

One-Pot Synthesis of Clay-dispersed Poly(styrene-co-acrylonitrile) Copolymer Nanocomposite using Poly(ϵ -caprolactone) as a Compatibilizer

Moon Bae Ko

Material Science and Technology Division, Korea Institute of Science and Technology, Seoul 130-650, Korea

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Abstract : Clay-dispersed nanocomposites have been prepared by simple melt-mixing of three components, i.e. poly(styrene-co-acrylonitrile) copolymer (SAN), poly(ϵ -caprolactone) (PCL), and an organophilic clay (Cloisite® 30A). In the present study, poly(ϵ -caprolactone) was added in the mixtures in order to facilitate the intercalation of SAN into the gallery of silicate layers, and the molecular weight effects of PCL on the dispersion of silicate layers were compared by changing the amount of added PCL. The degree of dispersion of 10-Å-thick silicate layers of clay in the nanocomposites was investigated by using an X-ray diffractometer and a transmission electron microscope. It was found that PCL added in the mixture facilitate the intercalation of SAN copolymers into the galleries of silicate layers modified with an organic intercalant, resulting in the better dispersion of clay. It was, also, observed that the processing temperature influences the degree of clay dispersion.

Introduction

Dispersion of smectite clays and other layered inorganic materials that can be broken down into nano-scale building blocks in polymer matrix is a good method for the preparation of organic-inorganic nanocomposites. While clay-dispersed nanocomposites can be made in a number of ways, this paper will report on studies of melt blending the clay into the polymer. Inorganic montmorillonite surface is modified by organic treatments to make the silicate layer more compatible with an organic polymer. There must be a strong interaction between a polymer chain molecule and the surface of silicate layer (and/or intercalant) in order for a long polymer chain to intercalate into a narrow gallery of silicate layers. Therefore the selection of intercalants and functional groups in the polymer plays a crucial role in accelerating the intercalation of the polymer with smaller strength of interaction with the surface of silicate layer. Ko and coworkers¹⁻⁶

reported some studies on clay-dispersed poly(styrene-co-acrylonitrile) copolymer nanocomposite. It was concluded that it was difficult to delaminate silicate layers perfectly in the SAN matrix, because SAN intercalates less rapidly into the gallery of silicate layers than oxygen-containing polymer such as Nylon. In the present study, clay/SAN hybrids have been prepared by adding PCL in the mixture as a compatibilizer, which was selected by two reasons. First, there are two oxygen atoms in a repeating unit of PCL, which can destroy the hydrogen bonding of the intercalant in an organophilic clay such as Cloisite® 30A by the Southern Clay Products Inc. Second, it is well known that SAN copolymers containing AN content of 8-28 wt% are miscible with PCL.⁷ Poly(ϵ -caprolactone)s with three different molecular weights were added in the mixtures in order to facilitate the intercalation of SAN into the gallery of silicate layers, and the molecular weight effects of PCL on the dispersion of silicate layers were compared by changing the amount of added PCL. Dispersion of 10-Å-thick silicate layers in the hybrids was investigated

*e-mail : mbko@kist.re.kr

by using a transmission electron microscope and an X-ray diffractometer.

Experimental

Materials. "Cloisite[®]" supplied by the Southern Clay Products Inc. is a trade name of organophilic clays. Methyl tallow bis-2hydroxyethyl ammonium (MT-2EthOH) treated organophilic clay (Cloisite[®] 30A) was used in this study. The characteristic properties of Cloisite[®] 30A are found in the previous papers.^{2,3,5} Poly(ϵ -caprolactone)s with three different number average molecular weights (PCL10K = 10,000, PCL43K = 43,000 and PCL 80K = 80,000) as compatibilizers were used as received from Aldrich Chem. Co. SAN copolymer (M_n = 56,000 and AN content = 25 wt%) was obtained from Cheil Industries Inc.

Preparation of Hybrids. Powdery organophilic clay and SAN polymer, and PCL in pellet form were dry-mixed, and then the mixture was melt-blended by using a twin screw extruder (Model TSE 16TC, Prism) to yield pale-yellow strand of hybrid. The obtained strands were chopped with a pelletizer. For this study the inorganic content in a hybrid was fixed at 5 wt%.

