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Melt-intercalation of sodium-montmorillonite with alkylamine and quarternized ammonium salts of sulfonated polystyrene ionomers

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Abstract

Na-Montmorillonite (Na-Mmt) was melt-intercalated with alkylamine and quarternized ammonium salts of sulfonated polystyrene ionomers (SPS) with no other organic modification. Mixtures of SPS and polystyrene (PS) also exhibited similar intercalation, indicating that the ionomer was an effective compatibilizer for a non-polar polymer such as PS. The materials were mixed in a co-rotating, non-intermeshing twin-screw extruder. The intercalation was relatively insensitive to the melt processing conditions. The key variable appeared to be the ratio of charge between the ionomer and the clay. Intercalation was assessed by wide angle X-ray diffraction and transmission electron microscopy.

Keywords: Nanocomposites; Ionomers; Intercalation

1. Introduction

Since the pioneering work on nylon-clay nanocomposites by the Toyota group in the early 1990's [1–6], considerable research has been conducted on the development of nanocomposites with a variety of polymers and modified and pristine silicate clays. The difference in the sizes of the filler particle and polymer dimensions, and the lower concentration of filler loadings required to achieve comparable properties with polymer layered nanocomposites (PLNs) and conventional composites, presumably due to much larger filler surface areas exposed to the polymer phase, has spurred considerable research and development of these materials. The literature on the subject is now quite extensive [7].

Layered silicates, such as montmorillonite, are commonly used for the inorganic filler. Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused with two external silica tetrahedra at the tip [8]. The layer thickness of the sheets is around 1 nm. These layers organize into stacks with a regular Van der Waals gap called the 'interlayer' with a spacing of 0.96 nm. Isomorphous substitution of the Al^{3+} by Mg^{2+} or Si^{4+} by Al^{3+}, within the silicate layer generates a net negative charge on the layer, which is counterbalanced by alkali or alkaline earth metal cations in the galleries. The interlamellar cations have one or two shells of water of hydration surrounding them; e.g. montmorillonite has the chemical formula $[M_x\ (Al_{4-x}\ Mg_x)\ Si_8O_{20}\ (OH)_4]$, where 'M' is a monovalent cation which resides in the intergallery spaces, and 'x' is degree of isomorphous substitution.

In situ polymerization of a monomer in the galleries [1], solution intercalation [9], and melt intercalation [10,11] are the most commonly used strategies for fabricating PLNs, though melt intercalation of the polymer into the clay by the application of shear forces is potentially the most versatile and useful technique for producing commercial materials. Melt processing is environmentally benign since no solvents are used, and it is compatible with common polymer processing techniques and equipment, which minimizes the

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capital costs. The silicates used for melt intercalation are usually organically-modified to improve their surface energy and interactions with organophilic polymers [12]. Organic modification is achieved by exchanging the interlamellar alkali/alkaline ions with long chain alkyl amines or quaternary ammonium ions. Without the aid of organic modification of the silicates it is difficult to disperse them in organic polymers, especially non-polar materials. However, organic modification has disadvantages. It not only requires an extra step in producing the polymer clay nanocomposites but also the organic modifiers commonly used degrade at the elevated temperatures needed to process the nanocomposites and thus causing the silicate layers to regain their hydrophilicity [13–17]. The instability of the organoclay can also adversely affect the stability of the polymer as well [18–20] and suppress intercalation of the polymer into the galleries [21,22].

This paper considers a modification of the polymer, rather than the clay, for promoting melt intercalation, specifically the introduction of alkyl ammonium salt groups along the polymer chain. The charged nature of the aluminosilicate surfaces makes it difficult to intercalate non-polar or slightly polar polymers without any surface modification. The edges of montmorillonite are positively charged and this charge constitutes about 20% of the cation exchange capacity (CEC) of the total clay [23]. Polystyrene (PS) is a common non-polar polymer that is immiscible with charged montmorillonite. However, PS can be easily sulfonated by a postpolymerization reaction [24], the ion-exchange capacity (IEC) and the average distance between the ionic groups can be varied and the ionic strength of the ion pairs can be manipulated by changing the nature of the counter-ion. Weiss et al. [25] previously studied the effect of the number of alkyl substituents and the length of alkyl chains on the properties of alkyl ammonium salts of sulfonated polystyrene ionomers (SPS).

The main objective of the current paper was to examine the use of alkylamine-neutralized SPS for promoting intercalation of the ionomer into unmodified sodium montmorillonite clay and its use as a compatabilizer for intercalating another polymer into unmodified silicate clay. The effect of the number of ionic equivalents in the melt, molecular weight of the ionomer, and the number and the length of the alkyl substituents of the counter-ion on intercalation capability was evaluated. The effect of processing variables such as mixing temperature, mixing time and shear rates was also investigated.

2. Experimental

2.1. Materials and synthesis

A commercial atactic polystyrene, Styron® 666, with $M_w = 280$ kDa and $M_n = 106$ kDa was provided by Dow Chemical Company and used as received. Low molecular weight polystyrene with a molecular weight range of 0.8–5 kDa was obtained from Polysciences Inc. Sulfonated polystyrene ionomers (SPS) were prepared by sulfonating polystyrene (PS) in 1,2-dichloroethane solution using acetyl sulfate at 50 °C following the procedure of Makowski et al. [24]. The sulfonation reaction is an electrophilic substitution reaction, which substitutes sulfonic acid groups randomly along the chain, primarily at the *para*-position of the phenyl ring. The ionomers were isolated from solution by distillation of the solvent, filtered, washed several times with deionized distilled water, and dried under vacuum. The sulfonation level of the ionomer was determined by titration of the sulfonic acid derivative (HSPS) in a mixed solvent of toluene/methanol (90/10 v/v) with methanolic sodium hydroxide of known normality to a phenolphthalein end-point. Ionomers with four different sulfonation levels were prepared: 1.3, 3.4, 4.2 and 8.3 mol% of the styrl rings sulfonated, which correspond to ion-exchange capacities (IEC) of 0.12, 0.32, 0.39 and 0.75 mequiv/g, respectively.

