Polymer Nanocomposites Formation by the Use of Sodium Montmorillonite Dispersion in Alcohol and a Cationic Surfactant

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ABSTRACT: To enhance the formation of nanocomposites, we pretreated montmorillonite clay with a high-boiling-point alcohol or a combination of the alcohol and a cationic surfactant prior to melt mixing. The polymer matrix was melt-mixed with sodium montmorillonite treated with alcohol or a combination of the alcohol and a cationic surfactant, and then, the alcohol was removed. This new method was applied to polymethyl methacrylate, polystyrene, polyethylene, and polypropylene compounds. The dual use of a surfactant and an alcohol for the treatment of montmorillonite enabled a high degree of intercalation of montmorillonite layers by polymethyl methacrylate chains, which was not obtained in untreated clay or clay treated with either the surfactant or alcohol individually. The process was not as successful with the polyhydrocarbons. There was some evidence for slightly enhanced intercalation for polystyrene, but there was less evidence for polyethylene and polypropylene. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1951–1957, 2004

Key words: nanocomposites; surfactants; melt; blending

INTRODUCTION

Nanocomposites have created great interest in polymer science and engineering. From an industrial point of view, nanocomposites made by the melt-blend method have been intensively studied. The polymers for which the melt-blend method has been used include polyamides,[1–3] polyvinyl chloride,[4,5] polyvinylidene fluoride,[6] and various other polar halogenated polymers.[5] It is not possible to produce polymer–clay nanocomposites by this method from polyolefins and other polyhydrocarbons. Some authors have had success with such polymers by making them more polar by introducing maleated materials.[7–9]

It is well known that montmorillonite can be intercalated by alcohols. Theng[10] summarized the relation between the basal spacing of calcium montmorillonite complexes with *n*-alcohols and the number of carbon atoms in the alcohol molecule. He collected various data by several researchers and found that wider spacing tended to be obtained with an increase in the number of the carbon atoms in the alcohol molecule. Weiss[11] conducted a similar study using *n*-tetradacanol as an alcohol. He studied the influence of the cation adsorbed in montmorillonite on the basal spacing. The cations they studied were Mg^{2+}, Ca^{2+}, and Li^+. The typical basal spacing of montmorillonite treated with this alcohol was 3–5 nm compared to the 1 nm of montmorillonite without treatment.

Our purpose in this study was to develop a new method for making polymer nanocomposites with montmorillonite intercalated by an alcohol or a combination of the alcohol and a cationic surfactant.

EXPERIMENTAL

Materials

In our experiments, sodium montmorillonite was used. The cation adsorbed in this clay was Na^+. This clay was supplied by Southern Clay (Closite Na^+) and was used as received.

For comparative study, pretreated montmorillonite with di(hydrogenated tallowalkyl)dimethyl ammonium chloride was also used. This pretreated montmorillonite was supplied by Southern Clay (Closite 20A). This was also used as received.

As an alcohol, *n*-octanol was used. The melting point and boiling point of *n*-octanol were −15°C and 196°C, respectively.

The cationic surfactant we used was di(hydrogenated tallowalkyl)dimethyl ammonium chloride. This surfactant was the exactly same as that used in pretreated montmorillonite (Closite 20A). This surfactant was supplied by Akzo Nobel under the trade name 2HT. 2HT consists of di(hydrogenated tallowalkyl)dimethyl ammonium chloride, isopropyl alcohol, and water in the ratio of 75/17.5/7.5 wt %. The structure of this surfactant is drawn in Figure 1.

$$CH_3—N^+—HT \quad anion; Cl^-$$

CH₃ (top)
HT (bottom)

(HT; hydrogenated tallow)
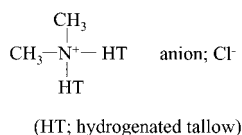
Figure 1 Di(hydrogenated tallowalkyl)dimethyl ammonium chloride.

The polymer matrices we studied were polystyrene (PS), poly(methyl methacrylate) (PMMA), linear low-density polyethylene (PE), and isotactic polypropylene (PP). They were also used as received. Their characteristics are summarized in Table I.

Treatment of sodium montmorillonite with *n*-octanol

Closite Na^+ was dispersed in *n*-octanol at room temperature. The weight ratio of Closite Na^+/*n*-octanol was 1/2.5. This dispersion was mixed with a spatula for 5 min.

