Exfoliation of Montmorillonite Clay by Mannich Polyamines with Multiple Quaternary Salts

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Introduction. Conventionally, the process for preparing the polymer/layered silicate (PLS) nanocomposites[1] requires two steps, organically ionic exchange of layered silicate clays and blending of organoclays into polymer matrixes. The advances of mechanical and physical properties are accomplished by the fine dispersion of exfoliated platelets in polymer matrixes. Since the successful development of Nylon 6/montmorillonite composites by Toyota research group,[2] the developments of other PLS nanocomposites such as polypropylene,[3] polystyrene,[4] polyurethane,[5] polyester,[6] epoxy,[7] and polyimide[8] have been widely reported. Recently, the increasing research efforts on clay usage has shifted to the importance of organic modifications and their compatibility with the target polymers as well as the interaction with biomaterials.[9]

The naturally occurring clays, such as the commonly utilized montmorillonite,[10] can be organically modified by ionic exchange with low-molecular-weight surfactants. For example, the metal ion species in the clay interlayer are exchangeable with cationic organic salts, such as amino acids, alkylammonium quaternary salt, or phosphonium salt.[11] The basal spacing, analyzed by X-ray diffraction, is subsequently widened from the pristine 12 Å to the range of 20−40 Å. Depending on the amount and the species of embedded organics, the modified clays become organophilic and compatible with the hydrophobic polymers. However, the problem of inappropriate compatibility may still be encountered when blending with target polymers. New approaches of selecting organic modifiers for facilitating a complete exfoliation and compatibility in polymer matrixes have been attempted. For example, the intercalating agents with a functionally reactive carbon−carbon double bond[12] and a high-molecular-weight polystyrene backbone[13] were found to improve the PLS properties.

The structure of 2:1 layered silicate/aluminum oxides such as montmorillonite (MMT) consists of two tetrahedron sheets sandwiching an edge-shared octahedral sheet.[14] The negative charges are generated by the isomorphous substitution of silicon or aluminum by lower-valance ions such as magnesium and balanced by the adsorbed counterions (calcium or sodium ions). The commercially available Na^+-MMT clay used in this study has a cationic exchange capacity of ca. 120 mequiv/100 g and an average 8−10 sheets in a primary stack.[15] Although widening the interlayer gallery can be easily achieved, an exfoliation of the layered structure through organic ion exchange is considerably difficult because of the intensive platelet ionic attraction and requires a tremendous force to overcome the inherent ionic bridges.

Previously, we found the intercalation of Na^+-MMT by using α,ω-poly(oxypropylene)-diamine (POP) quaternary ammonium salts afforded a high basal spacing enlargement up to 92 Å.[16] The enlargement is linearly dependent on the molecular weight of the intercalating agent in the range of 2000−4000 g/mol. The finding suggests that, at this spatial enlargement, the attracting force among the distant neighboring silicate platelets is considerably weak and at the verge of exfoliation. However, the intercalation with the high-molecular-weight (>4000 g/mol) POP diamine is limited by the commercial availability and the probable low solubility in water for a proper Na^+-MMT ionic exchange. Hence, we have adopted the synthesis of exfoliating agents from the Mannich reaction of POP-diamine (2000 M_w) with *p*-cresol and formaldehyde.[17] The synthesized amine-terminating Mannich oligomers (AMO) or polyamines, consisting of several POP segments and multiple amine functionalities, were used to modify the hydrophilic clays. The ionic exchange reaction of the AMO with Na^+-MMT was exploited and examined by using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Experimental Section. Sodium montmorillonite (Na^+-MMT), Na^+ type of layered smectite clay (theoretical formula $M^+_y(Al_{2-y}Mg_y)(Si_4)O_{10}(OH)_2{\cdot}nH2O$) with a cation exchange capacity (CEC) of 1.20 mequiv/g, was supplied by Nanocor Co. Polyoxyalkylene-amines including polyoxypropylene-(POP)- and polyoxyethylene-(POE)- backboned diamines were purchased from Aldrich Chemical Co. or Huntsman Chemical Co. The POP2000 is a poly(propylene glycol)-bis(2-aminopropyl ether) with a molecular weight of 2000 g/mol or 33 oxypropylene units in the structure. The POE2000 is an α,ω-diamine of poly(oxypropylene)-*block*-poly(oxyethylene)-*block*-poly(oxypropylene) of 2000 M_w with an average 39.5 oxyethylene and 5 oxypropylene repeating units, respectively.