Reagent grade butyl amine (BuA), di-butyl amine (DBA), tributyl amine (TBA), octyl amine (OA), and hexadecyl amine (HDA), were obtained from Aldrich Chemical Company and used as received. The alkyl amine salts of SPS were prepared by dissolving the HSPS in toluene/methanol solutions and neutralizing with stoichiometric addition of the appropriate alkyl amines. The neutralized ionomers were isolated by steam distillation, filtered, washed several times with deionized distilled water and dried under vacuum at 80 °C. The sodium montmorillonite (Na-Mmt) used was Cloisite Na^+, obtained from Southern Clay Products. The cation exchange capacity (CEC) cited by the manufacturer was 0.92 mequiv/g and the clay was used as received without any further drying.

The sample nomenclature used for the ionomer in this article is *rst*-SPS*x.y*, where *rst* denotes the alkylamine cation and *x.y* indicates the ion exchange capacity (IEC) of the ionomer in mequiv/g.

Quarternary sulfonated polystyrene (Quaternary SPS) were also synthesized in a similar manner as the secondary and tertiary amine neutralized sPS. Stoichiometric quantities of tetrabutylammonium and tetraoctylammonium were added to the reaction mixture of HSPS0.75 dissolved in toluene/methanol (90/10, v/v), and the reaction was continued for 12 h. The quarternary ammonium salts of sPS were isolated from the solution by steam-stripping, washed several times with deionized distilled water and dried under vacuum for 24 h. The sample nomenclature used for the quaternary salts was teBu-SPS*x.y* and teOc-SPS*x.y* for the tetra-butyl SPS and tetra-octyl SPS, respectively.

2.2. Melt processing

A DACA microcompounder (a vertical, recirculating co-rotating twin screw extruder) produced by DACA instruments, California, USA was used for melt-processing SPS/Na-Mmt and SPS/PS/Na-Mmt blends. The extrusion temperature in most of the cases was 50 °C above the glass transition temperature (T_g), the screw speed was 190 rpm and the mixing time was fixed at 10 min. In other experiments, the shear rate (i.e. screw speed) and melt temperature were varied. The polymers were added to the extruder using a lower screw speed, 70 rpm, than was used for the mixing. First, half of the polymer ($\sim$2 g) was added, followed by addition of the Na-Mmt after the polymer became molten and then the remainder of the polymer was added and the screw speed was increased to 190 rpm. During the mixing, the exit valve was closed and the recirculation valve of the DACA was opened, so that the DACA functioned as a batch mixer. After 10 min of blending the samples were pumped out through the exit valve. Any material left after that was removed from the screws and the barrel after stopping the extruder.

2.3. Materials characterization

Samples for materials characterization were prepared by compression molding 1 mm thick films with a Wabash two-platen press using a rectangular mold and the same temperatures used to process the blends. A preheating time of 3 min without pressure was followed by a compression molding time of 5 min at higher pressure ($\sim$90 kN). The samples were watercooled in the press at elevated pressure and removed from the press at room temperature. The blend nomenclature followed in this paper is *rst*-SPS*x.y*/Mmt for ionomer–silicate blends and (*m*/*n*) PS/*rst*-SPS*x.y*/Mmt for the PS/ionomer/Na-Mmt blends, where (*m*/*n*) denotes the PS/SPS*x.y* composition (w/w) based on the total polymer content. The composition of the silicate was fixed in all mixtures at 3 wt%.

Wide angle X-ray diffraction (WAXD) of compression molded specimens was done with a Bruker D8 Advance diffractometer using Cu Kα (λ=0.154 nm) radiation at a voltage and current of 40 kV and 40 mA, respectively. The scattering angle (2θ) was scanned from 3 to 12° at a scan speed of 0.1 °/min at room temperature. That angular range corresponded to values of the momentum transfer vector $q=4\pi \sin \theta/\lambda$ from 2.1 to 8.5 nm^{-1}. The basal spacings of the silicate layers (d) were calculated using Bragg's law $d=2n\pi/q$. Transmission electron microscopy (TEM) was carried out with a Philips 300 electron microscope using an operating voltage of 80 kV. Thin sections ($\sim$70 nm) were microtomed from compression molded samples at room temperature with a diamond knife using a LKB ultramicrotome. The sections were collected from water trough and floated directly onto Cu grids. No external staining was used; the contrast was provided by electron density differences between the silicate layers and the polymer matrix.

3. Results and discussions

3.1. Effects of IEC/CEC ratio

Fig. 1 shows the WAXD of pristine Na-Mmt as a function of temperature. The d_{001} peak shifted to higher q values with increasing temperature, which corresponds to a decreasing intergallery spacing. At a temperature as low as 60 °C, the d-spacing changed from 1.03 to 0.96 nm as a result of water loss [26], and that d-spacing remained constant until 150 °C. Additional water losses are reported to occur at much higher temperatures, >250 °C [27], but such high temperatures were not used in the present studies. In this study the PLNs were processed between 150 and 160 °C, so it was assumed that the weakly bonded water was already lost, and the base gallery spacing for the clay was assumed to be 0.96 nm. The large full width at half maximum (fwhm) of the as-received clay represents a large inhomogeneity of the intergallery spacings, which is a result of the poorly crystalline nature and the turbostratic packing of smectite minerals [8].

