Chem. Mater. **2003,** *15,* 1105−1110

New Poly(ethylene oxide)−Clay Composites

David J. Chaiko[†]

Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Avenue,
Argonne, Illinois 60439

Received August 19, 2002. Revised Manuscript Received December 18, 2002

This paper reports a new mechanism for the formation of clay intercalates containing poly(ethylene oxide) (PEO). This mechanism permits formation of a two-dimensional PEO crystal phase. Under acidic conditions, polymer adsorption occurs through an ion-exchange process that is mediated by oxonium cation formation. A single phase exhibiting a plateau in the d_{001} reflections of 19 Å is formed at a polymer/clay stoichiometry of 0.5 g/g. This two-dimensional PEO crystal phase has a higher melting temperature than its three-dimensional counterpart because it is confined within the clay galleries. Unlike previously reported methods for forming PEO/clay intercalates, oxonium ion exchange produces structures whose basal spacings increase with increasing polymer molecular weight.

Introduction

The adsorption of polyethers, such as poly(ethylene oxide) (PEO) and the lower molecular weight poly(ethylene glycol) (PEG), onto clays leads to the formation of hybrid structures with a wide range of interesting properties and important uses. For example, intercalation of PEO into the galleries of smectite clays has yielded an interesting new class of ionic conductors with possible electronic applications, such as solid-state electrolytes in batteries.[1−3] Recently, the adsorption of polyethylene-*block*-poly(ethylene glycol) copolymers onto Na^+−montmorillonite has been reported as a possible surface treatment to facilitate the formation of clay−polyethylene nanocomposites.[4] Water-soluble polymers, such as PEO, can be intercalated by treating the clay with an aqueous polymer solution[1] or by direct intercalation from the polymer melt.[3] In both approaches, the driving force behind PEO adsorption is entropic and involves at least partial replacement of the water of hydration associated with the exchangeable cations in the clay galleries.

Previous work[1−3] has found that intercalation of PEO within the galleries of Na^+-exchanged smectite clays results in hybrid structures that accommodate a maximum of 0.3 g of PEO/g of clay and display a characteristic d_{001} diffraction spacing of 17.7 Å. Polymer stoichiometries in excess of this ratio lead to the formation of two discrete phases—the clay/polymer intercalate, with 17.7-Å spacing, and a bulk PEO crystal phase.[3] In general, the intercalation of polymers beyond the monolayer depth is very difficult to achieve, and this limitation has impeded progress toward the commercialization of several of the most commercially interesting systems.[5−8]

Overcoming this limitation will require a better understanding of the factors that affect polymer adsorption, intragallery cation mobility, and clay exfoliation during production of nanocomposites. To that end, a study was initiated to determine the role played by the exchangeable cation in the adsorption of PEG onto smectite clays. Complexes were prepared with three clays: montmorillonite, saponite, and hectorite. These are 2:1 phyllosilicates with exchange capacities of about 50 mequiv/100 g of hectorite, 70 mequiv/100 g of saponite, and 125 mequiv/100 g of montmorillonite. In addition to the differences in exchange capacities, each displays a different assemblage of mineral impurities and thereby provides an opportunity to study how residual impurities in the processed clays may influence nanocomposite properties. In this paper, a new composite phase is reported for the PEG/clay system. This phase exhibits polymer stoichiometries greater than 0.3 and displays an endothermic melt transition.

Experimental Section

Materials and Methods. The clays used in this study were a Na^+−montmorillonite from Wyoming (Cloisite Na, Southern Clay Products), Na^+− and Ca^{2+}−saponites from Arizona (R. T. Vanderbilt Co. and GSA Resources, respectively), and a hectorite (Bentone MA, Elementis). Mineral impurities were removed from all of the as-received clay samples by dispersing the samples in deionized water at 40 °C and centrifuging. The clay samples were dispersed at a total solids concentration of 3−5 wt % with poly(ethylene glycol) 1450 (PEG-1450) as a dispersant (0.3 g of PEG/g of clay) along with 3 wt % (relative to the weight of the clay in the slurry) of the tetrasodium salt of 1-hydroxyethane-1,1-diphosphonic acid (Dequest 2016D, Solutia). This dispersant was used to (a) block the hydrogen-bonding sites on the edge of the clay particles in an effort to minimize edge−edge and edge−face interactions between clay particles and (b) to complex any calcium originating from the

---

[†] Phone: (630) 252-4399. Fax: (630) 252-4176. E-mail: chaiko@cmt.anl.gov.

