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Effect of Layer Charge on the Intercalation of Poly(ethylene oxide) in Layered Silicates: Implications on Nanocomposite Polymer Electrolytes

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The effect of layer charge on the intercalation of poly(ethylene oxide) (PEO) was investigated using a series of reduced-charge montmorillonites and smectites with varying layer charge. The amount of intercalated polymer initially increases with layer charge but then decreases. In contrast, the amount of water present continuously increases. This water is mostly coordinated with the gallery cations. When PEO is intercalated, it replaces water molecules filling the space between the hydrated exchangeable cations. Molecular simulations confirm the experiments and show that the polymer oxygen atoms do not directly associate with the exchangeable cations, which are mostly coordinated to water molecules and surface oxygen atoms.

Introduction

Improvements in rechargeable, high-energy density batteries are key to the development of products ranging from zero-emission vehicles to portable electronics. A key unsolved problem is the design and implementation of lightweight, chemically stable, and environmentally benign electrolyte/electrode combinations. Of particular interest are Li salts dissolved in flexible polymers such as poly(ethylene oxide) (PEO). A serious drawback in these systems is the precipitous decrease in conductivity at temperatures below the melting temperature, which is typically above room temperature. One of the most promising ways to improve the electrochemical performance of polymer electrolytes is to form composite electrolytes by adding inorganic fillers.

Polymer nanocomposites represent a radical alternative to conventional composite electrolytes. Previously we reported a nanocomposite polymer electrolyte based on intercalated PEO in a layered silicate with room-temperature conductivity several orders of magnitude higher than that of $LiBF_4$/PEO.[1] Polymer intercalation disrupts the normal, three-dimensional structure of the polymer chains and offers the means to suppress polymer crystallization. Furthermore, since the counteranions are the massive silicate layers, single-ion conduction is anticipated.

Intercalation of PEO in layered hosts, particularly in layered silicates, has been studied extensively.[1−16] Proposed arrangements for the intercalated chains up to this point have been based mostly on X-ray diffraction studies and generally assume a highly ordered polymer arrangement within the host gallery.

One proposed structure for the intercalated PEO is a helix. In this model, the cations are located in the center of the helix and are coordinated to the oxygen atoms of the PEO similarly to crown ethers. This arrangement was favored on the basis of infrared and nuclear magnetic resonance measurements. However, recent NMR work does not support the crown-ether-like association between the cations and the PEO oxygen atoms.[2] Furthermore, a helical structure would not allow full interaction of PEO chains with the silicate surface.

A second suggestion is that the PEO chains are organized in two extended, all-trans layers parallel to the silicate surface. Again the cations are assumed to be drawn to the center of the host gallery and coordinated by PEO oxygen atoms. This highly ordered structure is improbable on the basis of energetic considerations. Additionally, the structure would be perturbed by the presence of the exchangeable cations, which are heterogeneously distributed according to the layer charge distribution. This perturbation is much

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Table 1. Cation Exchange Capacities of Reduced-Charge Montmorillonites

sample	CEC (mmol/g)	CEC (% of CEC_{Mo1})	sample	CEC (mmol/g)	CEC (% of CEC_{Mo1})
Mo1	1.07	100	Mo5	0.71	66
Mo2	0.98	92	Mo6	0.52	49
Mo3	0.96	89	Mo7	0.24	22
Mo4	0.88	82	Mo8	0.11	10

greater when the hydration shell of the cations is taken into account. Fully replacing the water molecules in the coordination environment of the cations with less polar PEO oxygen atoms does not seem likely. PEO cannot play the role of a bridge in the electrostatic interaction between the cations and basal oxygen atoms of silicate, as water molecule dipoles may do.

In contrast to these proposals, some earlier reports have suggested that the gallery ions do not associate directly with PEO oxygen atoms and that their interaction with the polymer is mediated via the water molecules of their original hydration shells.[7] The above suggestions also do not take into account the heterogeneous nature of layered silicates such as layer charge density and ion location. These features give rise to hydrophobic and hydrophilic zones on the silicate surface. Thus, water and polymer molecules will absorb in these regions with varying affinity, producing a more disordered polymer structure than has been suggested so far.

In this paper we address the issues of cation coordination and silicate surface structure. We explore the effect of layer charge on PEO intercalation in layered silicates using a series of reduced charge montmorillonites and smectites. Additionally we focus on structure and interactions among the cation, the polymer, and the host surface and how these interactions affect the coordination shells of the cations.

Experimental Section

Synthetic Li-fluorohectorite (FH) (Corning Inc.) was used as received. Saponite (SapCa-1, Clay Mineral Society, Source Clays) was purified by sedimentation. Na-saponite was prepared by reaction with excess NaCl solution.