Fig. 2 compares the XRD of TBA-SPS0.75 and PS melt blended with 3 wt% silicate. The XRD of the PS/silicate sample shows a peak at the same position as for the neat silicate that corresponds to a gallery spacing of 0.96 nm. The peak moved to lower q (d=1.37 nm) for the ionomer/silicate nanocomposite, which indicates improved intercalation of the polymer within the gallery.

The IEC of the polymer in the composite was varied by either changing the sulfonation level of the ionomer and/or the amount of ionomer used in a PS/SPS blend—i.e. by diluting the ionomer with PS. Fig. 3 shows XRD results for three different values of IEC/CEC: 2.7, 6.8 and 27.2, that were achieved by mixing different ratios of PS with the TBA-SPS0.75. The neat ionomer had an IEC of

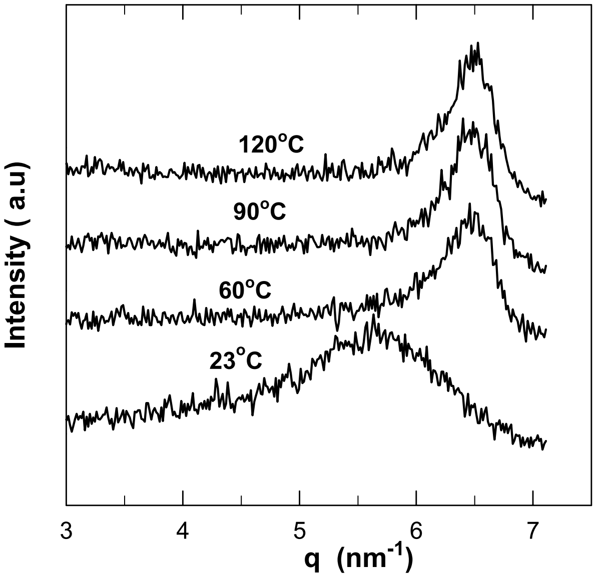

Fig. 1. WAXD of Cloisite Na$^+$ as a function of temperature.

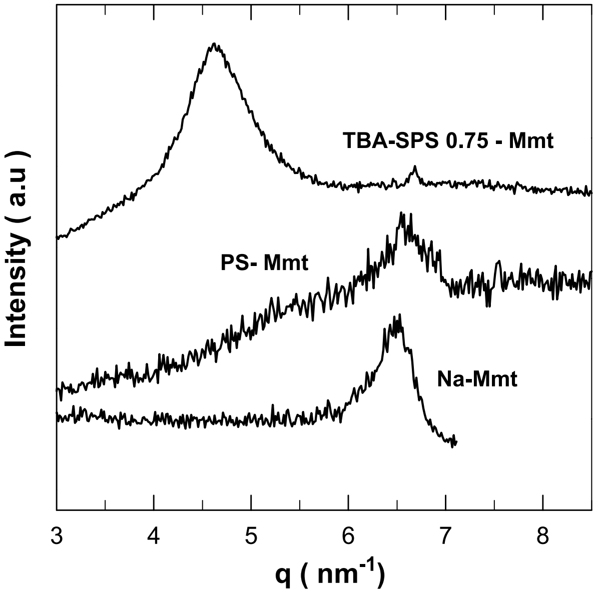

Fig. 2. WAXD of TBA-SPS 0.75 and PS with 3 wt% Na-Mmt. The blends were prepared in the twin screw extruder at 150 °C for 10 min. The bottom XRD is of Na-Mmt at 150 °C.

0.75 mequiv/g and the clay had a CEC of 0.92 mequiv/g. For each mixture containing the ionomer, the XRD peak moved from the intergallery spacing of the silicate at 0.96 nm to higher spacing, which indicates that the ionomer not only promoted intercalation, but it also appears to function effectively as a compatabilizing agent for the hydrophobic PS with the clay. For IEC/CEC = 27.2 and 6.8 the gallery spacing increased to 1.37 nm, while for lowest ratio, IEC/CEC = 2.7, the gallery spacing increased to 1.31 nm. A small peak corresponding to 0.96 nm was also seen at higher angles for the IEC/CEC = 27.2 and 6.8, indicating the presence of a small amount of unintercalated Na-Mmt.

Fig. 4 shows the XRD data as a function of the IEC/CEC ratio for mixtures of PS with the ionomers with lower IEC: TBA-SPS0.39 and TBA-SPS0.12. For the lowest IEC/CEC ratio of 0.42, the gallery spacing showed no change compared with that of Na-Mmt. For IEC/CEC = 1.08, curve (c) in Fig. 4, the gallery spacing increased compared to that in Na-Mmt, but the increase to 1.15 nm was much less than for the blends with IEC/CEC ≥ 3.5. The latter result was consistent with the changes that were observed for IEC/CEC ratios > 2.7 shown in Fig. 3 for the blends that used the higher IEC ionomer. Fig. 5 summarizes the change in the gallery spacing as a function of the IEC/CEC ratio for all of the blends studied using TBA-SPS*x.y*. It appears from these data that an IEC/CEC ratio of > 1 is necessary to achieve intercalation and a ratio of about 2.5 is needed to reach an upper limit on the increase in the gallery spacing.