Preparation of Polyamines from *p*-Cresol, Diamine and Formaldehyde. The typical experimental procedures for preparing the Mannich oligomers are described. To a 1-L round-bottomed flask, equipped with a mechanical stirrer, a thermometer, a heating mantle, and a Dean−Stark trap, was added *p*-cresol (6.8 g, 63 mmol), POP2000 (189 g, 95 mmol), and toluene (100 mL). The mixture became homogeneous when heated to 110 °C with stirring, which was followed by adding formalin (3.8 g, 127 mmol or 1.9 g, 63 mmol in another example) in a dropwise manner. After completing the formalin addition, the reactor was heated to 130−140 °C for 3 h and then to 160−170 °C for 1 h. During the process, the generated water, light materials, and toluene solvent were removed slowly through a Dean−Stark trap. Finally, the temperature was cooled to 90 °C and subjected to a vacuum to remove trace amounts of water and toluene. The recovered product was a viscous and yellowish liquid. Different amine oligomers can also be prepared and confirmed by using amine titration and gel permeation chromatography.

Intercalation of Na^+-MMT with Polyamine Quaternary Salts. The intercalation of Na^+-MMT with AMO was performed according to the procedures de-

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Scheme 1. Synthesis of AMO Polyamines from Hydrophobic and Hydrophilic Polyoxyalkylene-diamine, *p*-cresol and Formaldehyde at Molar Ratio of 2:1:2 or 3:2:4 (x = 1 or 2)

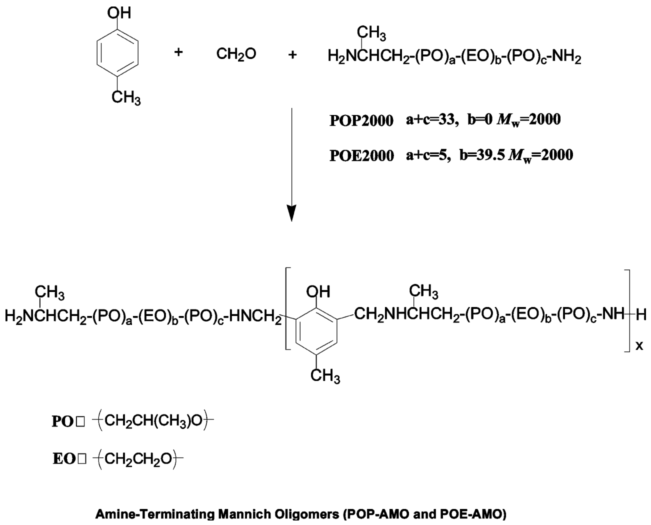

Table 1. Intercalation of Na^+-MMT by AMO Quaternary Ammonium Salt at Different Amine/Quart/MMT Ratios

	amine/H^+/MMT[a]	interlayer distance (Å)	organics/silicates[b] (w/w)
POP-AMO	6:1:1	18	63:37
	6:2:1	50	75:25
	12:2:1	featureless	82:18
POE-AMO	6:2:1	18	
	12:2:1	18	
Na^+-MMT		12	

[a] pH at 9.0 and 8.2 after adding HCl to form quaternary salts at equivalent ratios of 6:1 and 6:2 amine/H^+, respectively. [b] Organic/silicate fraction determined by TGA at 850 °C (in air).

scribed previously. Na^+-MMT (10 g, CEC = 1.20 mequiv/g) was dispersed in 1 L of deionized water at 80 °C by vigorously mixing. The prepared AMO (57.5 g, 24 mmol) and 37 wt % aqueous hydrochloric acid (1.2 g, 12 mequiv) were dissolved in 5 mL deionized water to form quaternary ammonium salts at room temperature and then poured into Na^+-MMT slurry in water. The mixture was continuously stirred at 80−85 °C for an additional 5 h. The precipitate was filtered, collected, and washed thoroughly with 400 mL of water/ethanol several times. The product was dried in a vacuum at 70 °C.