Treatment of sodium montmorillonite clay with a cationic surfactant in *n*-octanol

A similar procedure was carried out except with the use of a cationic surfactant (2HT). At first, 2HT was dissolved in *n*-octanol, and then, Closite Na^+ was added. The weight ratio of Closite Na^+/2HT/*n*-octanol was 1/0.67/2.33. This mixture was also mixed with a spatula for 5 min.

PS, PMMA, PE, and PP compounds

These compounds were prepared by four methods:

1. Mixing the polymer matrix and Closite Na^+.
2. Mixing the polymer matrix and Closite Na^+ treated with *n*-octanol.
3. Mixing the polymer matrix and Closite Na^+ treated with 2HT in *n*-octanol.
4. Mixing the polymer matrix and pretreated montmorillonite with 2HT (Closite 20A).

In these experiments, a batch mixer (Brabender Plasticorder laboratory internal mixer) was used.

In method 1, the polymer matrix and sodium montmorillonite were premixed and fed into the machine. The composition of polymer matrix/sodium montmorillonite was 95/5 wt %. The temperature of the mixer was set at 175°C. The materials as described previously were mixed for 10 min at 175°C.

In method 2, at first, sodium montmorillonite and *n*-octanol were mixed at a composition of sodium montmorillonite/*n*-octanol of 1/2.5 (w/w). Then, the polymer matrix and the sodium montmorillonite

treated with *n*-octanol were premixed at a composition of polymer matrix/sodium montmorillonite treated with *n*-octanol of 84.5/15.5 wt %. The temperature of the mixer was set at 175°C. The materials as described previously were fed and mixed for 5 min at 175°C. Then, the temperature was increased to 205°C, and the mixing was continued for another 5 min. The composition after *n*-octanol was removed of polymer matrix/sodium montmorillonite was 95/5 wt %.

In method 3, first, 2HT was dissolved in *n*-octanol. Then, sodium montmorillonite was added. The composition of sodium montmorillonite/2HT/*n*-octanol was 1/0.67/2.33 (w/w). Then, the polymer matrix and this montmorillonite complex were mixed at a composition of polymer matrix/montmorillonite complex of 87.7/12.3. The temperature of the mixer was set at 175°C. The materials as described previously were fed and mixed for 5 min at 175°C. Then, the temperature was increased to 205°C, and the mixing was continued for another 5 min. The composition of polymer matrix/sodium montmorillonite/2HT after *n*-octanol and other volatile materials (water and isopropyl alcohol in 2HT) were removed was 95/3.3/1.7

In method 4, the polymer matrix and pretreated montmorillonite with 2HT (Closite 20A) were premixed and fed into the machine. The composition of polymer matrix/pretreated montmorillonite was 95/5 wt %. The temperature of the mixer was set at 175°C. The materials as described previously were mixed for 10 min at 175°C.

Characterization

Wide-angle X-ray diffraction (WAXD) analysis was performed with a Bruker X-ray machine at room temperature. The operating conditions were 40 kV and 40 mA. The samples measured by this machine were dispersions and powders.

Transmission electron microscopy (TEM; Techna) was also used to directly observe the dispersion of montmorillonite in the polymer matrices. The acceleration voltage was 120 kV.

RESULTS

Treatment of sodium montmorillonite clay with *n*-octanol

n-Octanol and montmorillonite clay (Closite Na^+) were mixed at room temperature to make montmoril-

TABLE I
Polymer Matrices and Their Properties

Polymer	Company	Properties
PS	Sigma-Aldrich	$M_w = 2.3 \times 10^5$
PMMA	Sigma-Aldrich	$M_w = 1.2 \times 10^5$
PE	Dow	Melt flow rate = 1 g/10 min
PP	Equistar	Melt flow rate = 5 g/10 min

