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Effect of Textured Surfactant Brushes on Polymer-Layered Silicate Nanocomposite Morphology

by Mary K. Kurian, Arnab Dasgupta, Mary E. Galvin, and Frederick L. Beyer

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14. ABSTRACT

The morphological behavior of a series of polymer-layered silicate nanocomposites (PLSNs) has been investigated. The goal was to probe the effect of “textured” silicate surfaces on PLSN morphology. The nanocomposites were fabricated by mixing montmorillonite clay that was carefully modified with tailor-made polystyrene (PS) surfactants into a PS homopolymer matrix, where the chemical similarity of the matrix polymer and surfactants ensures complete miscibility of surfactant and homopolymer. To examine the effect of silicate surface “texture,” clay was modified with combinations of long and short surfactants. The samples, characterized by small-angle x-ray scattering (SAXS), were then melt-annealed to allow the equilibrium morphology to develop. Based on the implications of the Balazs model and other work on the wetting behavior of polymer melts, textured surfaces were expected to promote the intercalation of the homopolymer matrix material into the modified clay. Extensive characterization of both the modified clays as well as the resultant nanocomposites clearly showed that the modified clays exhibited a high degree of order, but also that only phase-separated morphologies were formed in the corresponding nanocomposites.

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1. Introduction

Polymer-layered silicate nanocomposites (PLSNs), as a class of materials, have generated significant research interest as a result of several important examples of dramatically enhanced properties including tensile strength, heat resistance, solvent resistance, and permeability (*1–8*). These properties were improved simply by the incorporation of small amounts of a suitable filler material such as montmorillonite clay mineral in the matrix polymer.

The clay minerals typically used for these purposes have been thoroughly described elsewhere (*9*). In brief, they are phyllosilicates akin to mica and talc, and are composed of particles called tactoids which are stacks of separate crystalline layers. Within the interlayer spaces, which are called galleries, are found cations such as Na^+, which can be readily exchanged with cationic organic molecules to render the clays organophillic.

PLSNs are dispersions of individual layers of a clay mineral in polymer matrices. This dispersion is normally achieved through one of three techniques: melt processing using extrusion (*10–15*), solution processing in a cosolvent (*16–18*) and *in situ* polymerization of the monomer in the presence of the silicate mineral (*19–24*). A significant impediment to the simple fabrication of PLSNs with well-dispersed clay layers is the hydrophilicity of the clay minerals. With the noted exception of polymers such as poly(ethylene oxide), it is usually necessary to modify the clay surface with an organic surfactant (*25–29*). Numerous research efforts to understand how to disperse a layered silicate clay mineral into a hydrophobic polymer matrix through the use of organic modifiers, in most cases alkylammonium compounds, have been made. Hasegawa et al. (*29*) reported the preparation and mechanical characterization of polypropylene-clay hybrids made by melt processing a mixture of stearylammonium-exchanged montmorillonite, maleic anhydride-modified polypropylene oligomer, and homopolypropylene (*29–31*). Other researchers have also reported similar work on polypropylene-based hybrids (*32*, *33*). Similar approaches have been employed to assist the dispersion of clay in thermosetting polymers where reports (*34*, *35*) describe epoxy-clay nanocomposites prepared by the reaction of epoxide resin and a curing agent in the presence of alkylammonium ion exchanged forms of montmorillonite clays. The melt-intercalation of polystyrene (PS) (*36–40*) into the interlayer gallery region of long chain primary and quaternary alkylammonium exchanged clays has also been investigated previously. In all cases, the use of modifiers was seen to assist in the formation of intercalated and partially exfoliated nanocomposite materials due to easier and more efficient dispersion of the inorganic clay in the polymer matrices.