Characterization. The molecular-weight distribution of the prepared Mannich amines was determined by using a Waters apparatus gel permeation chromatograph (GPC). XRD was recorded on a Shimadzu SD-D1 diffractometer with a Cu target (k = 1.5405 Å). The basal spacing (n = 1) was calculated according to Bragg's equation ($n\lambda = 2d \sin \theta$) on the basis of the observed peaks of n = 2, 3, etc. Thermal gravimetric analysis (TGA) was performed on a Seiko SII model SSC/5200 by heating the samples from 50 to 850 °C at 10 °C/min in air. TEM was performed on a Zeiss EM 902A and operated at 120 kV. The sample was prepared by encapsulation in epoxy material.

Results and Discussion. Synthesis of Polyamines as the Intercalating Agents. The Mannich synthesis, first reported[18] in the 1940s, has been well documented for their diversified applications, including epoxy curing agents, polyurethane rigid forms, fuel additives, dispersants, and surface-active agents.[19] The Mannich reaction is versatile in coupling of primary amines into secondary amines with the characteristic $-CH_2NH-$ linkages in the structure. Hence, the reaction is suitably adopted for preparing polyamines with multiple amine functionalities and the consequential quaternary ammonium salts for ionic exchange reactions. The requirements of high-molecular-weight and multiple functionalities can be achieved by the Mannich coupling of *p*-cresol, formaldehyde, and polyoxyalkylene-diamines with controlled molar ratios. To avoid cross-linking polymerization, the difunctional *p*-cresol is chosen instead of the trifunctional phenol in preparation of the desired linear oligomers (Scheme 1). When hydrophobic POP-amines and hydrophilic POE-amines were used as the starting amines, the synthesized AMO could be water-soluble and water-insoluble oligomers, respectively. With the diamine such as 2000 g/mol M_w POE2000 or POP2000 as the reactants, the product distribution is controlled by the stoichiometric molar ratio of the reactants. For example, at the 2:3:4 ratio of *p*-cresol, POP2000, and formaldehyde, the AMO are analyzed to have a GPC distribution of approximately 3:2:1 area distribution, while the 1:2:2 molar ratio also has a 3:2:1 distribution. Further characterizations by amine titration for POP-AMO and POE-AMO at 1.05 and 1.02 mequiv/g, respectively, are consistent with the theoretically calculated results. The comparative GPC analyses also showed a consistency for the coupled structures, consisting of POE or POP-segments, two terminal primary amines, multiple secondary amines ($-CH_2NH-$), and the phenol-linking functionalities.

Intercalation of Na^+-MMT with Hydrophilic and Hydrophobic AMO Salts. By treating with different equivalents of hydrochloric acid, the hydrophilic polyamines derived from the POE2000 Mannich reaction (POE-AMO) was converted into the corresponding quaternary ammonium salts. The water-soluble quaternary ammonium salts were allowed to intercalate Na^+-MMT. The results of X-ray diffraction for these intercalated MMTs were summarized in Table 1. The intercalation afforded the enlarged silicate interlayer from the pristine 12 Å to 18 Å. However, the silicate basal spacing remained the same for the intercalation of POE-AMO with different amounts of HCl treatment. This implies that the POE backbone associates flatly with the silicate surface despite the increase in quaternary ions in the polyamine structure. The hydrophilic intercalating agent molecules have a high affinity for the ionic silicate surface through a backbone $-(CH_2CH_2O)_x-/Na^+$ interaction, regardless of the multiplicity of quaternary salts in the AMO intercalating agent.