M_w = weight-average molecular weight.
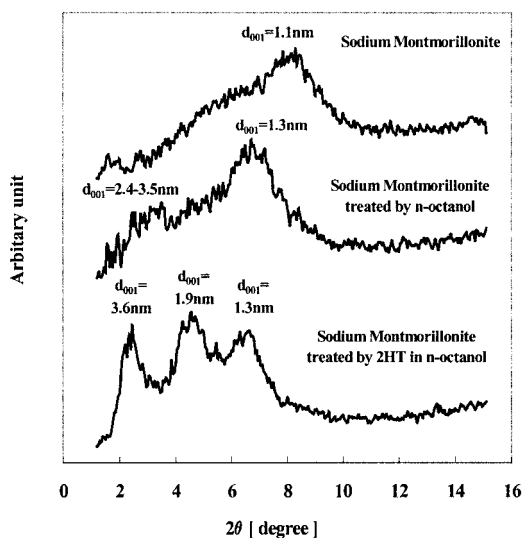
Figure 2 WAXD patterns for (1) sodium montmorillonite, (2) sodium montmorillonite treated with *n*-octanol, and (3) sodium montmorillonite treated with 2HT in *n*-octanol.

lonite complex. The mixture obtained was creamy. Figure 2 shows the WAXD patterns of the sodium montmorillonite (Closite Na$^+$) and its complex with *n*-octanol. The typical basal spacing (d_{001}) between the layers of Closite Na$^+$ was calculated as 1.1 nm on the basis of a peak at 8.0°. Closite Na$^+$ treated with *n*-octanol had a shoulder-type peak at 2.5–3.7° and a distinctive peak at 6.7°. The former peak corresponded to d_{001} = 2.4–3.5 nm and the latter to 1.3 nm. Our experimental results were in agreement with the study by Theng.[10]

Treatment of sodium montmorillonite clay with a cationic surfactant in *n*-octanol

Figure 2 also shows the WAXD pattern of the montmorillonite treated with 2HT in *n*-octanol. Interestingly, this had three distinctive peaks at 6.7, 4.6, and 2.5°, which corresponded to basal spacings of 1.3, 1.9, and 3.6 nm, respectively.

WAXD results

PS compounds

As shown in Figure 3, PS compounds made by methods 1–3 had a very broad peak at 8–13°. This broad peak came from PS itself because the diffraction pattern of PS also had the same broad peak. The PS compound made by method 1 did not have a distinctive peak, and presumably, a peak that corresponded to Closite Na$^+$ was overlapped by the broad peak mentioned previously. The PS compound made by method 2 had a small shoulder-type peak at 6.5°, which corresponded to a basal spacing of 1.4 nm.

n-Octanol, which was used to intercalate Closite Na$^+$, was removed from the compound. The spacing in this compound, which was wider than for Closite Na$^+$, came from the intercalation of the layers by PS chains. It is possible that the *n*-octanol existing in the layers helped some PS chains enter there during melt mixing. The PS compound made by method 3 had two peaks in the pattern, which corresponded to basal spacings of 2.8 and 1.7 nm. The dual use of *n*-octanol and 2HT made it possible to intercalate Closite Na$^+$ by PS chains much more than with method 2. As shown in Figure 4, the PS compound made by method 4 had the almost same diffraction pattern as the PS compound made by method 3. With methods 3 and 4, wider basal spacings than that of Closite 20A were obtained. We assumed that the intercalation by PS chains took place partially in both cases.

