Tailoring Basal Spacings of Montmorillonite by Poly(oxyalkylene)diamine Intercalation

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Introduction. The use of montmorillonite clay/polymer nanocomposites as advanced materials has been intensively studied because of their excellent thermal[1,2] and mechanical properties.[3−7] The process for preparing such materials typically involves intercalation of the layered silicates and a subsequent exfoliation via in situ polymerization.[8,9] Past research focused primarily on the exfoliation process. The intercalation is generally carried out using various amino acids or alkylammonium salts.[5,6,9,10] Multiple charged amine salts such as tallow diamine, triamine, and tetramine are also effective intercalating agents.[11] However, these intercalating agents can only achieve silicate basal spacings of less than 30 Å. In this paper, we reveal the preparation of layered silicates with *d* spacing as high as 58 or 92 Å by intercalating telechelic POP-diamines. To achieve a large basal height, the POP-diamines require a molecular weight greater than 2000 g/mol. These wide spatially enlarged silicates can encapsulate over 60% (w/w) of organic composition and display an unusual amphiphilic property in toluene/water.

Experimental Section. The preparation of the wide *d* spacing silicates is exemplified here. Na^+−montmorillonite (Na^+−MMT, 10 g, cation exchange capacity (CEC) = 1.15 mequiv/g, obtained from Kunimine Industries Inc.) was dispersed vigorously in 1 L of deionized water at 80 °C. The slurry was added to amine salts prepared from poly(propylene glycol)-bis(2-aminopropyl ether) with a molecular weight of 2000 g/mol or 33 oxypropylene units in the structure (obtained from Aldrich or Huntsman Chemical Co., abbreviated POP2000, 23 g, 11.5 mmol) and equivalents of hydrochloric acid in water. After being stirred vigorously at 80 °C for 5 h, the precipitate was collected at ambient temperature, washed thoroughly with warm water/ethanol, and dried under vacuum. The basal spacing of the intercalated MMT was analyzed by an X-ray powder diffractometer (Schimadzu SD-D1 using a Cu target at 35 kV, 30 mA).

Results and Discussion. Various oxyalkylene diamines including POP- and POE-amines were allowed to intercalate Na^+−MMT. In using POP-diamines of 230, 400, 2000, and 4000 g/mol as the intercalating agents, we found basal spacing of modified silicates at 15.0, 19.4, 58.0, and 92.0 Å corresponding to the molecular weight of the diamines used (Table 1). This implies these POP-diamines intercalate the layered silicates in a similar orientation. In the case of MMT/POP2000, the POP2000-intercalated silicates exhibited a series of Bragg peaks in a pattern from $n = 1$ to 5 (Figure 1), indicative of a more ordered gallery structure compared to the original Na^+−MMT. With the increasing POP-diamine molecular weights, the silicate complexes became highly organophilic.[12,13] For example, both MMT/POP2000 and MMT/POP4000 can be swelled and dispersed in toluene easily by simple mixing, while POP230 and POP400 derived silicates are dispersible only in polar ethanol solvent (Table 1). Dynamic laser particle size analyzer (Brookhaven 90 Plus Particle Sizer) revealed an average particle size of 3−4 μm diameter for MMT/POP2000 in toluene. For comparison, the nonmodified Na^+−MMT, dispersible in water rather than toluene, was reported to have primary structure of 0.1−10 μm.[14,15]

Table 1. Basal Spacing and Property of Na^+−MMT Intercalated by POP− and POE−Diamines

intercalation agent[a]	*d* spacing (Å)[b]	wt fraction (w/w %)[c]	solvophilicity[d,12] toluene	ethanol	water
none	12.4	0/100	−	−	+
POP230	15.0	23/77	−	+	−
POP400	19.4	35/65	−	+	−
POP2000	58.0	63/37	+	+	−
POP4000	92.0	72/28	+	+	−
POE2000	19.4	43/57	−	+	+

[a] POP: poly(propylene glycol)−bis(2-aminopropyl ether) at 230, 400, 2000, and 4000 g/mol. POE2000: poly(ethylene glycol)−bis(2-aminopropyl ether) at 2000 g/mol. [b] Basal spacing by X-ray diffraction. [c] Weight fraction: organic composition/silicate (measured by a thermal gravimetric analysis). [d] + = dispersible; − = aggregate.

