One-Step Exfoliation of Montmorillonite via Phase Inversion of Amphiphilic Copolymer Emulsion

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Introduction. Naturally occurring phyllosilicate clays such as montmorillonite (MMT) are well characterized and conventionally used for catalysts and adsorbent agents in the past.[1] Recently, the dispersion of layered silicates in polymer nanocomposites has been intensively studied[2] since the disclosure of nylon-6/montmorillonite nanocomposite by the Toyota research group.[3] Structurally, the MMT clay is multiple-layered with approximate dimensions of $100 \times 100 \times 1$ nm^3 for each platelet[4] and exist in agglomerates of 1−10 μm in diameter with primary units consisting of 8−10 layered silicate platelets in each stack.[5] In the primary structures, the neighboring platelets attract each other through multiple anionic charges and metal counterions with an exchangeable capacity as high as 80−115 mequiv/g.[2b] Hence, the multiple-layered structure possesses an enormous force of ionic attraction which proves difficult to disperse in hydrophobic organic polymers. Simple ionic exchange reactions by quaternary ammonium salts of low-molecular-weight surfactants could only incorporate the organics into the silicate gallery and widen the basal spacing; however, the structure remains stacked. Continued improvements of product performance for a polymer/layered silicate (PLS) nanocomposite require a fine dispersion of randomized silicate platelets in polymer matrices.[6]

In the conventional process, the PLS nanocomposites are prepared for first intercalating the clays with water-soluble surfactants to alter the hydrophilic characteristics. With consequent organic incorporations, the modified clays become organophilic and compatible with hydrophobic polymers. For instance, the intercalation of Na$^+$-MMT by the 2000−4000 M_w quaternary ammonium salt surfactants afforded organoclays that are highly organophilic with a wide basal spacing of up to 92 Å.[7] However, the exfoliation of multiple-layered silicates requires a second step, the polymer blending or monomer polymerization process, to exfoliate the layered structure into PLS matrix.[8] Overall, the extremely intensive barrier of surface energy between the layered silicates and polymers is resolved through this two-step manipulation.

A direct exfoliation is to delaminate the layered structure into random platelets in the ionic exchanging process and yet have been achieved by using conventional surfactants. A new strategic approach is engaged in order to overcome the enormous ionic forces between the neighboring platelets. Instead of using low-molecular-weight surfactants, we synthesize a family of amphiphilic copolymers capable of forming emulsions in toluene/water in order to interact with the clays. The amphiphilic block copolymers consisting of hydrophilic poly(oxyethylene) segments in the structures may behave as surfactants. In general, these block copolymers enable the formation of micelles and self-assembling structures.[9] By emulsifying the copolymer into a colloidal system, the incompatible materials are brought together to interact. To facilitate the clay ionic exchange, the required copolymer must have dual-functional abilities, self-emulsifying in toluene/water, and ionically exchanging with Na$^+$-MMT. In our previous study,[10] it was found that the comb-branch copolymers with multiple amine pendants could smoothly intercalate MMT at an approximate 19 Å and generated amphiphilic polymer/clay hybrids. However, the micelle-like hybrid is considered a water-in-oil type with a stack of ionic silicate platelets in the core, which is surrounded with hydrophobic polymer backbones in the corona phase. Here, we reveal the use of grafted copolymers with multiple quaternary ammonium salts for exfoliation of Na$^+$-MMT through a micelle phase inversion mechanism.