Evaluation of the Degree of Clay-dispersion. Dispersion of silicate layers in the hybrid was evaluated by using an X-ray diffractometer and a transmission electron microscope (TEM). An X-ray diffractometer (Model MXP18, MacScience) was adopted to monitor the change in peak intensity for the organophilic montmorillonite after intercalation. $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) was used as X-ray source at a generator voltage of 40 kV and current of 30 mA. TEM (Model CN30, Philips) observations of the hybrids were performed for injection-molded samples, and were operated at an acceleration voltage of 120 keV. Thin sections of 70 nm were microtomed with a diamond knife and then subjected to TEM observation without staining.

Results and Discussion

Figure 1 shows XRD patterns of the clay nanocomposites melt-mixed with the twin screw extruder. The (001) plane peaks are observed

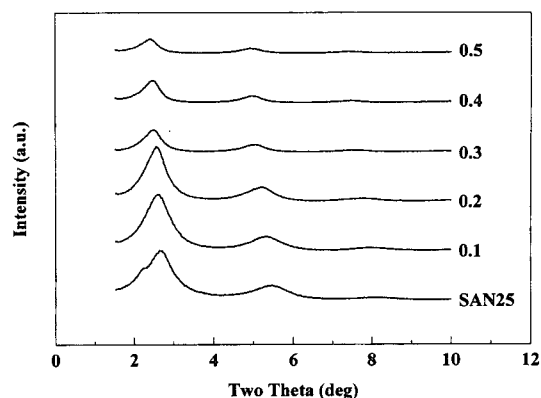


Figure 1. XRD patterns of the clay nanocomposites melt-mixed at 180 °C as a function of PCL10K content in the matrix. The values indicated in the figure represent the fractions of added PCL10K.

around 2.5° in XRD patterns of the hybrids. Therefore it can be said that polymer chains intercalate into the galleries of silicate layers. However, it is observed that the peak intensity of (001) reflection decreases as the fraction of added PCL10K increases. The peak intensity of (001) reflection becomes smaller when smaller fraction of silicate layers is intercalated with matrix polymer or much more intercalated silicate layers lose their crystallographic ordering by the external shear force after the intercalation of polymer chains takes place. It was reported that silicate layers are well delaminated and distributed in PCL matrix.⁶ Thus it could be thought that the dispersion of silicate layers becomes better in the hybrid as the fraction of added PCL10K increases. Hydroxyl groups of MT-2EthOH can form stable hydrogen bonding in the galleries of Cloisite[®] 30A because they act as proton donor/acceptor. It seems that SAN is less compatible with MT-2EthOH because the electronegativity of nitrogen atom in SAN is lower than that of oxygen atom in MT-2EthOH. Therefore SAN itself seems to be difficult to penetrate deeply into the galleries of Cloisite[®] 30A destroying the hydrogen bonding formed between the intercalant molecules, even though the intercalation of SAN can take place. Meanwhile, the oxygen atoms in PCL enable PCL molecules to penetrate more easily into the galleries of silicate layers, due to the stronger attractive

interaction between the intercalant molecule and PCL. Thus the easier penetration of PCL chain molecules into the galleries of silicate layers might be thought to induce the better dispersion of silicate layers.

The peak intensity of (001) reflection can be used as a measuring parameter for the crystallinity of silicate layers intercalated with matrix polymers in the hybrids. Thus the integrated intensity may be used as an exact form for the crystallinity considering the broad XRD peak as follows:

$$\text{crystallinity} \propto \int s^2 I(s) ds \quad (1)$$

where $s (= 2\sin\theta/\lambda)$ is a scattering vector. If we neglect the effect of peak position on the calculated crystallinity of silicate layers intercalated with matrix polymer, the crystallinity is assumed to be proportional to the area of (001) plane peak. Thus $\beta H/2$, in which H and β are the maximum peak intensity (in counts per second) and the full width at half-maximum (in radian), respectively, may be used as a measuring parameter for the crystallinity of intercalated silicate layers. Figure 2(a) is a plot of $\beta H/2$ for various hybrids. The plot shows that the crystallinity of intercalated silicate layers, $\beta H/2$, decreases as the fraction of PCL increases. The decreasing tendency of $\beta H/2$ with the fraction of PCL in the matrix might be resulted primarily from the decrease in the crystallinity of silicate layers intercalated with polymers. Also, an effect from the larger mass absorption coefficient of oxygen atoms in PCL on the XRD reflection rather than that of hydrogen, carbon, or nitrogen atoms in SAN copolymer, should be considered in the calculation of crystallinity. Suppose a material composed of several different kinds of elements whose fractional parts (by weights) are f_1, f_2, f_3, \dots , so that $\sum f_i = 1$. The intensity of transmitted light through all the layers constituting the total thickness, x of the material is well described