(1) Aranda, P.; Ruiz-Hitzky, E. *Chem. Mater.* **1992**, *4*, 1395.
(2) Wu, J.; Lerner, M. M. *Chem. Mater.* **1993**, *5*, 835.
(3) Vaia, R. A.; Vasudevan, S.; Krawiec, W.; Scanlon, L. G.; Giannelis, E. P. *Adv. Mater.* **1995**, *7*, 154.
(4) Liao, B.; Song, M.; Liang, H.; Pang, Y. *Polymer* **2001**, *42*, 10007.
(5) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.
(6) Akelah, A.; Salahuddin, N.; Hiltner, A.; Baer, E.; Moet, A. *Nanostruct. Mater.* **1994**, *4*, 965.
(7) Wang, M. S.; Pinnavaia, T. J. *Chem. Mater.* **1994**, *6*, 468.
(8) Akelah, A.; Moet, A. *J. Mater. Sci.* **1996**, *31*, 3589.

10.1021/cm020833j CCC: $25.00

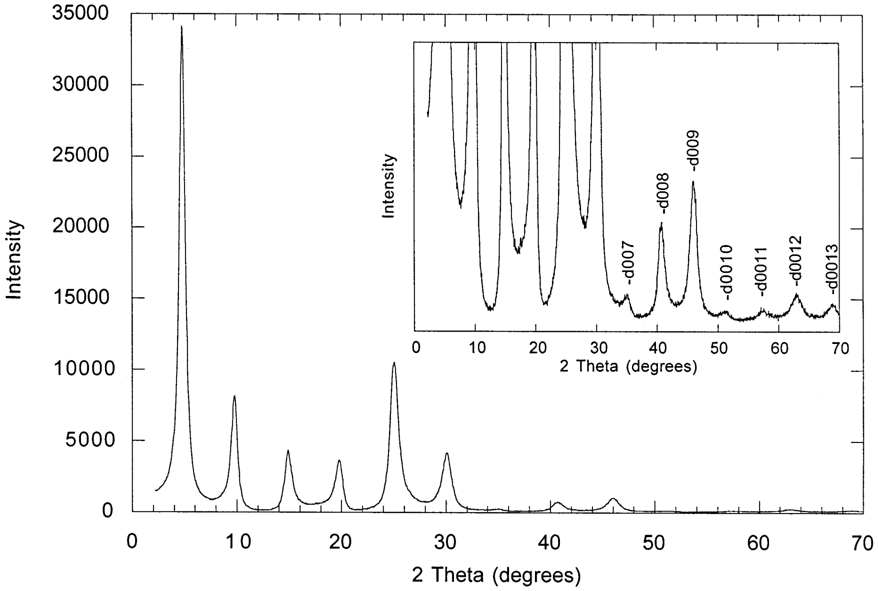

Figure 1. X-ray diffraction pattern of a PEG-1450/Na$^+$−hectorite nanocomposite.

exchange sites on the clay. The dispersant also helps to minimize defects in cast films by suppressing the viscosity for a longer period into the film-drying process—thereby minimizing misaligned or flocculated particles.

In sample preparations with varying polymer concentration, the purified clay slurry (a centrifuged product without added PEG) was treated with a cation-exchange resin (Dowex HCR-S) to replace the Na$^+$ and Ca^{2+} ions on the clay surface with H$^+$. Sufficient resin was used to ensure that with complete exchange of Na$^+$ or Ca^{2+} from the clay $<$10 mol % of the exchange capacity of the resin would be consumed. The clay slurries were processed at a dispersed solids concentration of 0.5 wt % to avoid blockage of the exchange column. Varying amounts of PEG or PEO were added to the treated clay slurries after H$^+$ exchange. The nanocomposite compositions reported below represent the mass ratio between measured clay concentration and added polymer. No further analysis of polymer stoichiometry was performed. All polymers used in this study were purchased from Aldrich.