Experimental Section. a. Materials. Sodium montmorillonite (Na$^+$-MMT), supplied by Kunimine Ind. Co., is a smectite silicate clay with a cationic exchange capacity (CEC) of 115 mequiv/100 g. The maleic anhydride (MA) grafted polypropylene (the meleated PP with a trade name MPP9100) was purchased from Eastman Chemical Co. The sample was titrated to have an acid number of 47 mg KOH/g and was estimated by gel permeation chromatography to have 9100 M_w and 3900 M_n molecular weights. The content of MA was calculated to be about 4.0 wt % or 3.7 MA units per polymer strain. Poly(ethylene glycol)- or poly(propylene glycol)-backboned diamines, or Jeffamine amines, were obtained from Huntsman Chemical Co. Poly(oxypropylene)bis(2-propylamine) of ∼2000 M_w (abbreviated POP2000, amine content 0.98 mequiv/g) is a water-insoluble or hydrophobic diamine with a backbone of 33 oxypropylene units in the structure. The diamine of poly(oxypropylene)-*b*-poly(oxyethylene)-*b*-poly(oxypropylene)-triblock is water-soluble or hydrophilic. The amine has a backbone of 39.5 oxyethylene units in the middle and a total of 5 oxypropylene units at both ends (abbreviated POE2000, white waxy solid, mp 37−40 °C, amine content 0.95 mequiv/g).

b. Characterization and Instruments. X-ray powder diffraction (XRD) analysis was performed on a Schimadzu SD-D1 diffractometer with a Cu target (λ = 1.5405 Å) at a generator voltage of 35 kV, a generator current of 30 mA, and a scanning rate of 2°/min. Thermal gravimetric analysis (TGA) was measured by using a Perkin-Elmer Pyris 1 model at a heating rate of 10 °C/min up to 800 °C under air flow to determine the weight loss of organic fraction. Interfacial tensions were measured by the Wilhelmy method using a Kruss-K10 digital tension meter equipped with a spherical ring. The data in correlation with concentration are graphed. The average particle sizes were estimated by using a Brookhaven 90 Plus particle sizer. Transmission electronic microscopy (TEM) was performed on a Zeiss EM 902 A and operated at 80 kV. A film sample was cut into a wedge shape and then embedded in a polyethylene mold using epoxy resin. The specimen was

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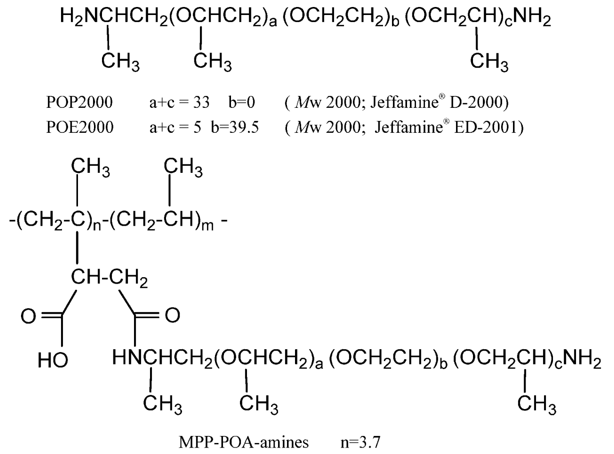


Figure 1. Chemical structures of POA-amines and the grafted PP copolymers.

trimmed into the shape of a trapezoid, cut into thin sections about 80 nm thick, and collected on a 200 mesh carbon-coated Cu grid for the analyses.

c. Intercalation of Na$^+$-MMT with the MPP-POA-Amines. Two poly(oxyalkylene)-amines (POA-amines), POP2000 and POE2000, were grafted onto the meleated polypropylene (MPP) according to the procedures described previously.[11] The grafted copolymers are abbreviated as MMP-POP2000 and MPP-POE2000, respectively. The typical procedures for the ionic exchange reaction of montmorillonite are described in the following example. To an autoclave equipped with a mechanical stirrer, nitrogen pressure lines, and a heating devise, Na$^+$-MMT (5.0 g, cation exchange capacity 1.15 mequiv/g) in 200 mL of deionized water was charged, heated to 80 °C, and kept stirring until swollen. A solution of MPP-POE2000 (25.6 g, 5.75 mequiv) in hot toluene (about 80 °C) was acidified with a portion of concentrated hydrochloric acid (0.59 g, 5.75 mequiv) and then charged into the autoclave. The mixture was stirred at 120 °C under 500 psig of N_2 pressure and maintained for 5−6 h. The reactor was allowed to cool to ambient temperature, and the product was recovered by decantation. The product was toluene/water washed, air-dried, and then analyzed for *d* spacing (XRD) and organic fraction (TGA).