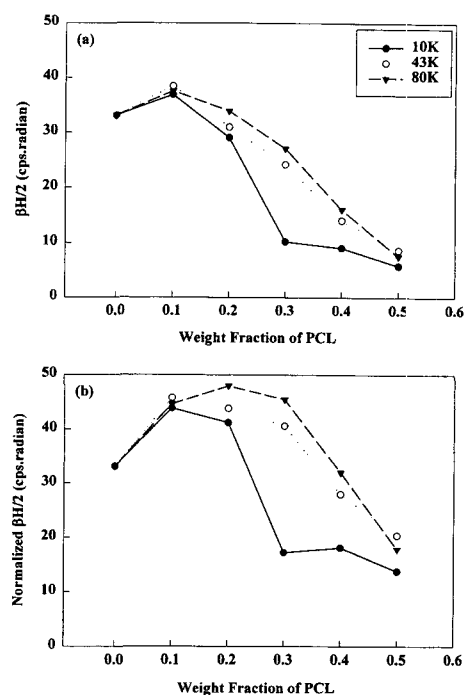


Figure 2. Plots of (a) $\beta H/2$ and (b) normalized $\beta H/2$ for various hybrids prepared at 180 °C.

as the following equation⁸:

$$I = I_0 e^{-(f_1\mu_1 + f_2\mu_2 + f_3\mu_3 + \dots)\rho x} \quad (2)$$

where I_0 is the intensity of incident beam, and μ_i and ρ are the mass absorption coefficient of i^{th} element and a density of the material, respectively. If we let the average values of mass absorption coefficient of materials A and B, φ_A and φ_B , respectively, the intensity ratio of transmitted beams through materials A and B is written as follows:

$$\frac{I_A}{I_B} = e^{-(\varphi_A M_A - \varphi_B M_B)} \quad (3)$$

where M_A and M_B indicate the mass per unit area of the samples A and B, respectively, so that

Table I. Normalization Procedure of XRD Peaks from the Hybrids Containing Different Contents of Poly(ϵ -caprolactone) with Respect to that of SAN Copolymer Hybrid

PCL Content	0 wt%	10 wt%	20 wt%	30 wt%	40 wt%	50 wt%
$\varphi_A(\text{cm}^2/\text{g})$	4.49	4.66	4.83	4.99	5.16	5.33
$M_A(\text{g}/\text{cm}^2)$	1.224	1.218	1.211	1.205	1.198	1.192
I_A/I_B	1.000	0.840	0.707	0.596	0.504	0.427

the normalization of $\beta H/2$ for a blend of SAN and PCL can be achieved with respect to a sample, e.g. a hybrid of SAN copolymer. Table I shows the normalization procedure for the hybrids by selecting SAN copolymer hybrid as a reference. Figure 2(b) is a plot for the normalized $\beta H/2$ of the hybrids. The normalized $\beta H/2$ increases slightly at the fraction of PCL10K, 0.1, compared with that for pure SAN copolymer. This may be resulted from the fact that some unexpanded galleries of silicate layers are expanded by the further intercalation with the addition of PCL10K. The abrupt decrease of normalized $\beta H/2$ at the fraction of PCL10K, 0.3, compared with that at the fraction, 0.2, indicates that PCL10K can act to induce the better dispersion of silicate layers. Meanwhile, the normalized $\beta H/2$ at the fraction of either PCL43K or PCL80K, 0.3, is larger than that at the same fraction of PCL10K. It is also noteworthy that the normalized $\beta H/2$ for the higher fraction of PCL 10K, either 0.4 or 0.5 does not decrease significantly, compared with that for the fraction of PCL10K, 0.3. This means that the further addi-

tion of PCL10K in the mixture does not induce the enhanced dispersion of silicate layers.

Figure 3 is TEM micrographs of the hybrids, revealing that nano-scale building blocks of clay are distributed in the hybrids. Nano-scale building blocks of clay in the SAN/PCL10K blends of 70/30 composition are shown to be smaller in size than those in the hybrid of either 100/0 or 80/20 composition. This shows that the dispersion of silicate layers becomes better losing their crystallographic ordering in the hybrid as the fraction of added PCL increases. However, it is observed that the size of nano-scale building block in the hybrid of 60/40 composition is larger than that in the hybrid of 70/30 composition. TEM micrographs of the clay-dispersed SAN/PCL43K and SAN/PCL80K hybrids of 70/30 composition are shown in Figure 4. Nano-scale building blocks distributed in the matrix are larger in size than those observed in the SAN/PCL10K blends of 70/30 composition. Thus it can be said that the clay dispersion in SAN/PCL10K of 70/30 composition is better than that in either SAN/PCL43K or SAN/PCL80K hybrid of the same composition, which is consistent with the result from the observation by XRD-analysis.