PMMA compounds

As shown in Figure 5, PMMA compounds made by methods 1 and 2 had the almost same pattern. They had a broad shoulder-type peak at 6–9°, corresponding to a basal spacing of 1.0–1.5 nm. The peak position was 7.5° for method 1 and 7.0° for method 2. We assumed that the mean basal spacing was larger in the PMMA compound made by method 2 than the corresponding compound made by method 1, which may have indicated that *n*-octanol helped PMMA chains enter the clay spaces during melt mixing. The PMMA compound made by method 3 had two distinctive peaks in the pattern, which corresponded to basal spacings of 3.3 and 1.7 nm. This phenomenon was
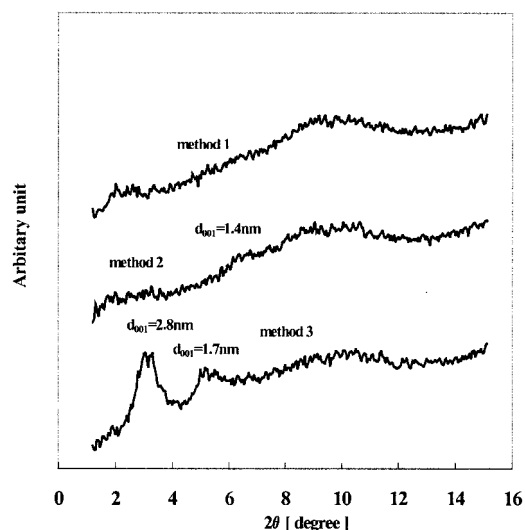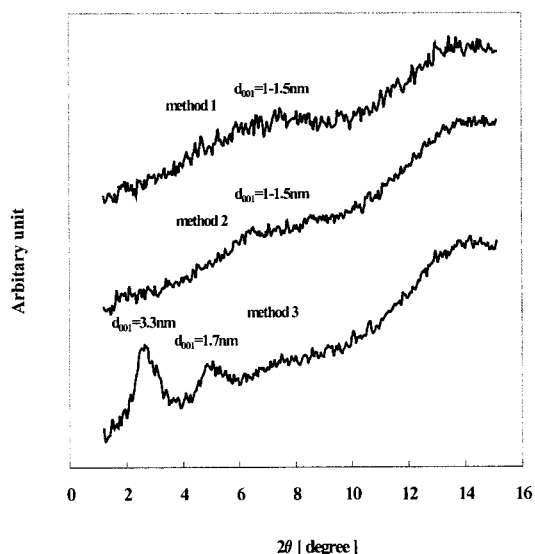

Figure 3 WAXD patterns for PS compounds: (method 1) mixing PS and sodium montmorillonite, (method 2) mixing PS and sodium montmorillonite treated with *n*-octanol, and (method 3) mixing PS and sodium montmorillonite treated with 2HT in *n*-octanol.
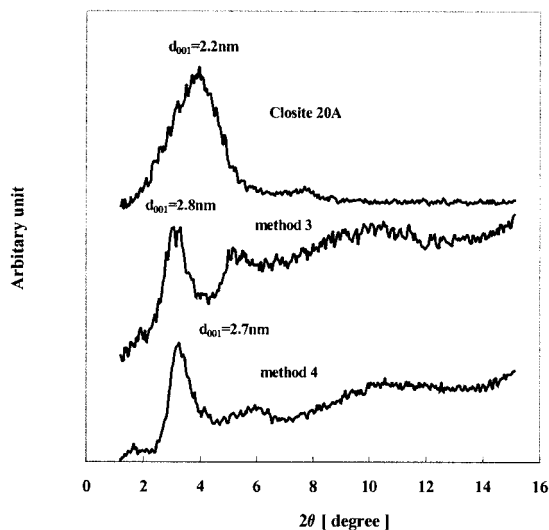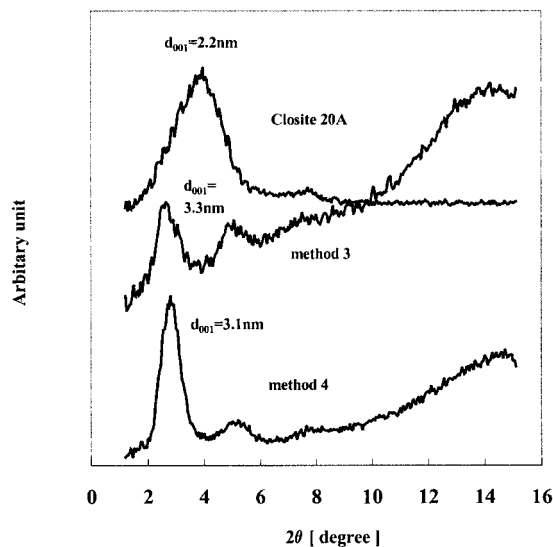
Figure 4 WAXD patterns for PS compounds: (Closite 20A pretreated montmorillonite), (method 3) mixing PS and sodium montmorillonite treated with 2HT in *n*-octanol, and (method 4) mixing PS and pretreated montmorillonite with 2HT (Closite 20A).