The TEM micrographs in Fig. 6(a) and (b) show the dispersion of the clay in the absence and presence of ionomer. Fig. 6(a) clearly shows the immiscible morphology of a PS, Na-Mmt mixture. The particle size of the clay tactoids was greatly reduced when the TBASPS0.75 was added to the PS, as seen in Fig. 6(b). Higher magnification of the (75/25)PSTBASPS0.75/Na-Mmt composite, Fig. 6(c) and (d), shows that the interlayer spacing of the intercalated clay increased to 1.3–1.4 nm, which agrees with the XRD data. The TEM images however, showed a mixed morphology, with some layers intercalated and some

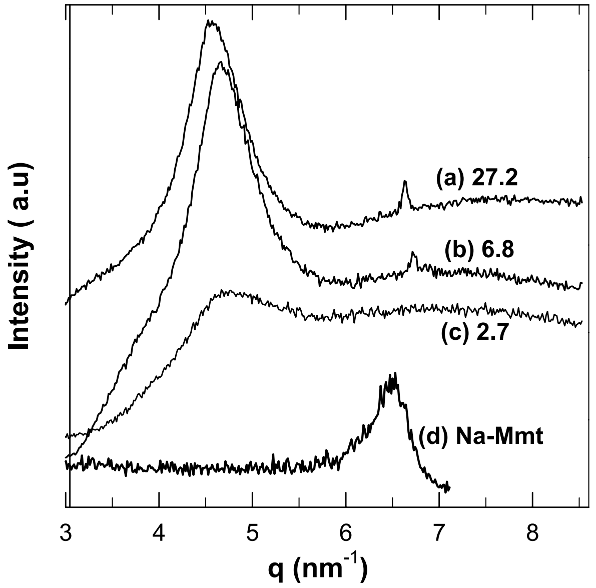

Fig. 3. WAXD for blends having varying IEC/CEC ratios. All blends constituted 3 wt% silicate. The specific blends were (a) (100/0)PS/TBA-SPS0.75/Mmt, (b) (75/25)PS/TBA-SPS0.75/Mmt, (c) (90/10)PS/TBA-SPS0.75/Mmt and (d) Na-Mmt at 150 °C.

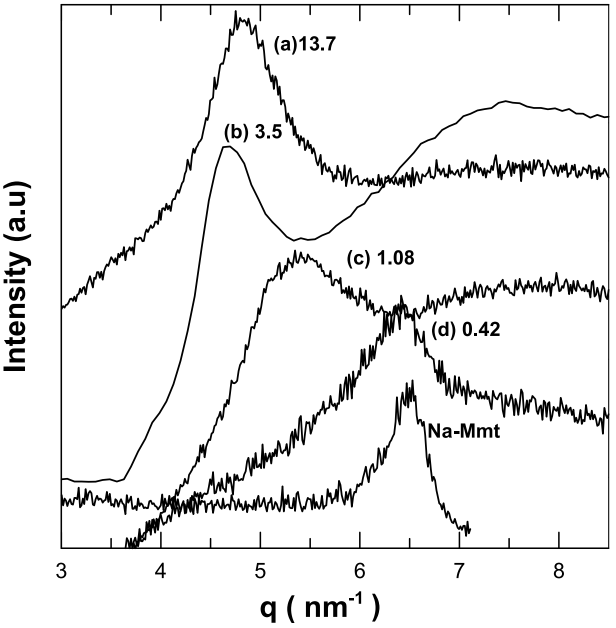

Fig. 4. WAXD for blends having varying IEC/CEC ratios. The specific blends were (a) (100/0)PS/TBA-SPS0.39/Mmt, (b) (75/25)PS/TBA-SPS0.39/Mmt, (c) (75/25)PS/TBA-SPS0.12/Mmt, (d) (90/10)PS/TBA-SPS0.12/Mmt and (e) Na-Mmt at 150 °C.

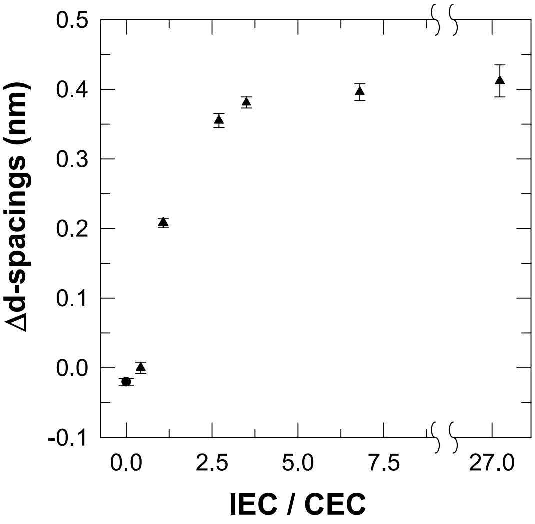

Fig. 5. Change in $d_{(001)}$ spacings as a function of IEC/CEC: (●) blend with PS; (▲) blends with TBA-SPS*x.y* ionomers.

not. The increase in spacing was observed at the edges of most of the larger particles and large numbers of 2–3 platelets stack were observed. Thus addition of the ionomer produced a more delaminated and dispersed nanocomposite. No exfoliation was seen in any of the samples studied.