The oxygen transmission rate was measured from cast films following the method described in ASTM D 3985-95 "Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor." Differential scanning calorimetry (DSC) measurements were performed with a Perkin-Elmer Pyris 1 calorimeter under an argon atmosphere and a scan rate of 20 °C/min.

The basal spacings of the clay−polymer intercalates were measured by X-ray diffraction using a Rigaku diffractometer with Cu Kα radiation, $\lambda = 1.541$ Å.

Results and Discussion

Transport in PEO−Clay Composites. To a certain extent, thermoplastic flow, gas diffusion, and cation transport in clay/polymer systems are all coupled to segmental motion of the polymer. However, past studies have shown that confinement of PEO within the clay galleries restricts polymer motion to such an extent that the melt transition of the polymer completely disappears, and the only observable event in DTA and TGA measurements is the polymer decomposition at 360 °C.[1,2] Not surprisingly, ionic conductivity in these systems, even at elevated temperatures, is extremely low—less than 10^{-5} vs 10^{-3} S/cm for nonintercalated polymer electrolytes.[9]

In addition to the influence of segmental polymer motion on diffusion processes, transport rates also depend on platelet orientation, which introduces anisotropy. Transport perpendicular to the platelet orientation is retarded because of the tortuosity introduced into the diffusion path by the presence of the clay platelets. While problematic in the production of solid-state electrolytes, these diffusion-barrier properties are of great value in flexible packaging applications, where increased resistance to gas transport is desirable.

Cast Films. An effective method for producing highly oriented PEG/clay nanocomposites is to cast thin films (i.e., $<$100 μm) from dilute aqueous suspensions. The resulting intercalated structures are in effect lamellar liquid-crystal composites. Thus, the optical properties of these films, when plasticized by water or other appropriate polar solvents, can be controlled by electric fields and shear.[10]

In the absence of defect structures in liquid-crystal films (i.e., misaligned or flocculated particles), these materials would be expected to be transparent, and their X-ray diffraction patterns should reveal highly regular and intense d_{00l} reflections. The pattern in Figure 1, which shows the expected features, is from a Na$^+$−hectorite nanocomposite containing a bilayer of PEG-1450 in the galleries (i.e., a monolayer of polymer per clay crystal surface). Similar diffraction patterns were obtained with montmorillonite and saponite.

Structural and optical defects were minimized by removing any remaining impurities by centrifugation at approximately 6000g for 10 min immediately prior to casting the films. This pretreatment always produced a small portion of particles which settled and are presumed to be either flocculated or unexfoliated clay impurities. The film quality was further improved by allowing slow evaporation of the solvent at ambient temperature. As a result, the clay platelets had time to self-assemble under gravitational and osmotic forces

---

(9) Srinivasa, R. R.; Riley, M. W.; Fedkiw, P. S.; Khan, S. A. *Chem. Mater.* **1998**, *10*, 244.

(10) Kawasumi, M.; Usuki, A.; Okada, A.; Kurauchi, T. *Mol. Cryst. Liq. Cryst.* **1996**, *281*, 91.

before the viscosity of the system impeded particle realignment. In Figure 1, only one-dimensional reflections are visible, and a total of 13 (00*l*) reflections can be observed by appropriate scaling of the plot. The clay gallery height is expanded to approximately 8.2 Å because of the presence of the polymer. The hectorite films, along with similar films made with montmorillonite and saponite, were flexible and strong despite being only 10−100-μm thick. The amazing flexibility of the composites, which are essentially polymer-modified ceramics, reflects the highly compliant nature of the aluminosilicate crystal lattice.[11]

Despite the centrifugation step and slow solvent evaporation, all of the cast films were translucent because of some long-range disorder on the scale of visible light. Interestingly, it was possible to deposit transparent and colorless hectorite films onto glass substrates by heating a dilute PEG/clay dispersion to temperatures above the cloud point of the clay/polymer exfoliate (i.e., 100 °C). With this approach, trace mineral impurities, which would otherwise contribute to defects in the films, can remain suspended in the aqueous dispersion during self-assembly. Cast films, in contrast, do not provide a mechanism for the segregation of defect-forming impurities.

