tensile Propertis

Tensile properties of the different composite materials containing 5 wt % of Na–MMT and organophilic MMT were tested and compared. Table IV summarized the stress–strain results obtained in elongation experiments. The values of modulus and elongation at maximum load obtained from those different composites are found to be comparable, whereas the stress of SSAN-5 at maximum load demonstrates quite a small value. Presumably, the polymer of low degree of polymerization and the small quantity of grafted polymer are considered to be the main reasons for the failure of reinforcement.

Regardless of the kinds of MMT, these experimental data indicate that the composite material can be reinforced by simply incorporating a large quantity of polymers having a high degree of polymerization into the MMT galleries.

Morphological Comparison

The morphological aspects of composite materials obtained by both the techniques have been examined using optical microscopy and scanning electron microscopy (SEM) in order to determine the final particle dispersibility in SAN copolymer matrix.
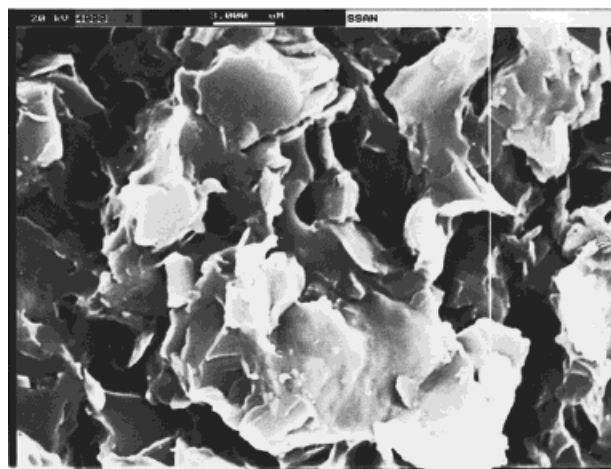
Figure 5 shows the optical micrographs obtained from the ESAN-5 [Fig. 5(a)] and SSAN-5 [Fig. 5(b)]. As evident from the Figure 5(a), clay particles sized around 0.5 μm are dispersed homogeneously in the polymer matrix, while the Figure

(a)

(b)
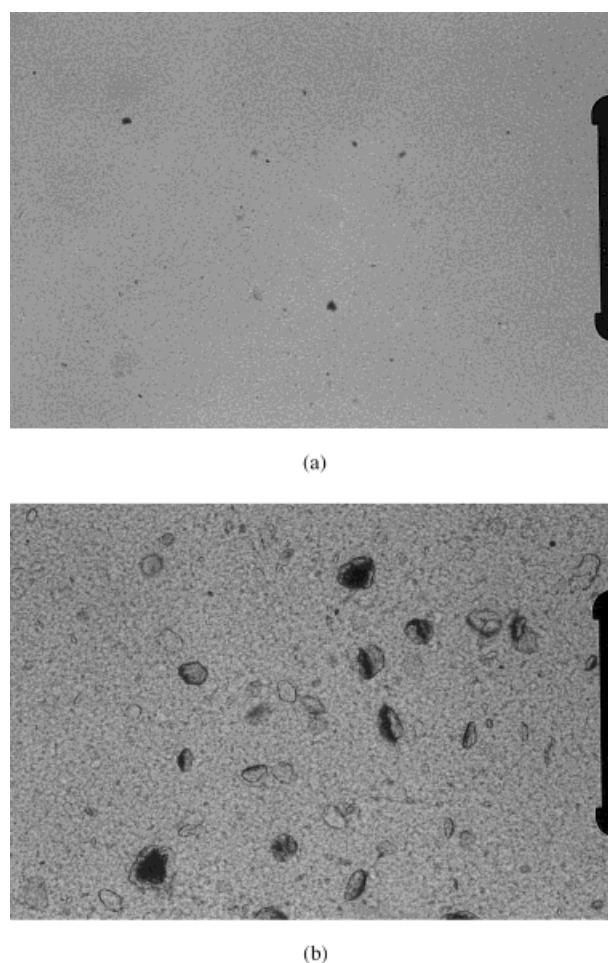
Figure 5 Unpolarized optical micrographs of nanocomposites of (a) ESAN and (b) SSAN-5.
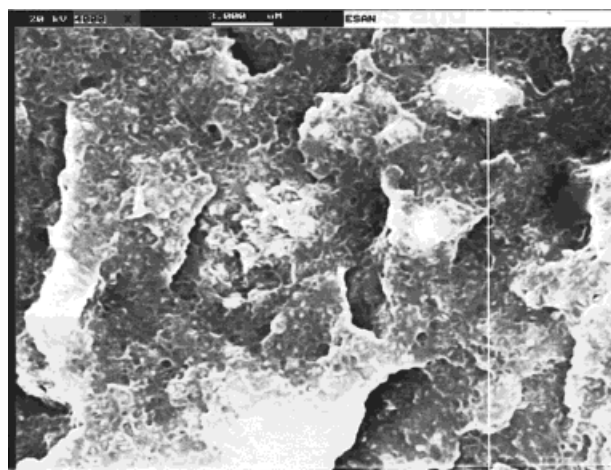
Figure 6 SEM images of fractured surfaces of nano-composites of (a) ESAN and (b) SSAN-5.