3.2. *Effect of processing conditions on nanocomposite morphology*

The intercalation behavior of the amine-neutralized SPS was also investigated as a function of the shear rate, mixing time and mixing temperature used. Though intermeshing extruders usually provide more shear intensive mixing than the non-intermeshing twin-screw extruders, a non-intermeshing co-rotating twin-screw extruder was used based on the findings of Dennis et al. [28] that such a screw configuration produced the best dispersions for nylon 6 nanocomposites. The effect of the screw speed, which is related to the shear rate, on the XRD of 3% silicate composites with TBASPS0.75 is shown in Fig. 7. Since the shear stress also increased with shear rate, increasing the screw speed was expected to improve the extent of intercalation. However, the XRD data in Fig. 7 show no distinguishable differences in the intergallery spacing with increasing screw speed for the system under consideration. Therefore, it appears that the melt intercalation of PS/TBA-SPS with Na-Mmt was not influenced by the magnitude of the shear rate for the screw speed range used in this study, and for the other processing studies, the screw speed was fixed at 190 rpm.

Fig. 8 shows the effect of the mixing temperature on the XRD (75/25)PS/TBASPS0.75/Mmt composites. The two temperatures used, 155 and 185 °C corresponded to 50 and 80 °C above T_g, respectively. Increasing the temperature of mixing had no effect on the intergallery spacing. Similarly, no differences were observed by varying the mixing time from 5 to 10 min (data not shown). As a result of the insensitivity of the intercalation to temperature, the mixing of these composites was, for the most part, carried out at $T = T_g + 50$ °C, which was conducive for higher shear stresses. Melt-mixing below that temperature was not possible, because of torque limits of the extruder.

For a limited number of samples, melt mixing was also accomplished using a Brabender Plasticorder intensive mixer. That instrument requires a larger feed, ca. 30 g of

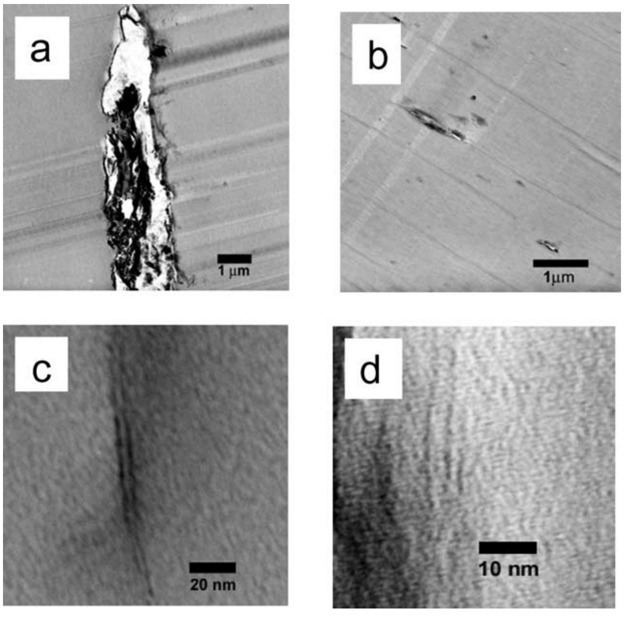

Fig. 6. TEM photomicrographs at low magnification of (a) PS/Na-Mmt (b) (75/25)PS/TBA-SPS0.75/Mmt and at high magnification of (75/25) PS/TBASPS0.75/Mmt (c) and (d).

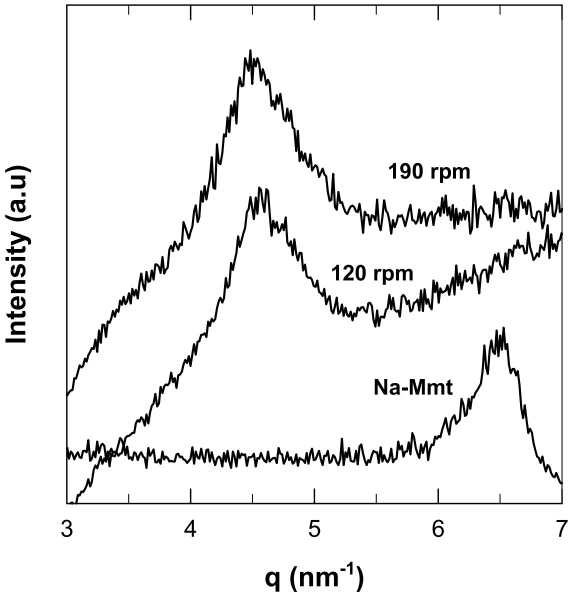

Fig. 7. WAXD of TBA-SPS 0.75/Mmt as a function of shear rate used in compounding, for 3 wt% Na-Mmt composites using the ionomer TBA-SPS0.75 as the polymermatrix. XRD of Na-Mmt at 150°C is shown for reference.

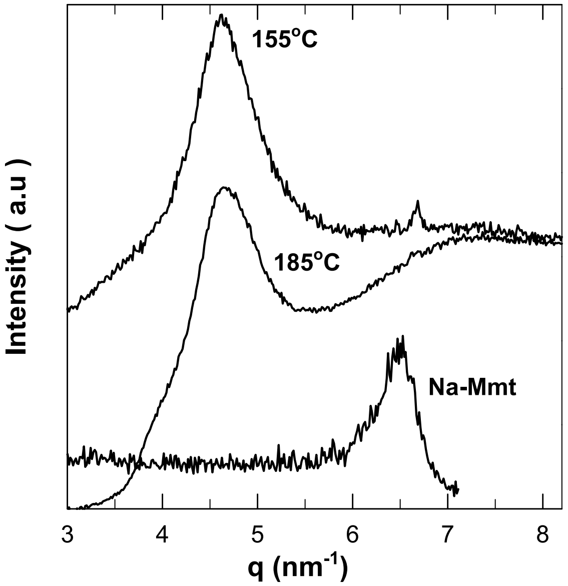

Fig. 8. WAXD of blends of (75/25)PS/TBA-SPS0.75/Mmt prepared at different processing temperatures.