Results and Discussion. a. Preparation of Amphiphilic Copolymers as the Ionic Exchanging and Exfoliating Agents. The maleated polypropylene (MPP), consisting of a PP backbone and multiple maleic anhydride (MA) functionalities, was subjected to the grafted reaction with POA-diamines according to the procedures reported previously.[11] The diamine grafting reaction onto a functionalized PP with an averaged 3.7 MA may cause cross-linking, which was minimized by using a highly dilute solution with a slight excess of the diamine equivalent. However, the variation in product distribution exists in different batches of the synthesis. The synthesized copolymers consist of two different kinds of functionalities: the hydrophobic PP backbone portion and the multiple POA-quaternary ammonium salts as the ionic exchanging sites (Figure 1). Both POE2000 and POP2000 grafted MPPs are amphiphilic and interact with the toluene/water mixture. Their relative emulsifying ability was measured by their micelle particle sizes in toluene and the toluene/water mixture. As summarized in Table 1, the MPP-POE2000 and MPP-POP2000 copolymers in hot toluene have average micelle sizes of 120 and 280 nm, respectively. With the conversion into the corresponding quaternary salts by treating with aqueous HCl, their particle sizes decreased to about 50 nm at 75 °C for the case of MPP-POE2000. The particle sizes became larger (1 μm) when cooled to 25 °C due to the serious aggregation or partial insolubility.

Table 1. Particle Sizes of MPP/POA-Amines in Toluene (1.0 wt %) at Different Temperatures

sample	acidification ratio (H^+/NH_2)	average diameter (nm) 25 °C[a]	average diameter (nm) 75 °C[b]
MPP-POE2000	0/1	260	120
	1/1	1000	50
MPP-POP2000	0/1	1600	280
	1/1	1200	150

[a] Sample was prepared by dispersion at 25 °C (cloudy solution). [b] Sample was prepared by dispersion at 75 °C (transparent solution).

b. Comparison of Intercalating and Exfoliating Na$^+$-MMT by the Copolymers. The intercalation was performed by mixing the swelled Na$^+$-MMT in water and the emulsion of copolymer amine salts in toluene/water. The pendent quaternary ammonium ions of the copolymers underwent an ionic exchange reaction with Na$^+$-MMT at 80 °C under atmospheric pressure or at 120 °C under 500 psig of N_2 for 5−6 h in a close system. The hybrid gallery incorporation of the organic fractions was measured by TGA, and the relative dispersing abilities were measured by a laser particle analyzer (Table 2). A fine emulsion, enhanced by the presence of quaternary ammonium ions in the structures, is crucial to the ionic exchange and the effective intercalation of Na$^+$-MMT. In comparison, the MPP starting polymer failed to affect the MMT *d* spacing (12.4 Å) because the ionic exchange reaction did not occur, while the MPP-POE2000 and MPP-POP2000 copolymers intercalated the layered silicates with a change in *d* spacing changes to 19.5 and 19.1 Å, respectively.[10] The ionic exchange was performed at a higher temperature (120 °C) in autoclave (500 psig N_2) and actually exfoliated Na$^+$-MMT into random platelets, which was observed by XRD as either a featureless pattern or a *d* spacing larger than 100 Å; furthermore, the direct exfoliation of MMT platelets is determined by the micrographs of TEM. In Figure 2c,d, the copolymer intercalated MMTs is shown to have stacks of layered structures with an average *d* spacing of ∼19 Å, consistent with the XRD analysis. In contrast, the exfoliated MMT (Figure 2a,b) exhibits an irregular form of silicate platelets which are well-dispersed in the matrix and also randomized without any significant regularity.