5(b) presents a coarse phase of dispersion with clay particles sized about several tens of micrometers. This is probably the consequence of increased surface area of fine clay particles that have been formed by sonication in water before emulsion polymerization.

SEM examination of the fracture surfaces for both the unextracted composites ESAN-5 and SSAN-5 yields quite different morphological phases, as shown in Figure 6(a,b). As is evident from Figure 6(a), the fractured surface of ESAN-5 shows a smooth surface having no voids, deformations, and traces of MMT particles, whereas the Figure 5(b) demonstrates an uneven fractured surface with the inclusion of voids and deforma-

tions. This may ascribed to the irregular dispersion of relatively large-sized MMT particles.

Although we have lost chances to characterize the particle size and morphology for the latex product from the reactor, a physical picture of intercalation by the emulsion technique is proposed in our previous article[2], which states, on the basis of the swelling characteristics of clay in an aqueous system, that the monomer-containing micelles sized as $2\sim10$ nm[14] can penetrate into the swelled interlayer of MMT and subsequently polymerize in an aqueous system. On the other hand, the large-sized monomer droplets ($10^3\sim10^4$ nm) are simply adsorbed or bound to the outer surfaces of the MMT particles and polymerized. If this physical picture of intercalation is truly possible, the particle sizes of latex products can be estimated as slightly larger than that of sonicated Na^+–MMT.

CONCLUSION

Two kinds of SAN–MMT composite materials have been prepared by different types of intercalation techniques. One is based on the emulsion polymerization using Na^+–MMT and water, and the other on the solution polymerization using organophilic MMT and cyclohexanone, both under the same conditions of polymerization. Comparison of those various properties and morphological aspects of the products made it clear that a proper selection of synthetic method appeared to be a matter of great significance in the resulting composite materials. Many physicochemical properties, such as polymer loading into the interlayer of MMT, molecular masses of intercalated polymer, gallery expansion, thermal stability, mechanical properties, and dispersibility of MMT in the polymer matrix of the emulsion product are found experimentally to far exceed those of products derived from the solution polymerization. This indicates that the use of emulsion polymerization is proven to be of great importance in preparing substantial polymer-clay hybrid nanocomposite. In addition, this emulsion technique can also contribute to eliminating toxicological and environmental problems.

REFERENCES

1. Lee, D. C.; Jang, L. W. J Appl Polym Sci 1996, 61, 1117.
2. Lee, D. C.; Jang, L. W. J Appl Polym Sci 1998, 68, 1997.
3. Akelah, A.; Moet, A. J Appl Polym Sci 1994, 55, 153.
4. Pillion, J. E.; Thomson, M. E. Chem Mater 1991, 3, 777.
5. Mehrotra, V.; Giannelis, W. P. Solid State Commun 1992, 51, 115.
6. Aranda, P.; Ruiz-Hitzky, E Chem Mater, 1992, 4, 1395.
7. Messersmith, P. B.; Stupp, S. I. J Mater Res 1992, 7, 2599.
8. Moet, A.; Akelah, A. Mater Lett 1993, 18, 97.
9. Moet, A.; Akelah A.; Hiltner, A.; Baer E. Proc Mater Res Soc, San Francisco, April 2–8, 1994.
10. Odian, G. Principles of Polymerization, 3rd ed.; Wiley: New York, 1991.
11. Wu, J.; Lerner, M. M. Chem Mater 1993, 5, 835.
12. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A. J Polym Sci 1993, Part A, 31, 983.
13. Fox, T. G.; Flory, P. J. J Polym Sci 1954, 14, 315.
14. Odian, G. Principles of Polymerization, 3rd ed.; Wiley: New York, 1991.