Figure 6 WAXD patterns for PMMA compounds: (Closite 20A pretreated montmorillonite), (method 3) mixing PMMA and sodium montmorillonite treated with 2HT in *n*-octanol, and (method 4) mixing PMMA and pretreated montmorillonite with 2HT (Closite 20A).

very similar to the PS compound prepared by method 3. However, the basal spacing obtained for the PMMA compound made by method 3 was larger than for the corresponding PS compound. As shown in Figure 6, the PMMA compound made by method 4 had a peak at a higher angle than that of the compound made by method 3. The PMMA compounds made by both methods 3 and 4 had wider basal spacings than Closite 20A. We assumed that intercalation by PMMA chains

took place in both cases. However, the basal spacing of method 3 (3.3 nm) was larger than that of method 4 (3.1 nm). The effect of the dual use of *n*-octanol and 2HT in the PMMA compound was confirmed.
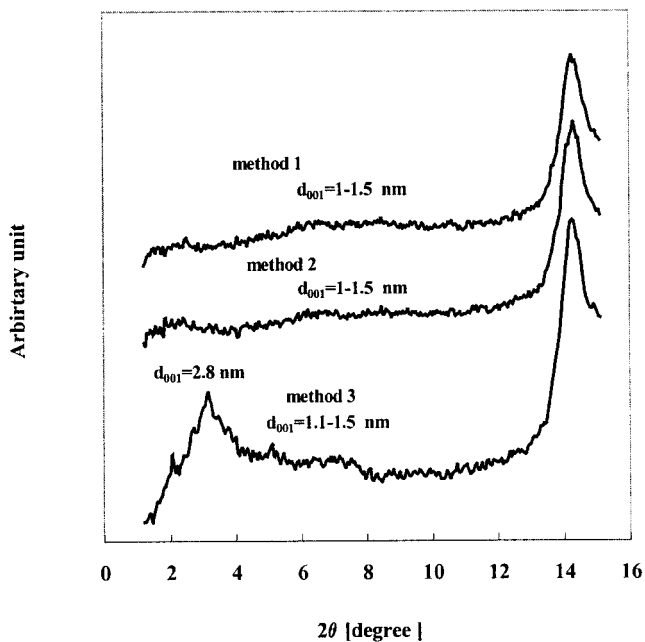
PE compounds

As shown in Figure 7, PE compounds prepared by methods 1 and 2 had a broad peak around at 6–9°, which corresponded to a basal spacing of 1.0–1.5 nm. No effect of *n*-octanol was observed in the PE compound made by method 2. Method 3 showed a peak around at 3.2°, corresponding to a basal spacing of 2.8 nm. Figure 8 compares the PE compounds made by methods 3 and 4. Method 4 showed a peak at the almost same position as for Closite 20A. We assumed that intercalation by PE chains did not take place in method 4. Method 3 had a peak at a lower angle than method 4 and Closite 20A. Intercalation was probably taking place only very slightly in the PE compound made by method 3.

Figure 5 WAXD patterns for PMMA compounds: (method 1) mixing PMMA and sodium montmorillonite, (method 2) mixing PMMA and sodium montmorillonite treated with *n*-octanol, and (method 3) mixing PMMA and sodium montmorillonite treated with 2HT in *n*-octanol.
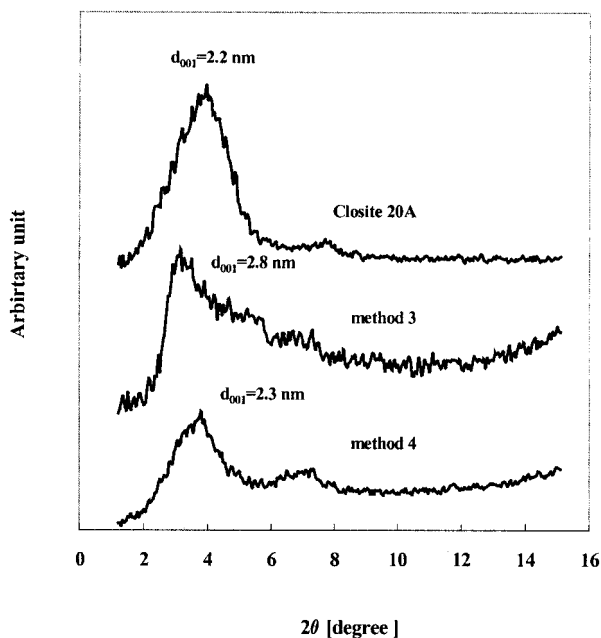
PP compounds