The studies previously mentioned show that an important requirement for reaching the goal of homogeneous dispersion of the layered clay mineral in the polymer matrix is the promotion of favorable interactions between the matrix and the silicate surfaces, achieved through the use of the "compatibilizing" surfactants. This is a classical problem in the physical sciences, and various approaches to improving the adhesion between two materials utilizing means such as van der Waals forces, physical entanglements, and chemical bonds have been investigated (*41*). Most studies probe the compatibility of a polymer film with a surface such as a silicon wafer, where incompatibility results in dewetting. A standard solution involves altering the surface-melt interaction by modifying the surface with suitable molecules. Reiter et al. (*42*) have reported on the dewetting of thin liquid films of PS from a surface modified with a polymer brush. They investigated the use of bimodal brushes on the surfaces formed by the incorporation of longer connector molecules into the polymer brush to promote wetting of a liquid film that was otherwise incompatible (*43*). Yerushalmi-Rosen and Klein (*44*) and Yerushalmi-Rosen et al. (*45*) have also conducted similar studies on the utilization of grafted molecules on a surface together with free polymer chains in the melt to promote the adhesion of an otherwise nonwetting, chemically similar liquid polymer film. In each of these studies, the complex behavior of the experimental system could not be definitely attributed to a particular phenomenon and was seen to depend on an interplay between a number of factors such as molecular weights of the brush, the connector, and the film polymer molecules, the density of grafting of the surface by the brush, and film thickness. Given the inherent incompatibility between the matrix polymer and the silicate at the molecular level, similar modification schemes, which have successfully been applied to promote adhesion between otherwise incompatible components, may provide routes to the successful formation of stable nanocomposite materials.

Though there have been numerous reports on PLS nanocomposite fabrication by various techniques, there are few reports probing the effect of fundamental interactions between nanocomposite components on the final nanocomposite morphology. Previously, we reported on the investigation of morphology formation in a model nanocomposite system based on PS (*46*). In that work, PS-based PLSNs were fabricated using direct melt-processing, a technique where a mixture of modified clay and homopolymer matrix materials are simply annealed together with no solvents or shearing to promote intercalation. To promote interactions between the silicate and the PS matrix, organically modified clays were prepared by exchanging most cation exchange positions in Na^+ montmorillonite with custom-made, quaternary ammonium ion-terminated PS surfactants of five different molecular weights. It was shown that the high levels of modification resulted in dense polymer brushes on the clay surfaces, preventing intercalation of PS homopolymer molecules; phase-separated morphologies were observed in all cases, irrespective of surfactant molecular weight. This can be understood within the framework of well-established theories of dewetting from dense polymer brushes (*47*, *48*). Here, in a continuation of that work, we describe results on an additional method of silicate modification, and the corresponding effect on PLSN equilibrium morphology.

In this scheme, termed “mixed coverage,” the silicate is modified using a mixture of PS-based surfactants to create a silicate surface grafted with a bimodal brush. This texturing of the surface is expected to allow intercalation of matrix molecules into the galleries by providing a favorable entropic gain to the intercalating polymer through interaction with the longer grafted molecules, and reduced enthalpic interaction with the clay surface. This concept of an increase in entropic gain with increasing surfactant length is also outlined in the theoretical model of Balazs and coworkers (*49*). This scheme of modification should allow a clearer interpretation of the effect of surfactant length on morphological behavior, without interference from the competing influences of a dense surfactant brush or enthalpic interactions with the silicate surface.

2. Experimental

The silicate mineral Na^+ montmorillonite (SWy-2) was purchased from the Source Clay Repository at the University of Missouri. Ten grams of clay were dispersed in 1-L deionized water, and the heavier impurity fractions were allowed to settle to the bottom of the beaker. The resulting suspension was decanted and centrifuged to further make it free of impurities. This cleaned clay was vacuum dried and then powdered using a mortar and pestle. The cation exchange capacity (CEC) of SWy-2 was given as 76-meq/100-g clay, but measurement of the CEC for the cleaned clay, using standard techniques (*50–52*) gave a value of 67 meq/100 g, and this value along with the reported total surface area (*9*) (internal and external) of 800-m^2/g clay was used in all relevant calculations. Low polydispersity PS of approximate molecular weight 10,000 g/mol was used as the matrix polymer in all nanocomposites and was purchased from Polymer Source Inc., Dorval, Quebec, Canada.