Figure 5 shows a phase diagram for the mixtures of SAN and the various PCLs. A transparent mixture becomes turbid at an elevated temperature as the temperature increases, indicating the existence of LCST. It can be, also, observed that the cloud point shifts to lower temperature at any composition of PCL as the molecular weight increases, due to the decrease in the change of

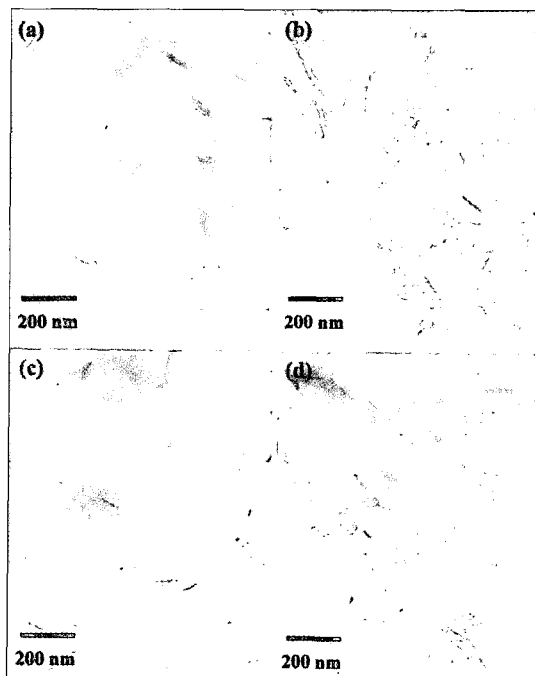


Figure 3. TEM micrographs for the clay/SAN nanocomposites with different contents of PCL10K : (a) 0 wt%, (b) 20 wt%, (c) 30 wt%, and (d) 40 wt%.

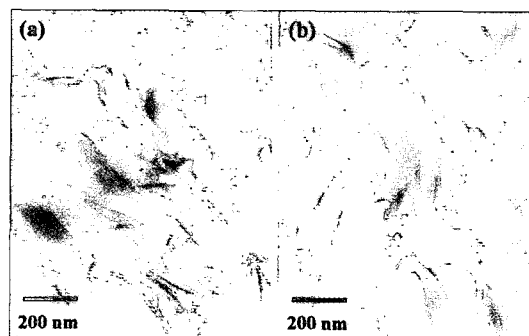


Figure 4. TEM micrographs of the clay-dispersed (a) SAN/PCL43K and (b) SAN/PCL80K hybrids of 70/30 composition.

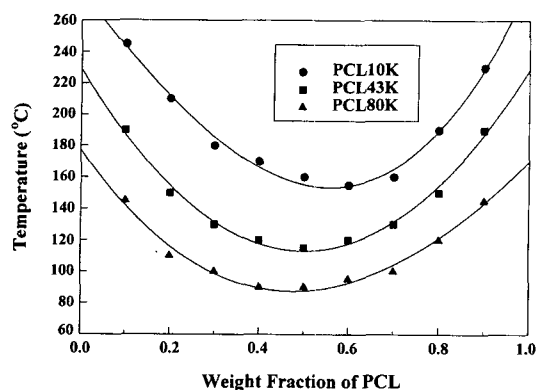


Figure 5. Phase diagram showing LCST behavior for the mixtures of SAN and the PCLs of different molecular weights.

combinatorial mixing entropy. It is necessary to delaminate the silicate layers perfectly in the matrix that SAN copolymer is well miscible with the PCL selected as a compatibilizer at the processing temperature. The silicate layers in SAN-rich domains, when extruding the mixture in thermodynamically immiscible state, is difficult to be intercalated with PCL molecules, so that it is hard to achieve a perfect delamination of silicate layers in the hybrids. As mentioned in the previous paragraph, the dispersion of silicate layers in the hybrid prepared at the fraction of PCL10K, 0.3 is better than that in the hybrid at the same fraction of either PCL43K or PCL80K. This might be due to the fact that the thermodynamic miscibility between SAN and PCL10K at a processing temperature, 180°C, is greater than that between SAN and either PCL43K or PCL80K. The SAN/PCL10K mixture of 70/30 composition at 180°C is located near the cloud point on the phase diagram, while the SAN/PCL43K and SAN/PCL80K mixtures of 70/30 composition at the same temperature lie in thermodynamically unstable region, in which liquid-liquid phase separation is easily induced. Also, the thermodynamically induced liquid-liquid phase separation in the mixtures of SAN/PCL43K, 0.4 and 0.5 is the cause that the further addition of PCL10K does not make the dispersion of silicate layers better, compared with the degree of dispersion of silicate layers in the mixture of 70/30 composition.