In contrast to the hydrophilic POE-AMO, the hydrophobic POP-AMO quaternary salts may behave differently in the layered silicate confinement. Previously, we have reported that the POP2000 amine by itself intercalated MMT at the basal spacing of 58 Å and the analogous POP4000 at an even wider spacing of 92 Å.[16] Because the AMOs are POP2000-coupled amines, the resultant structure is a high M_w POP-segmented amine with POP2000 as the block unit. With the hydrophobic POP backbones, the intercalating agent afforded silicates with 50 Å basal spacing, similar to that from the POP2000 intercalation.

The POP-AMO with a 2:3:4 molar ratio of the starting *p*-cresol/POP2000/formaldehyde, the major product has three POP segments, six amine functionalities (two

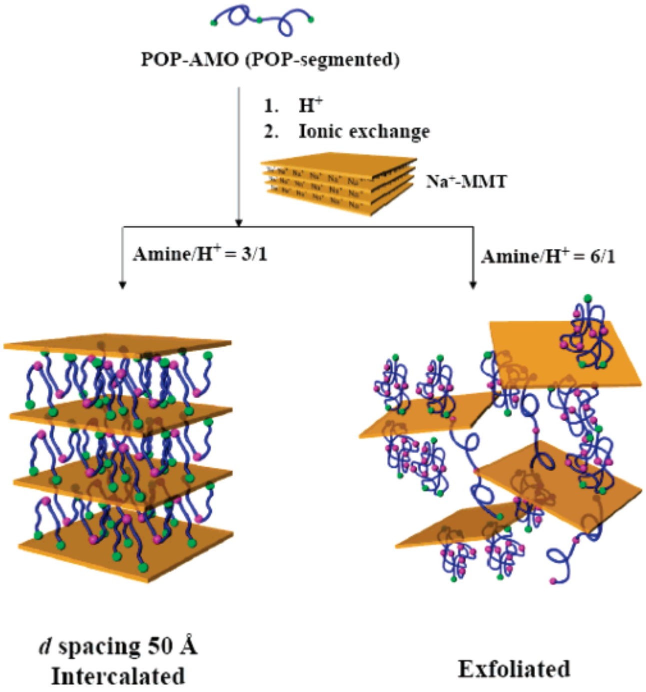

Figure 1. Conceptual representations of intercalated silicate stack and exfoliated platelets in association with the polyamines at different amine/quart ratios.

primary and four secondary), and three *p*-cresol linking cores, as illustrated in Scheme 1. In the structure, six amine-functional sites can all be possibly quaternized with the addition of hydrochloric acid. The formation of quaternary ammonium ions is evidenced by the pH changes during the process of amine acidification. The pH shifted from 11.1 to 9.0 and 8.2 by adding HCl at an equivalent ratio of 6:1 and 6:2 (amine/H$^+$), respectively. The presence of quaternary salt functionality also increases the molecular ionic character and, hence, the solubility in water. In ionic exchange reactions with Na$^+$-MMT, the intercalating mode is influenced by the number of quaternary ammonium cationic sites in AMO molecules for anchoring onto the silicate surface. By varying the quaternary salt/amine equivalent ratios, the AMO would widen the basal spacing in a different manner. The X-ray diffraction has shown a basal spacing of either 50 Å or completely featureless by using the same POP-AMO but with different quaternary salts. This is an indication of different conformations of the embedded AMO in the silicate gallery. In corresponding to the POP2000 intercalation in affording different basal spacing of 47 Å for 2 equiv HCl and 58 Å for 1 equiv HCl,[20] the conformation appears to be directly related to the quaternary ammonium ion sites that anchor onto silicate platelets. Specifically, at the equivalent ratio of amine/H$^+$/MMT at 6:2:1, POP-AMO afforded a basal spacing of 50 Å. On the other hand, with the addition of HCl at the equivalent ratio of 12:2:1, the XRD scan shows no readable diffractive peaks, indicative of complete exfoliation.