Gas Transport. Despite the relatively low level of optical defects in the hectorite and saponite films, their oxygen permeabilities were in excess of 10^{-16} mol/m·s·Pa. In contrast, the oxygen permeability of a PEG/Na^+−montmorillonite film (56-μm thick), measured at 0% relative humidity, was below the detection limit of approximately 1×10^{-21} mol/m·s·Pa. The reported oxygen permeability for PEO is about 8.6×10^{-16} mol/m·s·Pa.[12] To better understand the barrier mechanism introduced by the presence of the clay platelets, the tortuosity factor (τ) was estimated by using the Nielsen[13] equation,

$$\tau = 1 + (L/2W)V_f \tag{1}$$

where L is the average length of the clay platelets, W is the thickness, and V_f is the volume fraction of the clay in the nanocomposite. The estimated tortuosity factor of the PEG/Na^+−montmorillonite nanocomposite is 28−280. (This range was calculated by assuming a platelet thickness of 9.5 Å and average platelet lengths of 1 000 and 10 000 Å.) For one of the films tested, the oxygen permeability was actually 650 000 times lower than that of PEO, rather than ~280 times lower, as predicted by the tortuosity factor. Direct observation of montmorillonite platelets by atomic force microscopy reveals platelet diameters of 1000−2000 Å, with some platelets extending to 5000 Å.[11] Values of this order are not sufficient to account for the observed improvements in oxygen barrier properties. Even using a physically impossible aspect ratio (i.e., L/W) of 1 000 000 in eq 1 does not fully account for the measured reduction in the oxygen permeability. Clearly, the reduction in permeability is due to more than tortuosity effects alone. Deviations from the Nielsen equation have been observed in other nanocomposite systems,[13] and empirical correction factors that take into account the effects of polymer constraint within the galleries have been suggested.[14] However, it should be remembered that gas permeability is a function of both the diffusion and solubility coefficients. Since both can be expected to be sensitive to polymer constraint at high clay loading, their inclusion in a mathematical description of the transport process would provide a more direct approach to quantifying constraint factors. In the present system, the nanocomposite structure is somewhat simplified in the sense that all of the polymer is located within a highly constrained environment. Unfortunately, the nondetectable oxygen transport does not allow an estimation of oxygen diffusivity and solubility within the nanocomposite film.

The nondetectable gas transport observed in the PEG/Na^+−montmorillonite film is a result of extreme polymer constraint. It represents the largest deviation from the Nielsen model reported to date. The assignment of quantitative, physically meaningful factors to account for polymer constraint will undoubtedly require a better understanding of how segmental motion contributes to permeability. The larger issue, however, is whether effective methods can be developed to influence the interfacial phenomena that control solubility/diffusion in highly constrained systems.

Achieving extremely low gas permeability requires both long-range order within the film (i.e., minimal film defects such as cracks and pinholes) and severely restricted segmental motion of the intercalated polymer. Consequently, the PEG/clay nanocomposite films do not undergo thermoplastic flow unless they are plasticized by water. While the PEG/clay nanocomposites are impervious to nonpolar gases such as oxygen, they will swell in water. Without further modification, this sensitivity to moisture probably limits their utility as barrier films in packaging applications. Interestingly, the films that were prepared on glass by cloud-point deposition were unaffected by water and remained intact and transparent after several wet/dry cycles.

Ionic Transport. The confinement of PEG/PEO polymers within the clay galleries can lead to both low gas permeability and low ionic conductivity. For example, the highest values for Li^+ conductivities reported in the literature[15] for PEO/clay nanocomposites are $<10^{-5}$ S/cm, whereas corresponding conductivities in the absence of the clay are about an order of magnitude larger at temperatures above the melting point of the polymer.[15] Commercial viability as a solid-state electrolyte would require nanocomposite conductivities of about 10^{-3} S/cm or more.

To achieve the needed improvements in conductivity, it will be necessary to find ways to increase segmental motion of the polymer within the clay galleries. Increasing the intragallery distance would reduce polymer confinement and would likely lead to increases in ionic diffusion. Unfortunately, simply adding more polymer to the system does not lead to an increase in the gallery spacing. As shown in Figure 2, the excess polymer simply phase-separates upon removal of the water, and

---

(11) Kotov, N. A.; Magonov, S.; Tropsha, E. *Chem. Mater.* **1998**, *10*, 886.