It is expected that the selection of processing

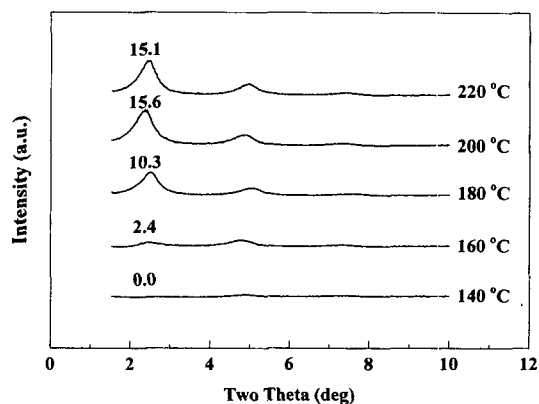


Figure 6. XRD patterns of the clay nanocomposites prepared at different temperatures indicated at the end of trace of XRD pattern. The value indicated near a peak represents $\beta H/2$ of the corresponding hybrid.

temperature is very important in controlling the degree of dispersion of silicate layers. In order to confirm how the miscibility difference between SAN and a compatibilizer affects the dispersion of silicate layers in the matrix, the hybrids of 70/30 composition of PCL10K were prepared by changing the processing temperatures from 220°C to 140°C. Figure 6 shows XRD patterns of the clay nanocomposites prepared at different temperatures indicated at the end of trace of XRD pattern in the figure. The (001) plane peaks are observed around 2.5° in XRD patterns of the hybrids, but the peak intensity becomes smaller and finally disappears at the lower processing temperature, indicating the perfect delamination of silicate layers. The thermodynamic miscibility increases as the processing temperature becomes lower in one-phase region of the phase diagram showing LCST behavior, so that the dispersion of silicate layers becomes better. Figure 7 is the TEM micrographs of the hybrids prepared at two different temperatures, 220°C and 140°C. The TEM micrographs show that while the nano-scale building blocks in the hybrids extruded at an higher temperature in the thermodynamically immiscible region are observed, the silicate layers in the hybrid prepared at a lower temperature of one-phase region are perfectly delaminated. This is consistent with the result from the XRD-analysis, so that it can be concluded that the greater ther-

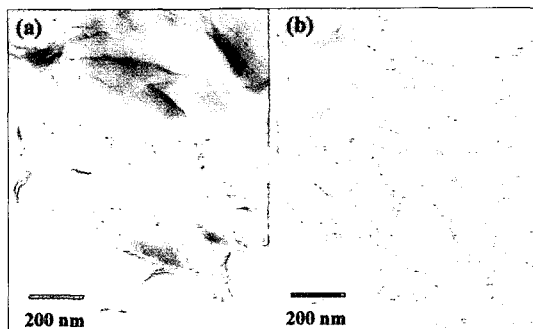


Figure 7. TEM micrographs of the clay-dispersed SAN/PCL10K hybrids prepared at two different temperatures, (a) 220°C and (b) 140°C.

modynamic miscibility between a matrix polymer and a compatibilizer is a necessary condition in selecting the compatibilizer for the clay-delamination by extrusion method.

Conclusions

Clay-dispersed nanocomposites have been prepared by simple melt-mixing of three components, i.e. poly(styrene-co-acrylonitrile) copolymer, poly(ϵ -caprolactone), and an organophilic clay (Cloisite® 30A). In the present study, poly(ϵ -caprolactone)s were added in the mixtures in order to facilitate the intercalation of SAN into the gallery of silicate layers, and the molecular weight effects of PCL on the dispersion of silicate layers were compared by changing the amount of added PCL. The PCL added in the mixture can facilitate the intercalation of SAN copolymers into the galleries of silicate layers modified with an organic intercalant. It was observed that the cloud point shifts to lower

temperature at any composition of PCL as the molecular weight increases, so that the selection of processing temperature is very important in controlling the degree of dispersion of silicate layers. It is necessary in order to delaminate the silicate layers perfectly in the matrix that SAN copolymer is well miscible with the poly(ϵ -caprolactone) at the processing temperature.

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