Quaternary ammonium end-functionalized PS surfactants of five different molecular weights were synthesized via a modification of the living anionic polymerization technique reported by Quirk and Lee (*53*). Complete details of synthesis and characterization of the surfactants have been reported elsewhere (*54*). Briefly, PS surfactants synthesized by living anionic polymerization were amine end-functionalized in nearly quantitative yields by using a terminating agent such as 3-dimethylaminopropyl chloride. The success of the reaction was confirmed by the presence of the $–N(CH_3)_2$ carbons in (*13*) C nuclear magnetic resonance (NMR) spectra of the terminated product. The amine-functionalized PS product was separated from residual unfunctionalized PS via column chromatography, and the product quaternized by refluxing overnight with a 100-fold excess of dimethyl sulfate in dry tetrahydrofuran (THF) solvent. The quaternized product was precipitated into methanol, was filtered, and dried. Complete conversion of the amine end-functionalized PS to the quaternary ammonium end-functionalized PS product was confirmed by thin-layer chromatography. Molecular weights for surfactants were measured using gel permeation chromatography (GPC) and in the case of the shortest surfactant (~2000 g/mol) by matrix-assisted laser desorption ionization (MALDI) mass spectrometry due to the inaccuracy of GPC in this low molecular weight range. GPC analyses were performed using THF as the solvent eluting at a flow rate of 1 mL/min through two PL gel 5-µm mixed-D columns connected in series and equipped with an HP 1047A RI detector. Mass spectra were obtained on a Bruker Biflex III MALDI time-of-flight mass spectrometer using delayed extraction in both reflectron (<5k m/z) and linear modes and were an average of minimum 50 spectra. Calibration was performed with PS standards, and at higher masses with protein standards. All solutions were prepared in toluene at 4 mg/mL. Dithranol was used as a matrix, and silver trifluoroacetate, when needed, as the cationization salt. Analyte solutions were premixed at an 8:4:1 ratio of matrix: sample: salt and applied in 1-µL aliquots to the probe. Calculation of molecular weights was performed using both the XMASS (Bruker) and Polymerix (Sierra Analytics) software packages. Surfactant nomenclature and properties are recorded in table 1. The nomenclature used is such that for any surfactant it provides information about its approximate molecular weight in thousands of grams per mole; for example, *Q-2* is a quaternary ammonium ion terminated PS surfactant of approximate molecular weight 2000 g/mol. The low polydispersity indices (PDI) indicate the ability to control molecular weight afforded by the anionic synthesis technique used in this work.

Table 1. Molecular weights for quaternary ammonium ion terminated PS surfactants.

Surfactant	**M_w (g/mol)**	**M_n (g/mol)**	**PDI**
Q2	1820	1735	1.05
Q3	2800	2700	1.04
Q7	7000	6800	1.03
Q11	11600	11200	1.04
Q18	18100	17600	1.03

The Na^+ cations in montmorillonite were easily replaced by the quaternized PS surfactants by a simple solution-phase cation exchange procedure as follows. A measured amount of Na^+ montmorillonite was dispersed in a 3:1 (v/v) mixture of acetone: water by stirring the mixture for 8 hr. The required amounts of surfactants needed to modify the clay were also dissolved in a similar solvent system. The surfactant solution was added to the clay suspension with rapid stirring, resulting in the immediate formation of a white precipitate. The mixed solution was further stirred for 8 hr. The precipitate was separated from the solvents by centrifuging, washed with THF to remove any unbound surfactant, and then dried under vacuum at 60 °C for 12 hr. Four different modified clays were thus made by treating a measured amount of Na^+ montmorillonite with a solution containing one of the longer four (*Q-3, Q-7, Q-11*, and *Q-18*) of five surfactants in combination with the shortest surfactant (*Q-2*). The relative amounts of surfactants in the mixture were adjusted such that in the final modified clay, of the total available CEC sites 17% would be occupied by the longer surfactant and rest 83% by surfactant *Q-2*. This scheme of clay modification provides surfaces that are in effect "textured" due to differences in the lengths of the modifiers used.

The composition of each of the modified clays was determined via thermogravimetric analysis (TGA). A 5–10 mg sample was analyzed using a Perkin Elmer TGA 7 instrument by recording the weight loss of the sample as a function of temperature in the range of 30 to 900 °C. The amount of residue that remains at the end of the experimental run provides a measure of the inorganic or ash content in the material.

Nanocomposites incorporating the modified clays were made by the following intercalation technique described previously as "direct melt intercalation" (*55*). Based on TGA results of the modified clays, amounts of modified clay and PS were measured such that the total inorganic content in the nanocomposite was 5% by weight and then gently mixed by hand. These mixtures were then pressed into pellets using only contact pressure. The pellets were annealed under vacuum at a temperature of 150 °C for 1 week. As shown previously (*46*), this time was calculated to more than an order of magnitude in excess of the length of time required for the diffusion of matrix homopolymer molecules to achieve their equilibrium morphology. The annealed samples were cooled to room temperature under vacuum and were observed to be fully coalesced solid samples.