(12) Braun, D. B. In *Handbook of Water-Soluble Gums and Resins*; Davidson, R. L., Ed.; McGraw Hill: New York, 1980.

(13) Nielsen, L. *J. Macromol. Sci. Chem.* **1967**, *A1*, 929.

(14) Beall, G. W. In *Polymer−Clay Nanocomposites*; Pinnavaia, T. J., Beall, G. W., Eds.; John Wiley & Sons: New York, 2000.

(15) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.

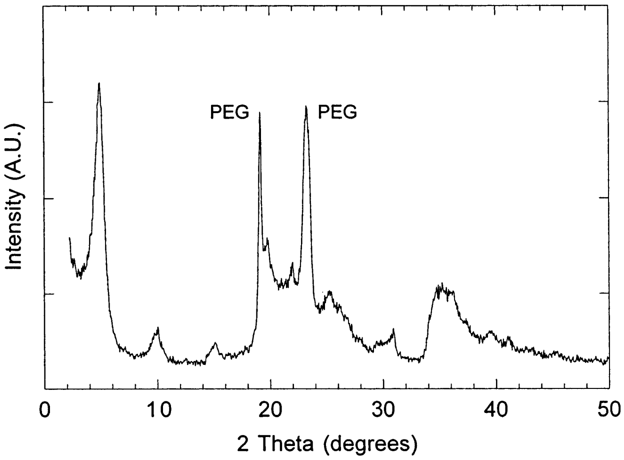

Figure 2. X-ray diffraction pattern of a PEG-1450/Na$^+$–saponite containing 50 wt % polymer.

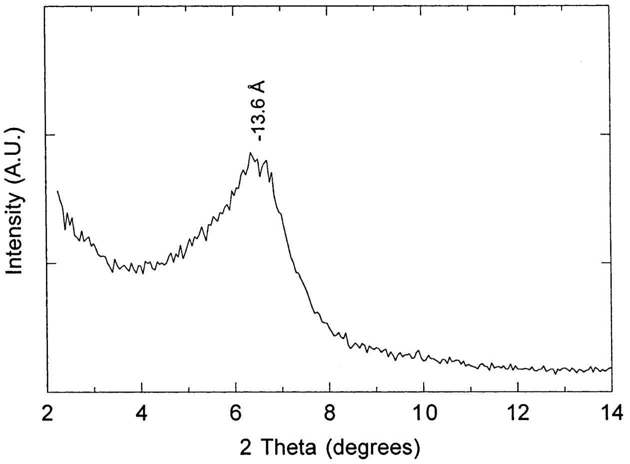

Figure 3. Basal spacing of a PEG-1450/ Na$^+$–saponite nanocomposite containing 27 wt % polymer.

the result is a solid solution containing a mixture of the 17.7-Å nanocomposite and the three-dimensional polymer crystal phase, which has characteristic diffraction peaks at 4.63 and 3.83 Å. Similar phase separation was observed in systems prepared by direct melt intercalation.

New PEG–Clay Composites. In one sense, the inability of PEO to form intercalates with greater than a monolayer depth can be viewed as an inability of the PEO molecule to wet the monolayer surface. If this nonwetting behavior represents a general phenomenon, it will have profound implications for the prospects of making single-phase clay/polymer nanocomposites with low clay loadings. Interestingly, when a nanometer-thick film of an aqueous PEG solution is spread on an immiscible, aqueous salt solution, the PEG film mimics certain aspects of the behavior exhibited in clay/PEO systems. In this system, the spreading of a thin PEG film is followed almost immediately by its collapse into a stable film approximately 40-Å thick, which is in equilibrium with macroscopic PEG-phase lenses floating on the aqueous subphase.[16] It would appear that the nonwetting behavior of PEG and PEO is induced by more general interfacial phenomena, rather than simply resulting from confinement within the clay galleries.