The effectiveness of exfoliating the layered MMT appears to be controlled by the emulsion size of copolymer. With different emulsion sizes, the copolymers undergo the ionic exchange reaction with Na$^+$-MMT to results on intercalation or exfoliation, conceptually illustrated in Scheme 1.

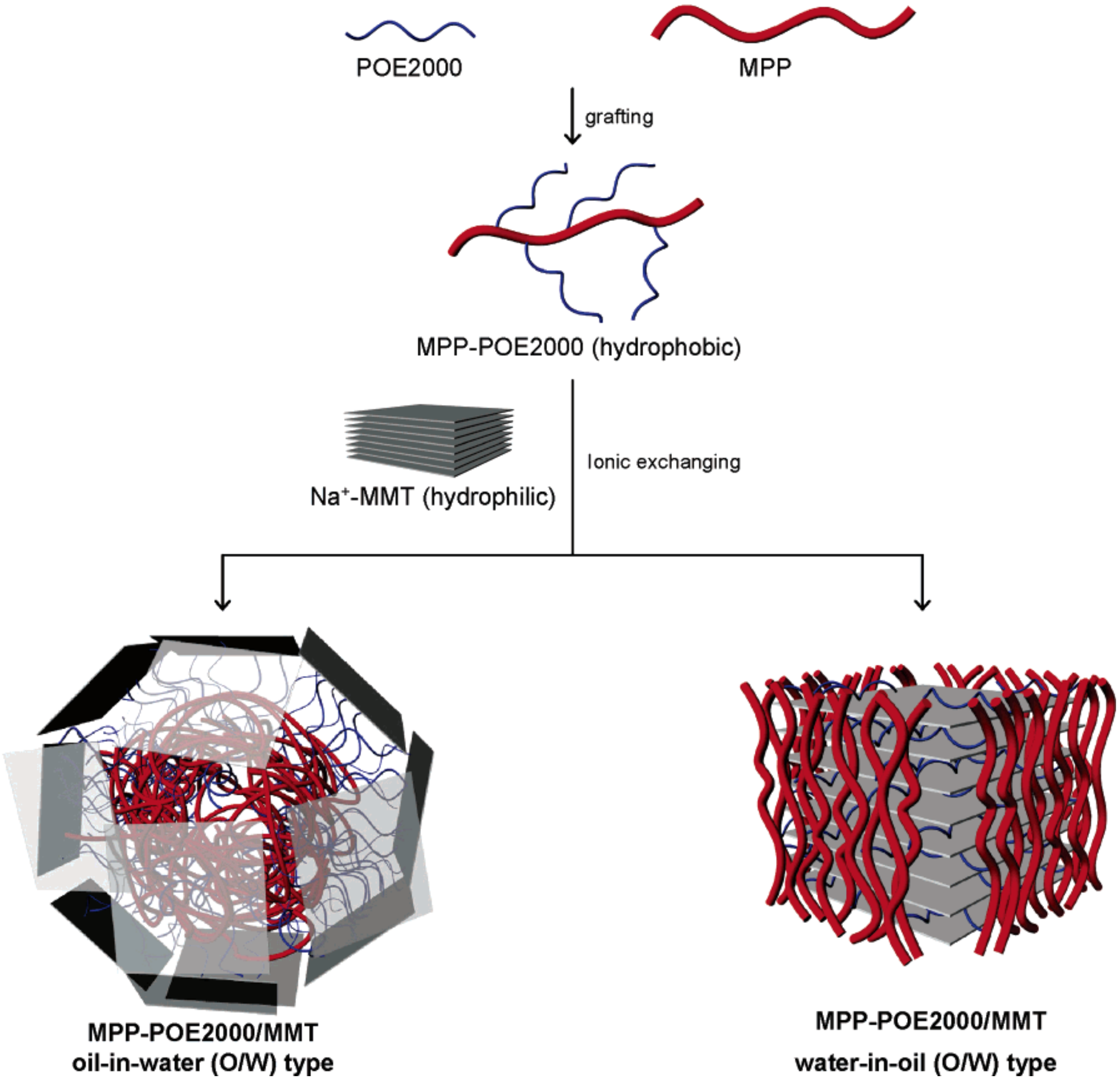
c. Explanation for the Direct Exfoliation by Finely Emulsified Copolymers. The requisite ionic exchanging agent is the comb-branched copolymer consisting of a hydrophobic polypropylene backbone and several pendant poly(oxyethylene)-tethered quaternary ammonium salts. The copolymers are soluble in hot toluene and form an emulsion in the toluene/water mixture. Hence, the ionic exchange reaction with the silicate sodium ions in the gallery is a function of temperatures. At 80 °C, the multiple quaternary am-