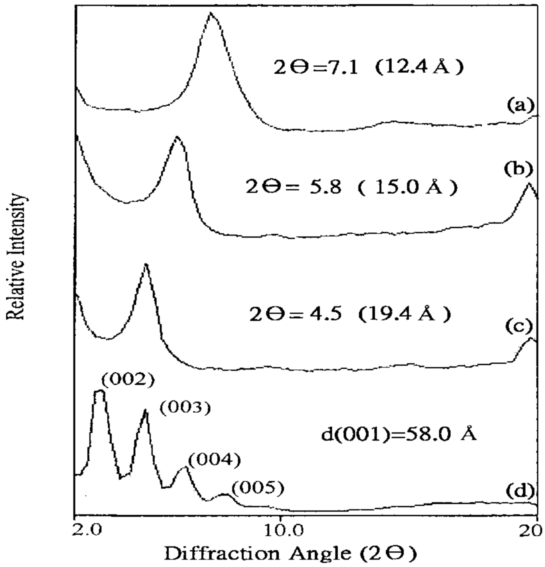

Figure 1. X-ray diffraction patterns of (a) Na^+−MMT, (b) MMT/POP230, (c) MMT/POP400, and (d) MMT/POP2000.

In contrast, the hydrophilic POE-diamine of M_w 2000 g/mol (POE2000) intercalation resulted in a 19.4 Å *d* spacing silicates. The complex consisted of a maximum 43% (w/w) of organic encapsulation and exhibited a stable dispersibility (0.3−0.7 μm) in water and ethanol, but not in toluene (Table 1). The crystallinity of MMT/POE2000 was analyzed by using differential scanning calorimetry (DSC). The enthalpy of crystallinity for the intercalated POE2000 was observed to be 15.0 J/g at

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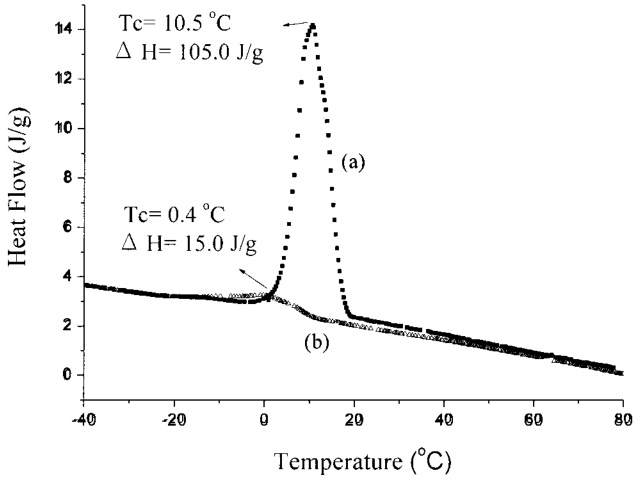

Figure 2. DSC cooling curve of (a) POE2000 and (b) MMT/POE2000.

0.4 °C, which was significantly lower than 105.0 J/g at 10.5 °C for the parent POE2000 (Figure 2). These data imply that the alignment of the POE-diamine orientation is restricted. This is consistent with the previously reported confinement of high molecular weight poly(ethylene glycol)s in clays.[15,16] However, the confined POE segments in MMT/POE2000 are still capable of entrapping ammonium-replaced sodium ions as analyzed to be 0.97% (w/w) for sodium content compared to 0.10% (w/w) for MMT/POP2000. The POE segments in silicates had a higher encapsulating ability for sodium ions than the POP.