Small-angle x-ray scattering (SAXS) data were collected to characterize the separation between individual clay sheets, a measure of the degree of intercalation in these materials (*56*). X-rays were generated using a Rigaku Ultrax18 rotating anode generator operated at 2.4-kW power, and the $Cu_{K\alpha}$ radiation was monochromated using a pyrolytic graphite crystal such that $\lambda = 1.5418$ Å. The sample to detector distance is 62.3 cm as calibrated using a silver behenate standard. Two-dimensional SAXS data were collected using a Bruker Hi-Star area detector. All data were azimuthally averaged for analysis in terms of intensity as a function of q, the magnitude of the scattering wave vector, where $q = 4\pi \cdot \sin(\theta)/\lambda$, with scattering angle, 2θ, and wavelength, λ. The length scale for a given value of q is simply $2\pi/q$.

3. Results

The sample nomenclature used in this report incorporates information about the exact silicate modification scheme, the surfactants and the matrix polymer used in a particular sample. For example, M-(2, 3)m-PS is a nanocomposite sample where "M" stands for montmorillonite clay, "*(*2, 3*)*" indicates that surfactants *Q-2* and *Q-3* (with approximate molecular weights 2000 and 3000 g/mol) were used to modify the silicate, "m" indicates mixed coverage, and "PS" indicates that PS homopolymer (always ~10,000 g/mol) was used as the matrix material. The modified clay alone without the matrix used in the above sample previously mentioned would be named M-(2, 3)m.

Table 2 lists the physical characteristics of all modified clays. As described in the procedure for silicate modification, surfactant amounts in the modifying solution were adjusted to achieve a "mixed" coverage where ~83% of the CEC sites on the silicate surfaces were occupied by the surfactant *Q-2* and the rest 17% by the longer surfactant. The feed compositions calculated based on the total amount of surfactants used to modify a measured amount of clay are recorded in table 2. TGA was used to determine the fractions of organic and inorganic matter in the

Table 2. Physical characterization data for the modified clays with "mixed" coverage.

Sample	Surfs.	Feed Composition		After Modification		Surf. Coverage	
		Clay (%)	Surf. (%)	Clay (%)	Surf. (%)	Q2 (%)	Long (%)
M-(2, 3)m	Q2, Q3	44	56	46	54	83	17
M-(2, 7)m	Q2, Q7	36	64	38	62	83	17
M-(2, 11)m	Q2, Q11	31	69	32	68	83	17
M-(2, 18)m	Q2, Q18	25	75	26	74	83	17

modified clays and comparison of these compositions with the feed compositions shows good agreement. This allows the calculation of the coverages by each of the surfactants in the modified clays. Knowledge of the composition of a modified clay also allows the calculation of the exact amount of matrix homopolymer required to make a nanocomposite which contains 5% by weight inorganic matter.

Figure 1 reports the morphological characterization data collected using SAXS. The data are presented in pairs, where the lower set of each pair is from the modified clay without any homopolymer, and the upper set in each pair is from the corresponding PLSN, containing modified clay and PS homopolymer after direct melt-intercalation (5 weight-percent total inorganic content). The data are plotted on a log-linear scale and scaled vertically for clarity of presentation. Table 3 records the scattering vector *q* for the first-order Bragg reflection, the associated real space length *d*, where $d = 2\pi/q$ and the corresponding gallery height *h*, where $h = (d\text{-}10)$ Å, for each of the modified clays and nanocomposites.

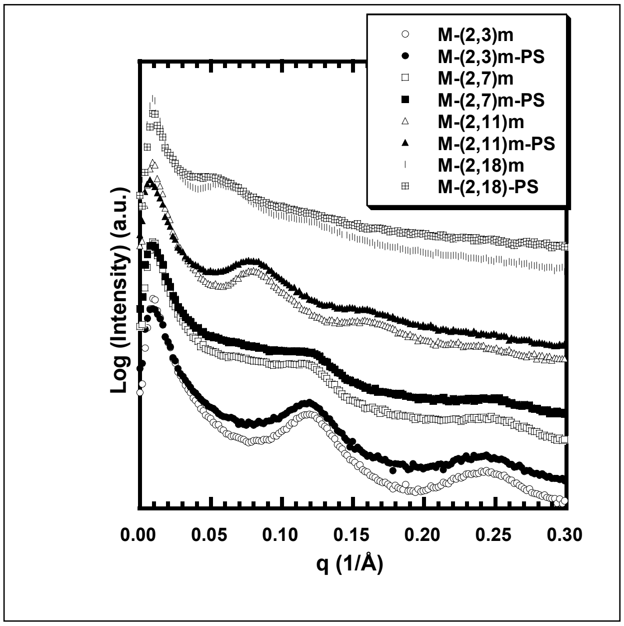

Figure 1. SAXS data for the modified clays with "mixed" coverage and the corresponding annealed nanocomposites.