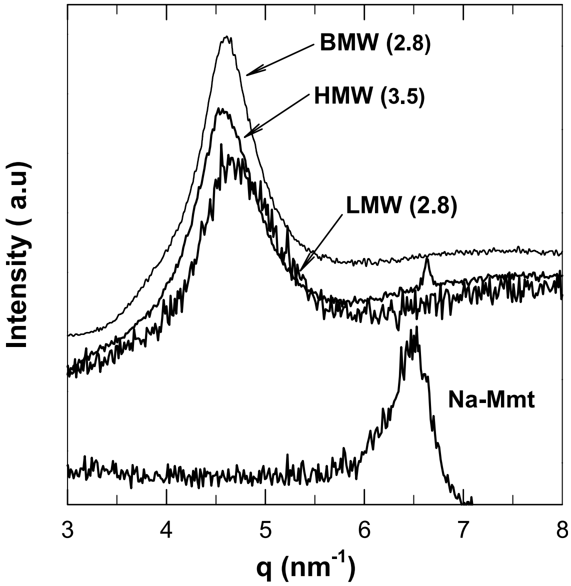

Fig. 9. WAXD as a function of molecular weight of the ionomer. The high molecular weight TBASPS(HMW) was used in a blend of (75/25) PS/TBASPS0.75/Mmt, and the low molecular weight TBA-SPS(LMW) was used in a blend of (75/25)PS/TBASPS0.66/Mmt. The bimodal distribution molecular weight (BMW) blend consisted of 25 wt% ionomer TBA-SPS0.66 of low molecular weight (0.8–5 kDa) and 75 wt% PS of high molecular weight (280 kDa). The figures next to the curves are the IEC/CEC ratios. All blends contained 75/25 (w/w) PS and ionomers as the polymer composition and 3 wt% silicate.

polymer. Like the DACA, it also possesses a non-intermeshing screw configuration, but in this case, it is counterrotating. The screw speed for the Brabender was maintained at 90 rpm and the torque was monitored during the entire duration of mixing. A steady torque was achieved after about 2–3 min of mixing. The changes in the intergallery spacings of Na-Mmt obtained from similar sample mixed in the two different mixers was almost identical.

Lyatskaya and Balazs [29] predicted that exfoliated nanocomposites were favored by lower molecular weight polymer. Vaia et al. [10] however, showed that molecular weight only affects the kinetics of intercalation and does not change the extent of intercalation. Fig. 9 compares the effect of molecular weight of the ionomer used for two different TBA-SPS*x.y* with similar sulfonation levels ($x.y = 0.75$ and 0.66) on the level of intercalation. The higher molecular weight (HMW) polymer ($M_w = 280$ kDa) had a much higher melt viscosity, which translates into higher shear stresses that may aid dispersion. The lower molecular weight (LMW) polymer ($M_w = 0.8$–5 kDa), however, should have a higher diffusion coefficient, which may aid transfer into the silicate galleries. But, the XRDs shown in Fig. 9 indicate no effect of the molecular weight of the ionomer on the gallery spacing of the melt mixed composites. The use of a bimodal molecular weight distribution, achieved by blending HMW PS with LMW TBA-SPS0.32 ionomer, had no effect on the intercalation, as shown in Fig. 9. In that case, the HMW PS was chosen to increase the shear stresses and the LMW ionomer to optimize diffusion to the silicate galleries and to allow the use of lower processing temperatures than would be possible with the much higher viscosity high molecular weight ionomer. The IEC/CEC ratio was 2.9.

The results for the intercalation of the molten ionomer into the Na-Mmt were relatively insensitive to the processing variables. Further, the magnitude of the increase in *d*-spacings of the silicate indicates that the degree of penetration of the ionomer into the galleries is not substantial, and the increase in the gallery spacings might actually be due to the intercalation of smaller molecules than polymer. One possibility is that the counter-ion from the ionomer is exchanging with the Na^+ initially present in the galleries, and that the net result of the melt intercalation process, in this case, is to produce an organically modified clay—albeit, by a meltphase reaction.

3.3. Effects of the amine counter-ion

The effect of the alkyl amine counter-ion on the ability to intercalate the SPS ionomers into Na-Mmt was assessed by studying a series of amine neutralized polystyrene ionomers with varying number of alkyl substituents and alkyl chain lengths. Previous work showed that the nature of the alkyl amine counter-ion can greatly affect the rheological properties of the ionomer by providing differences in the strength of ion association and/or steric hindrance of the ionic groups [25].

A series of mono-substituted *n*-alkyl amine salts with increasing alkyl chain length: butylamine (BuASPS), octylamine (OASPS) and hexadecylamine (HDASPS) were prepared from SPS0.75. These were melt mixed with PS to form 75/25 (w/w) blends with the ionomer and 3 wt%

silicate composites in the DACA microcompounder using a screw speed of 190 rpm and a temperature of 50 °C above T_g. The XRD data of the composites are shown in Fig. 10. The *d*-spacings of the galleries increased as the alkyl chain length increased from butyl to octyl, but it decreased for the hexadecylamine salt. The increased *d*-spacing values for OA-SPS0.75 compared to BuA-SPS0.75 suggest that it was the amine, and not the polymer, that was intercalating into the clay. The values of the intercalation for those two salts agree well with those reported for direct intercalation of the two alkylamines into Na-Mmt [30,31]. The increase in the gallery spacing for the HDA-SPS may be due to the longer alkyl chain, which shields the N atom from interacting with the negative silicate layers.