As shown in Figure 9, in the patterns of methods 1 and 2, a broad peak appeared at 6–9°, corresponding to a basal spacing of 1.0–1.5 nm. The effect of *n*-octanol was not observed in the PP compound made by method 2. Method 3 showed a sharp peak at 3.1° and a broad peak at 6–8°, which corresponded to basal spacings of 2.8 and 1.1–1.5 nm, respectively. As shown in Figure 10, methods 3 and 4 showed a sharp peak at
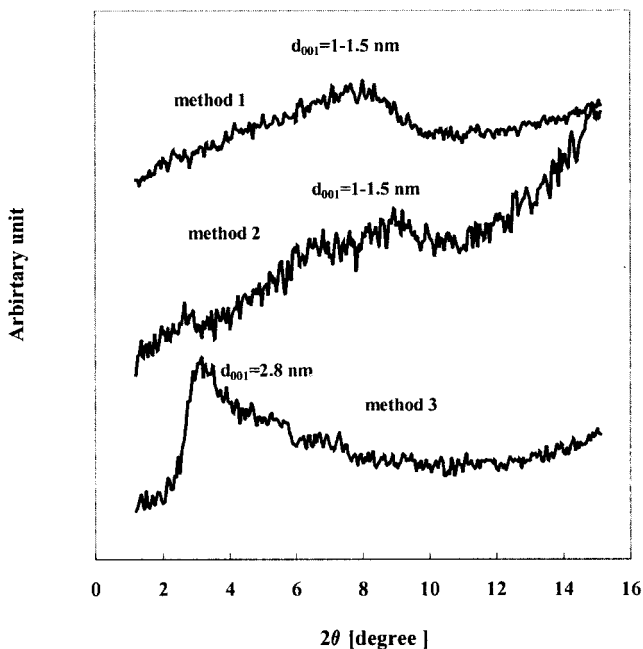
Figure 7 WAXD patterns for PE compounds: (method 1) mixing PE and sodium montmorillonite, (method 2) mixing PE and sodium montmorillonite treated with *n*-octanol, and (method 3) mixing of PE and sodium montmorillonite treated with 2HT in *n*-octanol.
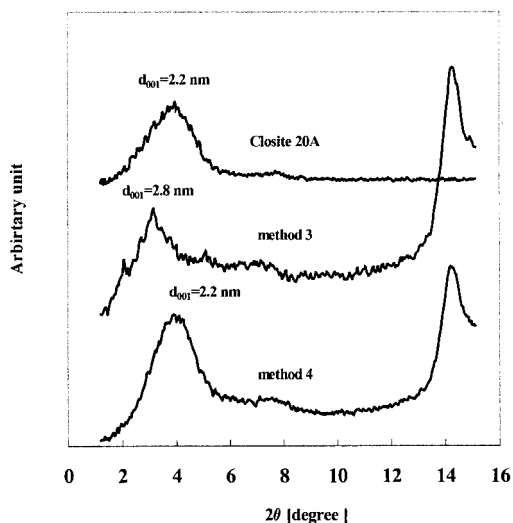

Figure 9 WAXD patterns for PP compounds: (method 1) mixing PP and sodium montmorillonite, (method 2) mixing PP and sodium montmorillonite treated with *n*-octanol, and (method 3) mixing PP and sodium montmorillonite treated with 2HT in *n*-octanol.

different positions. Method 4 showed a sharp peak at the same position (4°) as for Closite 20A. In this case, intercalation did not take place at all. However, method 3 showed a sharp peak at a lower angle than method 4 and Closite 20A. The peak at 3.1° in the pattern of method 3 corresponded to a basal spacing

Figure 8 WAXD patterns for PE compounds: (Closite 20A pretreated montmorillonite), (method 3) mixing PE and sodium montmorillonite treated with 2HT in *n*-octanol, and (method 4) mixing PE and pretreated montmorillonite with 2HT (Closite 20A).