The structural differences between POP- and POE-diamine affect the intercalating manners. The hydrophilic POE backbones tend to flatly "adsorb" onto silicate surfaces, due to the polar nature of the $-(CH_2CH_2O)_x-$ structure. On the other hand, the POP-diamines associate with the silicate surfaces via the tethered quaternary amine salts, but not with POP backbone $-(CH_2CH(CH_3)O)_x-$. Therefore, two noncovalent forces, the ionic telechelic amine/clay association and the hydrophobic effect of POP backbone, influence the POP stretching and orientation in the confinement. Consequently, wide spaced silicate platelets were observed to be 58.0 and 92.0 Å by 2000 and 4000 g/mol of the POP-diamines, respectively. To understand the POP arrangement in the confinement, the theoretical length of the fully stretched POP backbone was estimated on the basis of bond length (1.54 Å for C−C and 1.43 Å for C−O) and the bond angles (109.6° and 112°). This amounts to 77 Å for 33 units of $(-CH_2CH(CH_3)O-)$ for POP2000. The theoretical length is much longer than the observed 58.0 Å. Hence, it is reasonable to assume that the POP-diamines arrange in a tilting and perhaps lateral bilayer orientation in the gallery confinement.[11]

These POP-diamine-modified silicates can be considered as cluster of stable micelles, consisting of multiple silicate platelets arranged between the filled POP-amines. The dispersion of MMT/POP2000 in toluene has demonstrated the ability to reduce the interfacial tension in toluene/water, measured by using a Kruss K10 tensiometer. An unusually low concentration of 2−5 dyn/cm indicated the strong tendency for the complexes to self-assemble in the toluene/water interface. The critical micelle concentration (cmc) was estimated to be 0.01 g/100 g or 100 ppm in toluene. For comparison, the MMT/POP230 and MMT/POP400 complexes were shown to have an inferior interfacial property due to their insufficient hydrophobic interaction of short POP hydrophobes. At the toluene/water interface, MMT/POP2000 was able to self-assemble into a thin film, which was dimensionally stable and melted at 160 °C. Under scanning electronic microscopy (SEM), a treelike crystal was observed (Figure 3). The formation of such a crystalline structure is unusual, since POP2000 is inherently amorphous.

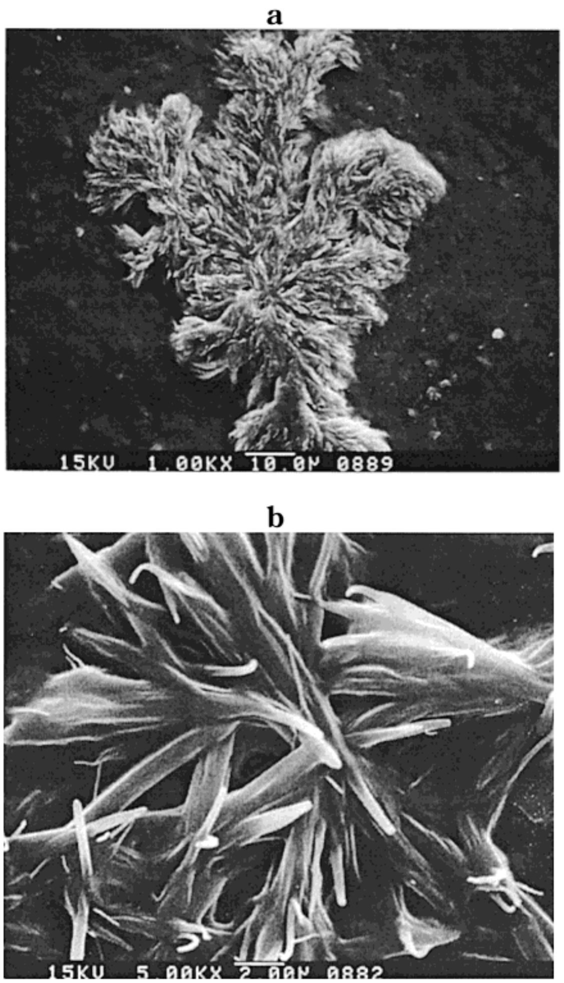

Figure 3. SEM images of MMT/POP2000 film formed at the toluene/water interface (1000× and 5000×).

In summary, the use of telechelic POP-diamines as the intercalating agents allows us to tailor highly ordered and enlarged basal spacing silicates. The wide galleries encapsulating hydrophobic POP-amines rendered the layered silicates amphiphilic and self-assembling.

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