The effect of increasing the number of substituents on the N of the counter-ion was studied using butylamine (BuA-SPS0.75), dibutylamine (DBA-SPS0.75) and tributylamine (TBA-SPS0.75) ionomers in composites with PS and 3 wt% Na-Mmt. Fig. 11 shows XRD data of those melt-mixed and compression molded samples. The gallery spacing increased as the number of alkyl substituents increased—that is, as the salt progressed from primary amine to secondary amine to tertiary amine. This, again, is consistent with an ion-exchange of the alkylamine salt for the Na^+ in the galleries; the larger, more bulky TBA produced the greatest separation of the gallery spacing.

3.4. Quarternary ammonium salts

Fig. 12 shows the XRD of mixtures of Na-Mmt with a polymer blend of 25 wt% of teBu-SPS or teOc-SPS and 75 wt% PS. For the blend with teBu-SPS0.75, the first order silicate reflection was at the same position as was obtained when tributyl amine was the counter-ion. However, for teOc-SPS0.75, there was a substantial increase in the gallery spacing; the $d_{(001)}$ reflection shifted from 0.96 nm for Na-Mmt to 1.96 nm for the composite. The TEM micrographs in Fig. 13 confirm the increased silicate gallery spacing and a much improved dispersion of the silicate layers when teOc-SPS0.75 was used. The lower magnification images in

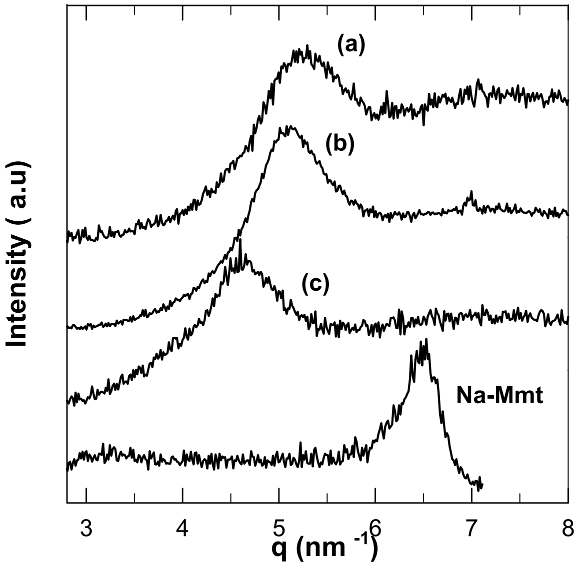

Fig. 11. WAXD of Mmt composites with alkylamine neutralized SPS as a function of the number of alkyl substituents on the amine: (a) (75/25) PS/BuASPS0.75/Mmt (b) (75/25)PS/DBASPS0.75/Mmt (c) (75/25) PS/TBASPS0.75/Mmt. All blends contained 3 wt% Mmt and 97 wt% polymer composed of 75/25 (w/w) PS/ionomer.

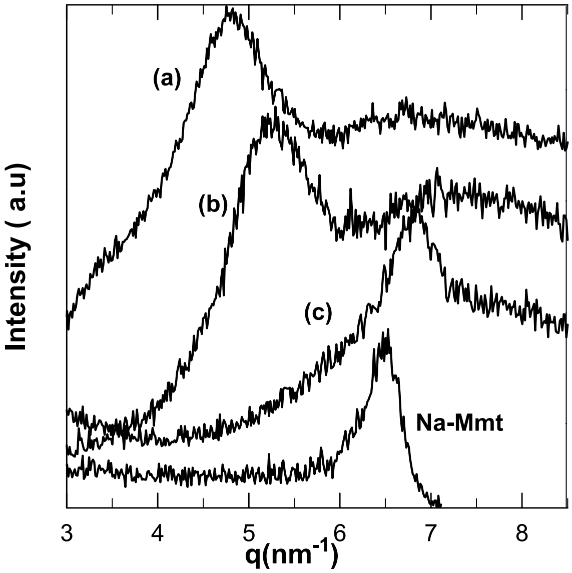

Fig. 10. WAXD of Mmt composites with alkylamine-neutralized SPS as a function of the alkyl chain length: (a) (75/25)PS/OASPS0.75/Mmt (b) (75/25)PS/BuASPS0.75/Mmt (c) (75/25)PS/HDASPS0.75/Mmt. All blends contained 3 wt% Mmt and 97 wt% polymer composed of 75/25 (w/w) PS/ionomer.

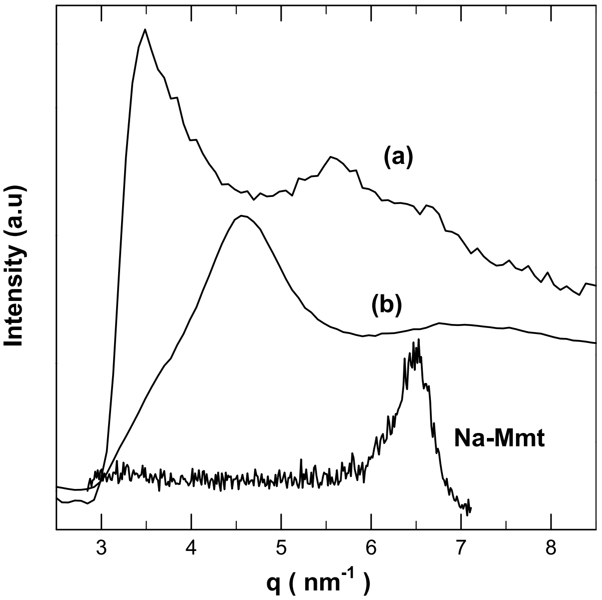

Fig. 12. WAXD of a Mmt composites with quarternary ammonium salts of SPS as a function of the alkyl chain length: (a) (75/25)PS/teOcSPS0.75/Mmt and (b) (75/25)PS/teBuSPS0.75/Mmt. All blends contained 3 wt% Mmt and 97 wt% polymer composed of 75/25 (w/w) PS/ionomer.