Figure 10 WAXD patterns for PP compounds: (Closite 20A pretreated montmorillonite), (method 3) mixing PP and sodium montmorillonite treated with 2HT in *n*-octanol, and (method 4) mixing of PP and pretreated montmorillonite with 2HT (Closite 20A).
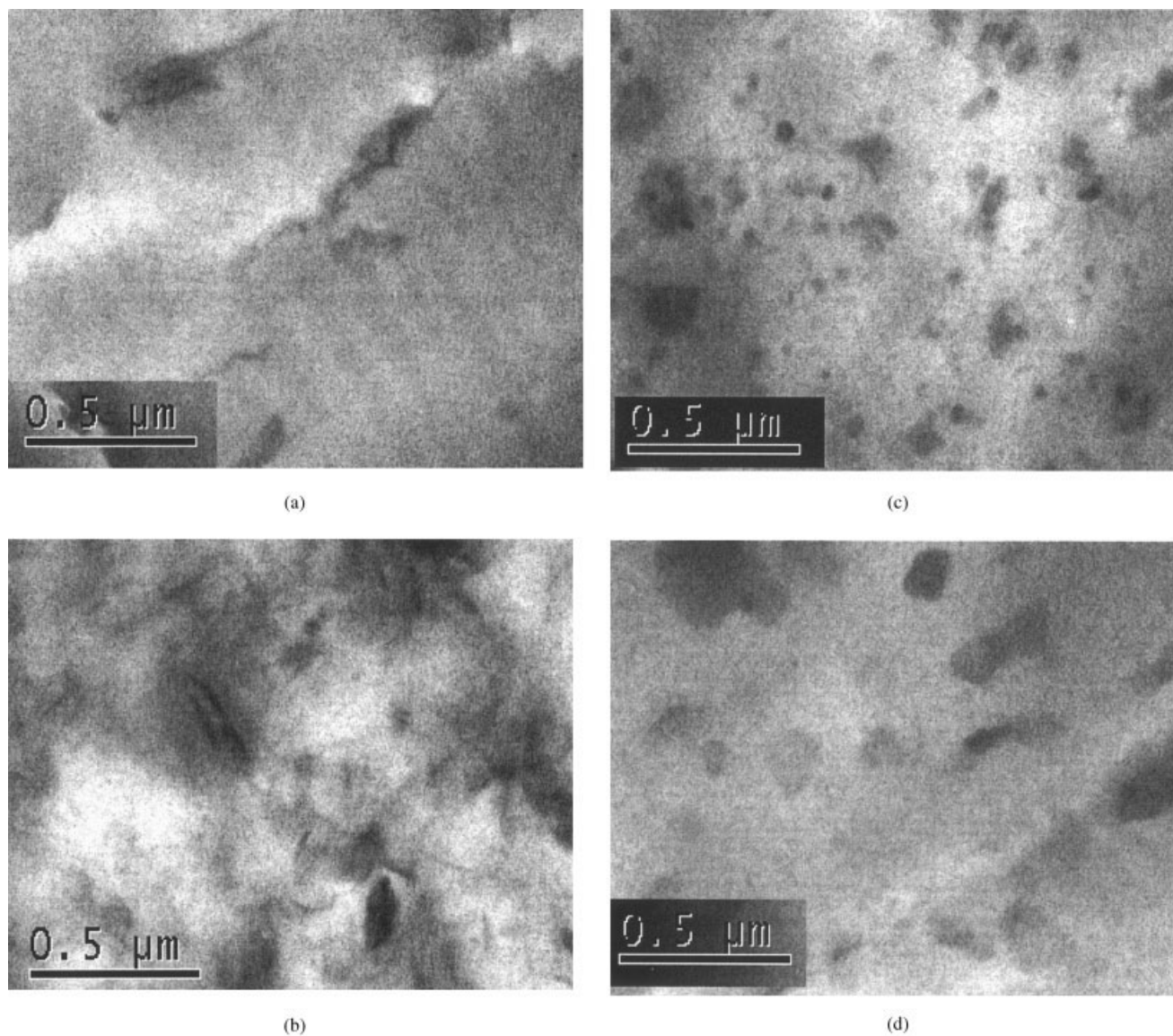
Figure 11 TEM image of compounds made by method 3: (a) PS, (b) PMMA, (c) PE, and (d) PP compounds.

of 2.8 nm. This means that some intercalation by PP chains was taking place in method 3.

TEM study

We compared TEM images of the PS, PMMA, PE, and PP compounds prepared by method 3, where *n*-octanol and 2HT were used. Figure 11(a) shows the image of the PS compound made by this method. The clay existed as tactoids; however, in some parts, exfoliation were seen a little. Figure 11(b) shows the image of the PMMA compound made by this method. There were still some tactoids; however, in some parts, intercalation and exfoliation were seen. Clay dispersion in the PMMA compound made by this method was better than that of the corresponding PS compound. Figure 11(c),(d) shows the images of the PE and PP com-

pounds made by this method. Most clay particles existed as tactoids, and exfoliation was not observed at all.