High-charge montmorillonite SAz-1, middle-charge montmorillonites HD and JP, and low-charge montmorillonite M40A (Wyoming), nontronite SWa-1, and iron-rich beidellite ST, were obtained from the collection of the Institute of Inorganic Chemistry, Slovak Academy of Sciences (Bratislava, Slovakia). More information about the purification and properties of these samples has been published elsewhere.[17,18]

The reduced-charge montmorillonites (RCMs) were prepared as described previously.[19] Briefly montmorillonite (Jelšový Potok, Slovakia) was first purified by sedimentation. The obtained dispersion of particles <2 μm was repeatedly saturated with a lithium chloride solution, washed several times to remove excess salt, and dried before being heated to 100−200 °C. Through this heat treatment the Li cations are driven inside the silicate framework and become immobile and nonexchangeable. As a result a series of montmorillonites with reduced charge and well-controlled cation exchange capacity (CEC) but similar particle size can be produced. Table 1 lists the different RCMs prepared in this manner and their nominal charge.

Nanocomposites were prepared by solution or melt intercalation. PEOs with molecular weights (MWs), 7500 (Polysciences Inc.) and 100 000 and 5 000 000 (Aldrich) were used. For melt intercalation a mixture of PEO and the silicate host was ground and mixed for 2 min. Equal weights of PEO and silicate were used, which enabled full polymer saturation of the host with some excess polymer. Pellets were pressed using a hydraulic press at 450 MPa for 20 s and subsequently heated to various temperatures for 15 h. Polymer intercalation was monitored using X-ray diffraction (XRD).

Solution intercalation was accomplished by slowly adding a 0.25% aqueous solution of PEO to 50 mL of a 0.1% suspension of the silicate in water to a final polymer/silicate weight ratio of 1:1. The resulting dispersions were allowed to age for 3 days with occasional shaking. Nanocomposite films were prepared by drying a small amount of the resulting suspension on a glass slide. The remaining dispersion was centrifuged, and the excess polymer was washed away by repeated dispersion in distilled water and centrifugation. Samples were washed 10 times to remove all nonadsorbed polymer and dried under vacuum at 50 °C for 2 days. The amount of irreversibly adsorbed polymer was determined by thermogravimetric analysis (TGA).

XRD patterns were collected on a Scintag Inc. diffractometer equipped with an intrinsic germanium detector using Cu Kα radiation. TGA was carried out on a Perkin-Elmer thermogravimetric analyzer (TGA 7) in air. A heating rate of 5 °C/min was used.

Canonical ensemble (NVT) computer simulations were performed using Cerius^2 software. The d spacing and polymer loading were input from XRD and TGA experiments, respectively. The simulation box parallel to the silicate layer measured 4.224 nm × 3.656 nm with periodic boundary conditions. Accurate force fields were adopted from literature studies of silicate hydration[20,21] and PEO/LiI mixtures.[22,23] These force fields have been carefully fit together to model this new system. Details of the simulation are given elsewhere.[32]

The amount of adsorbed water was determined by Monte Carlo simulations at 300 K. In these simulations a water vapor pressure of 100 kPa (1 atm) was imposed, and water was adsorbed through Grand Canonical Monte Carlo (GCMC) insertion, deletion, translation, and rotation trials. After water adsorption the system was equilibrated using molecular dynamic (MD) simulations. The water molecules were subsequently deleted and readsorbed through a second GCMC run to ensure thermodynamic equilibrium.

Water coordination to Li^+ was studied by considering the mass distribution plot of the entire GCMC simulation to

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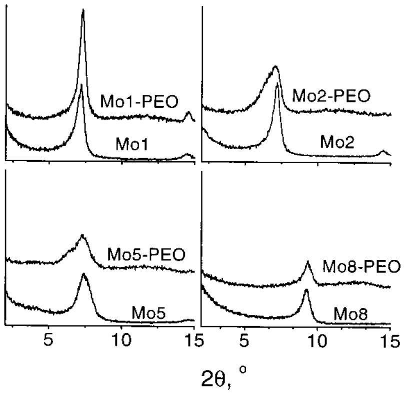

Figure 1. X-ray diffraction patterns of some reduced-charge montmorillonites and their unheated mixtures with poly(ethylene oxide) (MW 100 000).

ensure good statistics. The mass distribution was calculated in the projected plane parallel to the silicate walls. From this the number of Li ions coordinated to each water molecule was calculated.