Table 3. Physical characterization data for the modified clays with "mixed" coverage and the corresponding PS-based nanocomposites.

Sample	**q** **($Å^{-1}$)**	**D** **(Å)**	**h** **(Å)**
M-(2, 3)m	0.1191	53	43
M-(2, 7)m	0.1191	53	43
M-(2, 11)m	0.0818	77	67
M-(2, 18)m	0.0551	114	104
M-(2, 3)m-PS	0.1191	53	43
M-(2, 7)m-PS	0.1191	53	43
M-(2, 11)m-PS	0.0817	77	67
M-(2, 18)m-PS	0.0551	114	104

4. Discussion

The underlying premise of this research effort, including previously published results (*43*), is to investigate the possibility that given the proper combination of matrix polymer, surfactant, clay and processing conditions, a PLSN material could be created in such a way that there would exist a thermodynamic driving force that would favor the formation of intercalated and exfoliated morphologies. As calculated by Balazs and coworkers, it may be possible to engineer a system that would have as its equilibrium morphology an intimate mixing of polymer and individual clay sheets (*49*, *57*). Developing a system of this nature could significantly alter the economics of polymer-layered silicate nanocomposite materials because requiring the polymer matrix to be synthesized either *in situ* or forced into intercalation dramatically limits the feasibility of making PLSNs that can be commercialized.

To that end, and as an extension of our previous efforts, the current series of polymer-layered silicate hybrid materials was fabricated. This series, containing clays modified simultaneously with two PS-based surfactants, was devised to explore the possibility of avoiding the morphological behavior of the series of PLSN materials fabricated for the earlier work. In that study (*46*), PS-based surfactants were used to modify montmorillonite clays as fully as possible, but the result was a "phase-separated" morphology, where no intercalation or exfoliation of the clay layers was observed. This was attributed to autophobic dewetting of the matrix polymer molecules due to formation of a dense polymer brush by the surfactant molecules on the silicate surfaces. To compensate for this behavior, a strategy for overcoming autophobic dewetting was adopted from an experiment where the adhesion between a PS-brush coated surface and an otherwise nonwetting PS liquid film was improved by using connector polymer molecules (*43*). Different amounts of these connectors, 5–14 times longer than the brush molecules, were anchored to the surface to form 'bimodal brushes' that stabilized the film by penetration of the connectors into the nonwetting film. The authors reported that the grafting of a small number of end-functionalized connector molecules into a dense polymer brush resulted in a reduced dewetting velocity for a subsequently deposited nonreactive homopolymer film, with longer connectors being more effective in reducing this velocity. Here, the longer surfactants were hoped to provide the entropic benefit to the intercalating polymer as predicted by the Balazs model, while the short surfactants would provide a screen between the hydrophobic PS and the hydrophilic silicate surfaces, a repulsive force expected to impede intercalation (*39*). The data shown in figure 1 indicate that the actual behavior of this series of samples was to remain in a phase-separated morphology, with no indication of intercalation or exfoliation of the layered silicate in the PS matrix. Examination of the SAXS data reveals that no significant change in the shape or location of the Bragg reflections occurred upon annealing, which would be expected if there were any significant changes in morphological structure.

Several probable explanations for this morphological behavior are available. First, there are obvious differences between this experiment and that of Reiter et al. (*43*) regarding autophobic dewetting from a model polymer brush. Here, a natural clay mineral, with variations in composition, size, and texture was used, while the model experiment worked with a carefully prepared silicon wafer substrate. Here, all the surface modification occurred in one batch step, while the model experiment involved careful deposition of each component separately. In the model study, the polymer melt was observed in transition from a wetted state to a dewetted state, while in this experiment, only the transition in the opposite direction is of interest.