DISCUSSION

Treatment of sodium montmorillonite with *n*-octanol

Considering the basal spacing (1.3 nm) obtained in this complex and the chain length of the *n*-octanol molecule, we suggest that the chains were lying almost parallel to the silicate layers. However, we also found a shoulder-type peak corresponding to a basal spacing of 2.4–3.5 nm. Some molecules of *n*-octanol presumably extended at a higher inclined angle.

Treatment of sodium montmorillonite with a cationic surfactant in *n*-octanol

As mentioned earlier, we found three peaks in the pattern of montmorillonite treated with 2HT in *n*-octanol. In the space where the basal spacing of 1.3 nm was obtained, only *n*-octanol intercalated, and the alcohol chains were lying parallel to the silicate layers. The basal spacing of 1.9 nm suggested that only *n*-octanol intercalated, and the alcohol chains may have extended at a certain inclined angle. In the place where a basal spacing of 3.6 nm was obtained, both *n*-octanol and the surfactant presumably intercalated.

PS, PMMA, PE, and PP compounds made by method 2

The PS and PMMA compounds made by method 2 had a small shoulder-type peak, which may have indicated the occurrence of intercalation by the polymer chains. This was not observed for the PS and PMMA compounds made by method 1, where *n*-octanol was not used. In the PE and PP compounds made by method 2, we did not see the occurrence of intercalation.

PS, PMMA, PE, and PP compounds made by method 3

Each compound made by method 3 had a wider basal spacing than the pretreated montmorillonite with di-(hydrogenated tallowalkyl)dimethyl ammonium ion (Closite 20A). This means that at least partial intercalation occurred in each case. In method 4, where no *n*-octanol was used, intercalation did not occur for PE and PP compounds, but it did occur for PS and PMMA compounds. Even though the level of the intercalation was not high in PE and PP compounds made by method 3, the effect of the dual use of n-octanol and 2HT was observed. The PS compounds made by method 3 and method 4 had almost same spacing (2.7–2.8 nm). The effect of the dual use of *n*-octanol and 2HT was not clearly detected in PS compounds. The PMMA compound made by method 3 had a wider spacing than the corresponding compound made by method 4. The dual use of *n*-octanol and 2HT in this PMMA compound enabled further intercalation than in method 4, where only 2HT was used.

Significant but not complete exfoliation was also confirmed by TEM analysis in the PMMA compound made by method 3. No exfoliation was observed for the PE and PP compounds made by this method. The level of clay exfoliation in the PS compound prepared by method 3 was lower than in the PMMA compound and higher than in the PE and PP compounds.

CONCLUSIONS

Sodium montmorillonite (Closite Na$^+$) treated with *n*-octanol had a wider basal spacing than sodium montmorillonite itself. When a cationic surfactant was also dissolved, the complex had three distinctive peaks corresponding to basal spacings of 3.6, 1.9, and 1.3 nm.

The PS and PMMA compounds made by the mixing of the polymer with montmorillonite treated with *n*-octanol (method 2) indicated partial intercalation. This was not observed for the PE and PP compounds.

The dual use of *n*-octanol and 2HT enabled further intercalation. The PMMA compound made by method 3 had a very wide basal spacing (3.3 nm). This was larger than that obtained for the PMMA compound made by the mixing of the polymer with pretreated montmorillonite (method 4). The *n*-octanol used in method 3 definitely helped more PMMA chains enter the space between the clay layers than did method 4. In the case of PE compounds, the compound made by method 3 had a basal spacing of 2.8 nm. This value was larger than that of the PE compound made by method 4. Even though the intercalation was not high in the PE compound made by method 3, an effect of the dual use of *n*-octanol and 2HT was observed. Similar phenomena observed for PE compounds were detected for PP compounds. The basal spacing of the PP compound made by method 3 was 2.8 nm. This was larger than that for the PP compound made by method 4, where *n*-octanol was not used and intercalation did not occur at all.

TEM analysis revealed that the PMMA compound made by method 3 had the best quality of clay dispersion among the PS, PMMA, PE, and PP compounds prepared by this method.

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