Cation Substitution. In the course of preparing PEG intercalates with a Na$^+$–saponite (R. T. Vanderbilt), anomalous basal spacings were observed with d_{001} values of 13.6 Å at 27 wt % PEG loading (see Figure 3) instead of the expected 17.0-Å spacing. Systems with polymer stoichiometries that lie between a monolayer and a double layer, as in Figure 3, typically show d_{001} broadening due to the formation of two discrete nanocomposite phases: a 13.6- and 17.7-Å phase, respectively.[2] Indeed, the peak width at half-height is quite large (i.e., 2.2° 2θ), suggesting that two products are present within the galleries. However, redispersion of the intercalate in deionized water and the addition of a few milliequivalents of Na$^+$ per 100 g of clay resulted in a significant expansion of the clay galleries and produced an intercalate exhibiting the expected d_{001} value.[17] This result suggests the presence of a new intercalate phase containing the PEG double-layer structure but exhibiting slightly lower than expected d_{001} values.

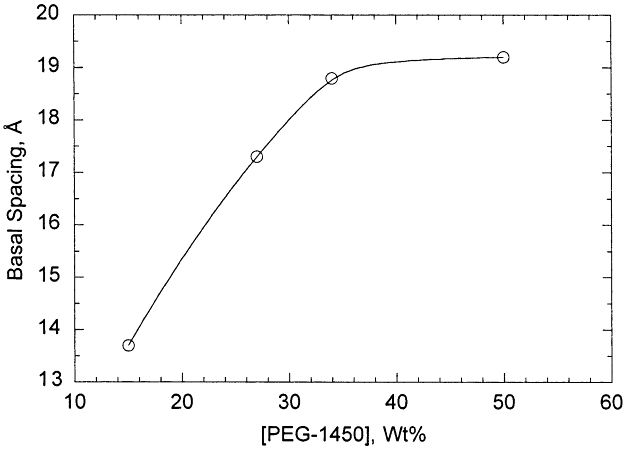

Figure 4. Basal spacing for PEG-1450/H$^+$–saponite nanocomposites as a function of polymer loading.

It is known that the interlayer cations of PEO/Na$^+$–clay intercalates are easily replaced by NH_4^+ or short-chain quaternary amines.[1] In an attempt to explain the unusual d_{001} spacing of the PEG/saponite intercalate in Figure 3, a series of PEG/clay complexes were prepared with cation substitution. The goal was to explore the extent to which the size of the exchangeable cation influences both interfacial adsorption capacity and d_{001} spacing. The results for H$^+$-exchanged materials are reported here.

To find out if the phase-formation behavior observed in the Na$^+$–saponite samples is a more general phenomenon, a Ca^{2+}–saponite (GSA Resources), purified by centrifugation, was treated with a cation-exchange resin in the H$^+$ form to replace the exchangeable ions on the clay surface. Varying amounts of PEG-1450 were then added to aliquots of the slurry. The samples were dried overnight at 100 °C, producing translucent, birefringent nanocomposites. The X-ray diffraction patterns were measured to determine the d_{001} spacings as a function of polymer loading. The data in Figure 4 reveal a higher than expected[2] plateau in the d_{001} values at about 19.2 Å and corresponding to a polymer loading of about 50 wt %.

---

(16) Li, M.; Tikhonov, A. M.; Chaiko, D. J.; Schlossman, M. L. *Phys. Rev. Lett.* **2001**, *86*, 5934.

(17) Ciullo, P. Personal communication, 1999.

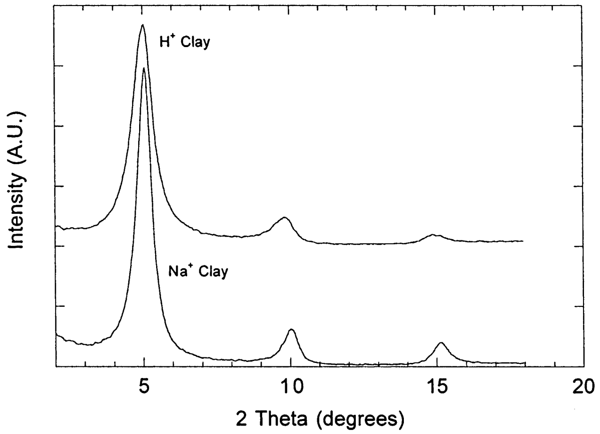

Figure 5. X-ray diffraction patterns for dimethoxy-PEG/montmorillonite nanocomposites.