Explanation for Intercalation vs Exfoliation. With the varied equivalent ratios of HCl to AMO, that is, quaternary salt to amine ($\equiv NH^+/-NH_2$), the intercalating agents possess different numbers of ionic exchanging sites or anchoring sites onto the silicate surface and, hence, altering their conformations in the silicate confinement. With the ionic exchange sites tethering on the silicate platelet surface, the POP segments could be bent in different conformations. Each anchoring site, representing a quaternary ammonium salt functionality, is an ionic site in exchanging with the sodium counterions within the silicate gallery (Figure 1). Besides the ionic bridge formation, the hydrophobic interaction among the POP2000 segments may self-aggregate into a separate phase that consequently stretches out the platelet distance. The intercalated basal spacing is widened incrementally by the POP segments from 50 Å to possibly over 100 Å or complete exfoliation.

The exfoliation process is evidenced by the TEM observation, as demonstrated in Figure 2, parts a-c with different magnifications for the exfoliated POP-AMO silicates. Particularly in Figure 2c, the fine dispersion

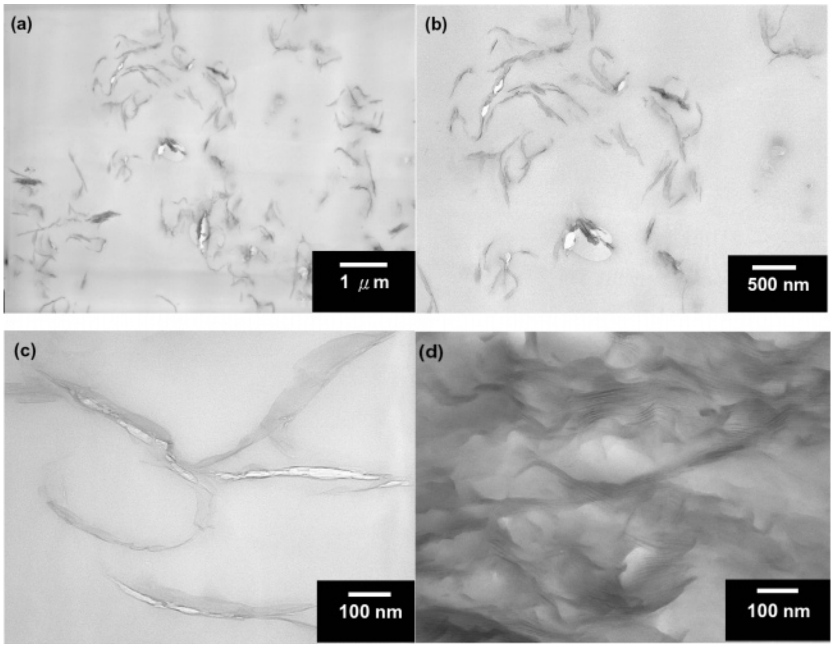

Figure 2. Comparative TEM micrographs of (a−c) the exfoliated POP-AMO/MMT (with featureless XRD pattern) at different magnifications, and (d) the intercalated POP2000/MMT (XRD of basal spacing 58 Å[21]).

of the exfoliated silicates at 1 or 2 individual silicate platelets is observed. For comparison, the POP2000 intercalated MMT (XRD 58 Å) shows the existence of layered silicate parallel lines with interlayer spacing around 50 Å (Figure 2d).[21] The TEM micrograph comparison provides direct evidence for the clay exfoliation, which is consistent with the observation of the amorphous XRD pattern.

In conclusion, the difference between the synthesized hydrophilic and hydrophobic polyamines for the Na^+-MMT intercalation was observed. The hydrophobic POP-AMO affected the layered silicate intercalation to a wide 50 Å basal spacing. With the formation of low quaternary salt/amine ratio (preferred 1:6 molar ratio), the polyamine salt with multiple POP segments in the structure may exfoliate the layered silicates into individual platelets. The POP-segmented quaternary salts undergo an ionic exchange reaction and, consequently, stretch out the layered silicates into the exfoliation. The mechanism for overcoming the intensive silicate platelet attraction provides a new insight for the clay exfoliation.

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