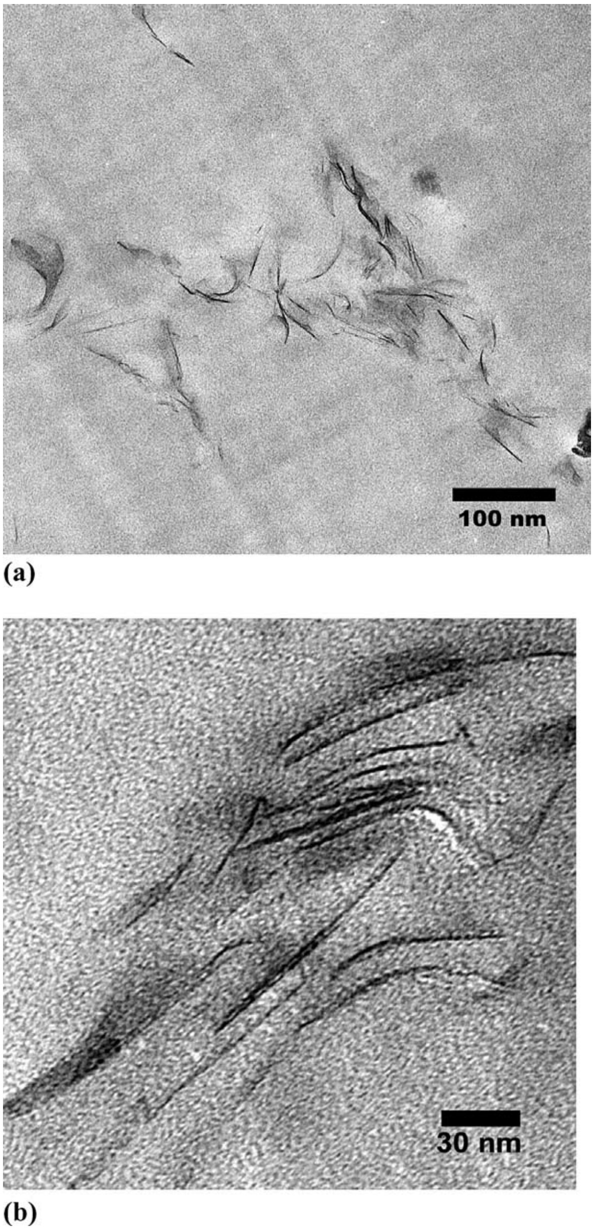

Fig. 13. TEM photomicrographs of (75/25)PS/teOcSPS0.75/Mmt at low magnification (a) and at higher magnification (b).

Fig. 13(a) also show a partially exfoliated morphology consisting primarily of individually dispersed clay platelets and/or silicate layers arranged in small groups. The higher magnification images in Fig. 13(b) show a large number of objects having 2–3 layers of silicate stacked together. These micrographs are in contrast with the large clay tactoids of the sizes of μm observed when the Na-Mmt was dispersed only in PS, cf. Fig. 6(a).

4. Conclusion

The melt mixing of pristine Na-Mmt with alkyl amine and quarternized ammonium salts of lightly sulfonated polystyrene ionomers resulted in an increase in the silicate gallery spacing consistent with intercalation. Mixtures of the ionomer with polystyrene exhibited similar gallery spacing increases, indicating that the ionomer is an effective compatibilizing agent for mixing of hydrophobic polymers into the clay. The extent of intercalation was independent of the melt processing conditions employed in this study and also did not change as the molecular weight of ionomer was varied. Intercalation appeared to be dependent on the charge ratio between the ionomer and the clay; when the ratio was greater than 1.0, interaction occurred. The increase in gallery spacing achieved was a function of size of the alkylamine counter-ions used. The more bulky, tri-substituted amine salts exhibited the largest gallery spacing increase. The extent of intercalation was consistent with an ion-exchange of the alkylamine counter-ions with the originally present Na^+ ions in the gallery, rather than intercalation of polymer, though no direct proof of that was obtained. More intercalation and even some exfoliation was achieved when a tetra-octyl ammonium salt was used.

A tentative mechanism for the melt intercalation may be rationalized on the basis of charge distributions in clay tactoids [32] and the presence of Lewis and Bronsted acid sites on the clay surfaces. The anionic sulfonated polystyrene is attracted towards the positively charged edges of the silicate layers. This association of SPS with silicate layers brings the counter-ions of SPS in proximity to the counter-ions of silicate layers, resulting in ion-exchange. This mechanism is speculative and further work is needed to completely understand the cause of the gallery spacing increase. Complete ion-exchange is not necessary, and it is more likely that only the cations which form 20% of CEC [23] and are loosely bound are exchanged. That would explain the mixed morphology that was observed—that is, with some interlayers interspersed with amine counter-ions and some with the original counter-ions.

An important aspect of this work is the finding that in situ formation of an intercalated nanocomposite without the aid of any organic modification of pristine montmorillonite is possible by the use of appropriate ionomers.

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