Table 2. XRD *d* Spacing, Organic Fraction, and Dispersing Size of MPP/POA-Amine Intercalating MMTs

intercalating agent	*d* spacing[a] (Å)	weight fraction (w/w)[b]		average diameter (nm)	
		based on CEC	based on TGA	25 °C	75 °C
none	12.4	0/100			
at 80 °C[d]					
MPP	12.4	74/26	32/68		
MPP-POE2000	19.5	84/16	82/18	570	580
MPP-POP2000	19.1	84/16	76/24	500	430
at 120 °C[e]					
MPP-POE2000	featureless	84/16	84/16	125	150
MPP-POP2000	featureless	84/16	84/16	115	120

[a] *d* spacing by X-ray diffraction. [b] Organic fractions (weight ratio of organics/silicates), based on CEC stoichiometric calculation (1.15 mequiv/g × M_w of intercalant) or TGA analyses. [c] Laser particle size analysis of MPP/POA-amine copolymer intercalating MMT in toluene (1.0 wt %). [d] The intercalation was stirred at 80 °C under atmospheric pressure for 5−6 h. [e] The intercalation was stirred at 120 °C under 500 psig of N_2 pressure for 5−6 h.

Scheme 1. Amphiphilic Copolymer for Na$^+$-MMT Exfoliation and Intercalation



monium sites intercalated with the layered silicates forming a 19 Å basal spacing. The configuration of a silicate stack in the core and PP aggregates in the surrounding corona represents a water-in-oil (W/O) micelle-like structure, as illustrated in Scheme 1. At the elevated temperature (120 °C under 500 psig of nitrogen in an autoclave), the copolymers not only intercalated but also exfoliated the Na$^+$-MMT, with a featureless XRD pattern. A transformation of copolymer/silicate micelles from W/O into O/W type of configuration is envisioned. The transformation is favored by the presence of water, in which the silicate stack is readily converted into the O/W structure with the ionic silicate platelets surrounding the corona phase. The transformation drives the intermediate micelle into a thermodynamically more stable form and renders the clay into exfoliated silicate platelets during the process. Ultimately, at a high temperature and with fine copolymer particles, the ionic exchange reaction facilitates the stepwise mechanism in overcoming the energy barrier of platelet ion attraction and delaminating the layered arrays.

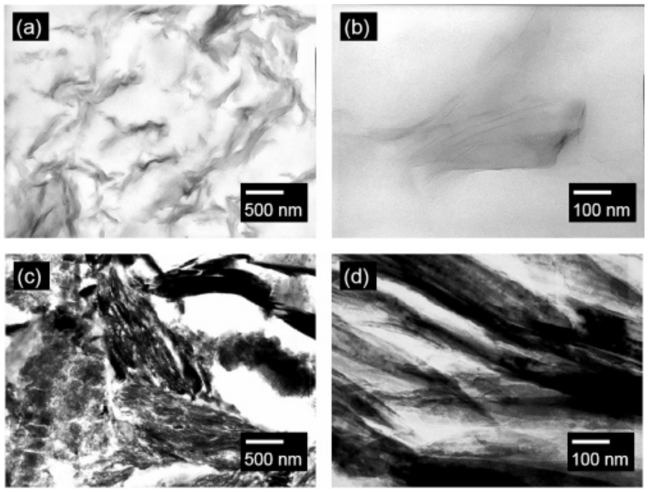


Figure 2. TEM images of exfoliated and intercalated MPP-POE2000/MMT microstructure: (a, b) nearly randomized and well-dispersed structure (featureless); (c, d) aggregated and layered structure (XRD *d* spacing = 19 Å).