Second, despite the bimodal nature of the brushes in this experiment, it is still possible that the brush is still effectively dense. This would be important only if the long surfactant fraction were being ineffective in fostering wetting and intercalation, which could be the case. Figure 2 shows a schematic of this scenario. In figure 2a, a long surfactant is illustrated at a low coverage over a surface that is repulsive to the homopolymer. In this case, the surfactant will stretch away from the surface until the energy required to stretch is no longer less than that of the repulsive enthalpic interactions. This is the scenario for a typical surfactant modified clay. In the bimodal brush, the shorter surfactant at full coverage (83%) effectively replaces the silicate surface. As illustrated in figure 2b, the surface now can be thought of as being composed of the dense brush. When a small fraction of those surfactants are replaced with longer surfactants, the situation may become something like that illustrated in figure 2c. Now, the length of the longer surfactant is important, but the conformation of the longer surfactant must also be considered. If the longer surfactant is similar in length to the shorter surfactant, one has effectively a short surfactant at low coverage. As the difference between the longer and shorter surfactants increases, the effective surfactant becomes longer, but does this longer brush actually assist in the wetting and intercalation processes? It is possible that it does not because there is now no enthalpic repulsion causing the surfactant to stretch away from the effective surface. The effect of conformation is clear for at least two samples examined here. Samples M-(2, 3)m-PS and M-(2, 7)m-PS both show primary and secondary Bragg reflections at the same spacings, in addition to showing no evidence of intercalation. When compared to the data collected for the PLS nanocomposite

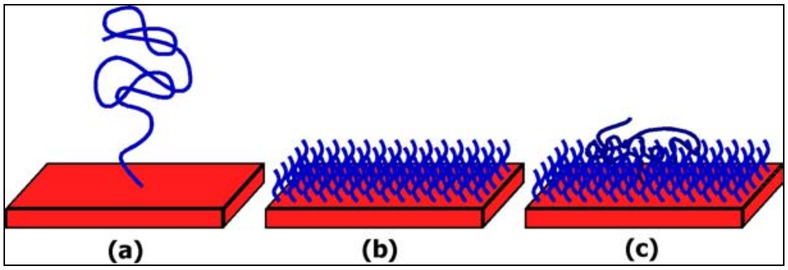

Figure 2. Illustration for a bimodal surfactant brush of one possible outcome on longer surfactant conformation of the densely packed brush of shorter surfactant.

fabricated in the previous study, where the surfactant was also Q-2, one finds that the gallery heights of the two PLSNs here are only slightly larger than those of clay modified solely with the Q-2 surfactant (sample M-2 in the previous report). That the gallery height does not change between M-(2, 3)m-PS and M-(2, 7)m-PS is remarkable given the 3-fold increase in surfactant molecular weight, and could only occur if the majority of the longer surfactant is remaining close to the dense surfactant brush formed by the Q-2 surfactant. This image also helps explain the significant breadth in the SAXS data for the M-(2, 7)m samples. The breath is consistent with disordering of the second kind (*58*), where fluctuations in the gallery height distort the Bragg reflections. The most readily found reason for this variation in gallery height would be a non-uniform distribution of longer surfactants where their effective length is sufficient to add volume in their locality unevenly between the silicate layers. As the longer surfactants become significantly longer, in samples M-(2, 11)m-PS and M-(2, 18)m-PS, the effect of the bimodal brush on the breadth and number of Bragg reflections is still evident. The Bragg reflections observed here are fewer and far broader than those observed for the fully exchanged clays. Still, no evidence of a change in morphology is observed, though, indicating that even these highly textured surfaces are not enough to cause intercalation to occur.

5. Conclusions

Polymer-layered silicate nanocomposites based on a PS matrix were prepared using montmorillonite clays that were modified with blends of PS-based surfactants. In these samples, 17% of the cations available for exchange in the clay mineral were replaced with a long surfactant, while the remaining 83% of the cations were replaced with a short surfactant ~2000 g/mol in molecular weight. Low molecular weight PS homopolymer was used as the matrix material to ensure miscibility and mobility. The incorporation of a small amount of longer surfactant molecules in a brush of short surfactants did not promote intercalation of the matrix polymer into the clay galleries, and only phase-separated morphologies were observed, regardless of surfactant length used. Though entropic gain is provided to the intercalating molecules through the longer surfactant chains, this compensation is insufficient to prevent the autophobic dewetting behavior favored because of the dense brush conditions that still exist on the silicate surfaces.

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