It is believed that the presence of H^+ ions in the exchange sites of the clay led to protonation of the terminal −OH groups of the adsorbed PEG, thereby generating an oxonium cation. This hypothesis is supported by the fact that oxonium cation formation by PEG has been reported in the solvent extraction literature.[18] The protonated PEG complex is stabilized by the formation of a five-membered ring through hydrogen bonding with the terminal ether oxygen. Indeed, nanocomposites prepared from dimethoxy PEGs with molecular weights of 750 and 2000 produced nanocomposites with basal spacings of 17.7 Å. The X-ray patterns for Na^+− and H^+−montmorillonite containing 50 wt % polymer are shown in Figure 5. These results are especially interesting because the low-molecular-weight dimethoxy PEG is a liquid at room temperature and therefore lacks any driving force for phase separation as a result of polymer crystallization. Due to the influence of the methoxy groups, the 2000 molecular weight polymer (which is a solid at room temperature) shows only weak diffraction peaks at 4.63 and 3.83 Å—both of which were visible in the nanocomposite sample.

Loss of the hydrated metal ions in the exchange positions of the clay surface would explain the anomalously low basal spacings of Figure 3 since the volume that would otherwise be occupied by the metal cations has become vacant.

Further evidence in support of an oxonium-exchange mechanism is presented in Figure 6, where the d_{001} reflections of a series of PEG/clay composites are plotted as a function of polymer molecular weight. Interestingly, these data show a molecular weight dependency that has not been observed in previous PEO adsorption studies. These data suggest that the oxonium cation is adsorbed to the extent necessary to satisfy the cation-exchange capacity of the clay. Increasing the molecular weight of the polymer therefore results in further expansion of the clay galleries to accommodate the increasing mass of the oxonium cation. Further studies are planned to examine the effect of clay-exchange capacity on the PEG molecular weight dependency.

Properties of Oxonium-Exchanged Clays. Evidence that the nanocomposite containing 50 wt % PEG-1450 is a single phase is presented in Figure 7, which clearly shows the d_{00l} reflections, whereas the 4.63- and 3.82-Å reflections from the PEG crystal phase are absent. There is an enhanced scattering intensity between 15° and 35° 2θ, suggesting the presence of an amorphous phase—possibly due to portions of polymer chains hanging over the edges of the platelets.

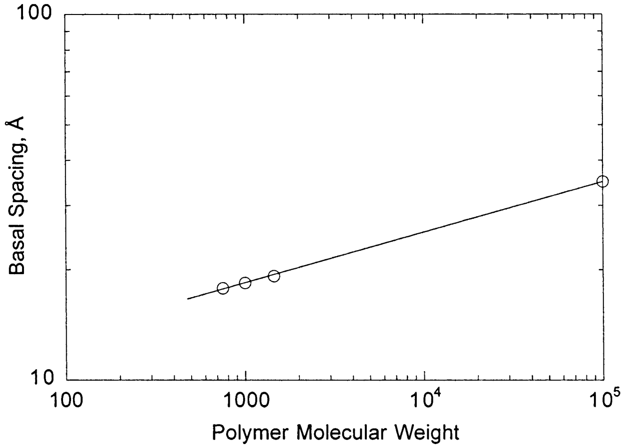

Figure 6. Basal spacing as a function of PEO molecular weight for H^+−saponite nanocomposites containing 50 wt % polymer.

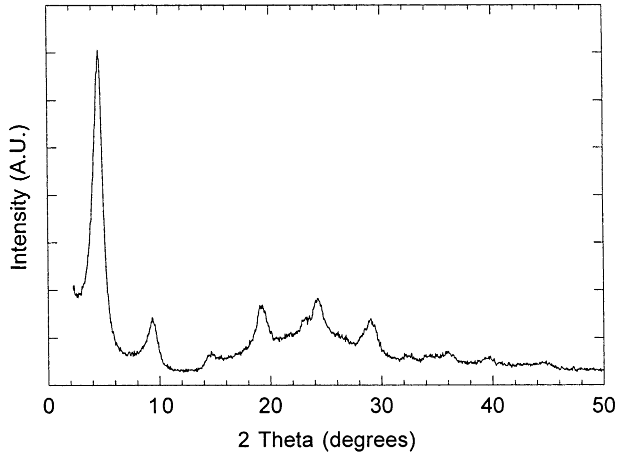

Figure 7. X-ray diffraction pattern of PEG-1450/H^+−saponite nanocomposite containing 50 wt % polymer.