d. Regular (Intercalated) vs Irregular (Exfoliated) Platelet Cluster. Both the MPP-POE2000- and MPP-POP2000-exfoliated MMT hybrids are amphiphilic and have demonstrated a fine dispersion with particle size of 150 and 120 nm, respectively. For comparison, their intercalated counterparts were measured to be 580 and 430 nm, accordingly. It is noteworthy that these particle distributions are insensitive to the temperature variation between 25 and 75 °C, implying thermal stability (Table 2).

The differences in the ability of lowering the toluene/water interfacial tension between the exfoliated and the intercalated hybrids were also compared. As reported previously,[10] the MPP-POE2000 and MPP-POP2000 copolymers demonstrated a low interfacial activity while their respective intercalated MMT derivatives showed surfactancy by lowering the toluene/water interfacial tension from 28 to 5 mN/m for both of the intercalated MPP-POP2000/MMT and MPP-POE2000/MMT. In these structures, the POE or POP pendant groups are embedded in the interlayer space rather than exposed in the MMT surrounding. While in the exfoliated MMT or the O/W type structures, the POE2000 segments along with silicate platelet ions were exposed to the water continuous phase. Having behaved differently from the intercalated, the exfoliated MPP-POE2000/MMT can further lower the tension (2.5 mN/m) and reach its critical aggregation concentration (CAC) before 0.01 wt % (Figure 3).

Conclusions. The conversion of layered silicates into random silicate platelets generally occurs only in polymer matrices by a two-step process: surfactant intercalation and a subsequent polymer blending. We found that a direct process can be achieved by using colloidal particles of multiple quaternary ammonium salt grafted on a PP backbone copolymer as the ionic exchanging agent. The synthesized exfoliating agents are dual-functional copolymers, enabling the formation of colloidal particles of less than 100 nm in diameter in toluene/water under elevated temperatures in an autoclave. During the ionic exchange, the intercalated intermediates undergo a phase inversion from a copolymer/silicate hybrid of water-in-oil to oil-in-water micelle structures. The phase inversion is accompanied by the intensive ionic attracting force being overwhelmed and platelet delamination. This process offers a new methodology for modifying the naturally abundant clays for applications of nanocomposite.

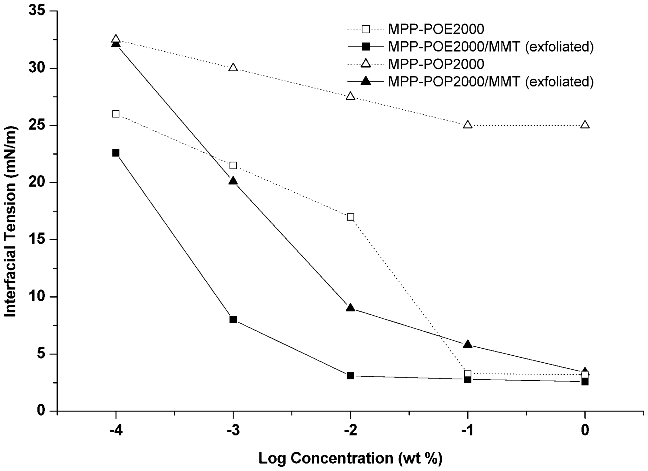


Figure 3. Interfacial tensions of copolymers/MMT hybrids in toluene/water of exfoliated MMTs.

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