Differential scanning calorimetry measurements of the nanocomposites containing 27, 34, and 50 wt % PEG-1450 were made to gain further insight into the physicochemical properties of the oxonium-exchanged clays. With 27 wt % polymer loading on the H^+-exchanged saponite, a melt transition was absent, indicating that the adsorbed polymer is confined within the clay galleries and is highly immobile. (The X-ray diffraction pattern of this sample also showed enhanced amorphous scattering.) The DSC trace did, however, show a decomposition endotherm at approximately 215 °C. For reference, the decomposition temperature for PEO/Na^+−clay nanocomposites in an inert atmosphere is approximately 360 °C. This saponite sample, when Na^+-exchanged and containing 27 wt % PEG-1450, showed the expected decomposition temperature of 360 °C. The lower decomposition temperature of the oxonium-exchanged clay is an indication of slightly enhanced mobility of the polymer within the clay galleries. (Nuclear magnetic resonance measurements to confirm this conclusion are planned.)

---

[18] Rais, J.; Sebestova, E.; Selucky, P.; Kyrs, M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1744.

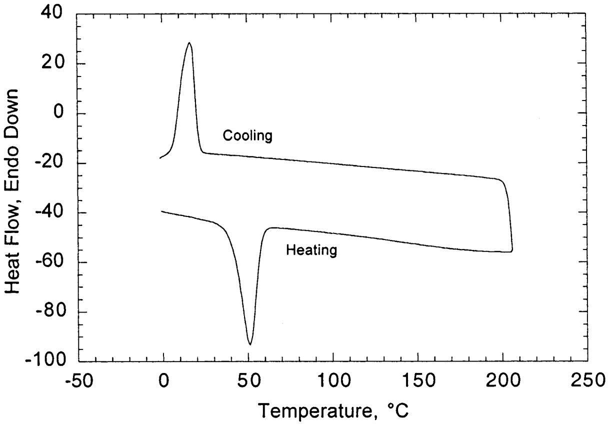

Figure 8. DSC plot of PEG-1450/H$^+$−saponite with 50 wt % polymer.

The DSC data for the nanocomposites containing 32 and 50 wt % PEG-1450 were identical and displayed a reproducible melt transition at approximately 50 °C and a recrystallization transition at approximately 18 °C. The DSC trace for the nanocomposite containing 50 wt % PEG is shown in Figure 8. The presence of the melt/freeze transitions indicates that at higher polymer loadings (e.g., >27 wt %) the oxonium cation behaves like a discrete, two-dimensional crystalline phase. However, the X-ray data in Figure 7 indicate that all of the polymer is firmly attached to the basal surface since the characteristic reflections for the PEG crystal phase at 4.63 and 3.82 Å are absent. In addition, the melt transition of 50°C is approximately 5−7 °C higher than that of the unconfined polymer and is consistent with the increase in melt transition that has been observed with poly(vinyl alcohol)/Na$^+$−montmorillonite nanocomposites.[19] Additionally, the increase in melting point indicates that the polymer in excess of 27 wt % is indeed located within the galleries and not merely attached to external surfaces of the intercalates or at the edges of the platelets.

The presence of a melt transition signals the appearance of enhanced segmental motion within the galleries. This change should increase gas diffusion within the galleries and, as a corollary, ionic diffusion as well. The results obtained with PEG indicate that, by extension, the adsorption of PEO as an oxonium cation may provide a new and useful route to the preparation of solid-state electrolytes with enhanced ionic conductivities. Further work is in progress to evaluate the ionic conductivities of mixed H$^+$−, Li$^+$−PEO/clay nanocomposites as possible solid-state electrolytes.

Acknowledgment. Support for this work was provided by R. T. Vanderbilt Co., GSA Resources, and the Chemical Technology Division of Argonne National Laboratory. This work was supported by the U.S. Department of Energy, Nuclear Energy Research & Development Program, under Contract W-31-109-Eng-38.

CM020833J

---

[19] Straehecker, K. E.; Manias, E. *Chem. Mater.* **2000**, *12*, 2943.