Results and Discussion

Figure 1 compares the XRD patterns of different RCMs and the corresponding PEO–RCM mixtures ($\mathrm{MW}_{\mathrm{PEO}} = 100\,000$). The 001 basal reflection for the Mo1–Mo8 samples is in the range of 7–9°. The corresponding d_{001} value for the Mo1–Mo4 samples is about 1.2 nm.[19] Taking into account the montmorillonite layer thickness of 0.95 nm, the remaining corresponds to a monolayer of water molecules.[24] Further decrease of the layer charge (Mo5–Mo7) causes a nonswelling phase to appear. Mo8 contains only a nonswelling phase with a *d* spacing of 0.95 nm. In the others (Mo5–Mo7) a mixture of expandable and collapsed layers is present, evidenced by the broadening of the basal reflection. The number of collapsed layers in the mixed-layer structure (0.95/1.24 nm) increased gradually with decreasing charge (Mo5–Mo7).[19,25]

No apparent difference between the diffraction pattern of Mo1 and the PEO–Mo1 mixture was observed. On the other hand, a small change was observed for the mixtures containing the lower charge silicates (Mo2–Mo6). The reflections for these samples were broadened toward lower angles, i.e., higher interlayer distances. This change indicates partial but detectable intercalation of the polymer chains probably near the particle edges. Note the XRD patterns were obtained before any heating of the polymer/silicate mixtures. The collapsed layers, dominant in the structures of Mo7 and Mo8, remained unchanged in the presence of PEO. The same behavior was observed for the Mo7 and Mo8 samples under other intercalation conditions.

Heating at 60 °C (Figure 2a), which is still below the melting point of the bulk polymer ($T_{\mathrm{m}} = 66$ °C), led to polymer intercalation in Mo1–Mo6. As the layer charge of the RCMs decreased, the value of the basal spacing increased from 1.78 (Mo1) to 1.87 nm (Mo6), a small but reproducible difference. The *d* spacings correspond roughly to intercalation of two layers of PEO in the interlayer space. The small variations in the *d* spacing could be due to differences in the arrangement of the PEO chains. Alternatively a mixed-layer structure containing a polymer-intercalated phase and a phase with lower spacing might be present. The presence of mixed-layer structure was supported by the absence of 002 reflections in Mo1 and Mo2 and only very-low-intensity peaks in the Mo3- and Mo4-containing samples. Further decrease in layer charge (Mo5, Mo6) results in a more uniform hybrid structure characterized by relatively intense and narrow diffraction peaks. The collapsed phase found in pure Mo5 and Mo6 was reexpanded partially in the presence of the polymer. The ability of many polar organic compounds (glycol, glycerol, ethanol, etc.) to expand a nominally nonswelling interlayer in water has been previously reported.[26]

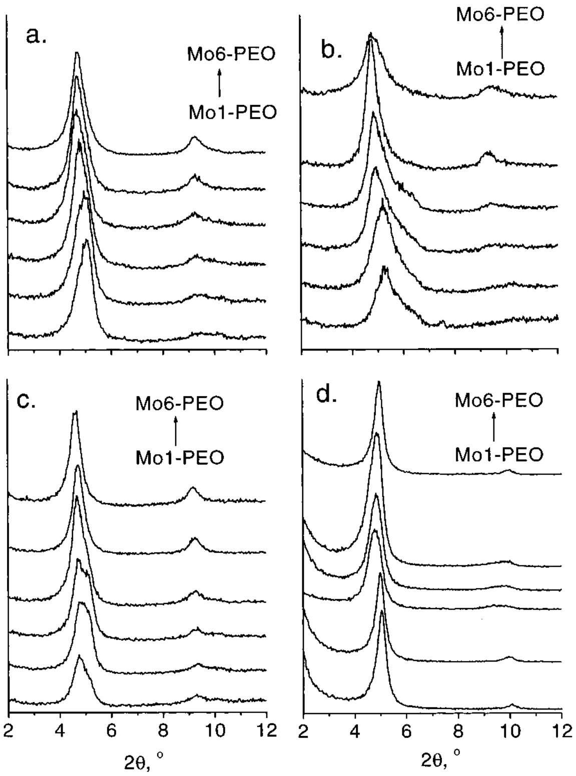

Figure 2. X-ray diffraction patterns of poly(ethylene oxide)-reduced-charge montmorillonite mixtures: (a) pellets with the polymer of MW 100 000, heated at 60 °C (b) pellets with the polymer of MW 7500, at room temperature; (c) pellets with the polymer of MW 5 000 000, heated at 75 °C; (d) films with the polymer of MW 100 000, prepared from solution intercalation.

Similar trends were observed in the intercalation of low MW PEO (7500) at room temperature (Figure 2b), and of very high MW PEO (5×10^6) at 75 °C (Figure 2c). Intercalation of low MW PEO takes place even at room temperature due to the higher mobility of relatively small PEO chains (Figure 2b). The broad band of the Mo6–PEO hybrid (Figure 2b) may indicate the presence of a collapsed phase, which is not fully reopened by polymer intercalation at low temperatures. Finally the same dependence of the *d* spacing on layer charge was also observed in the samples prepared by solution intercalation (Figure 2d).

High molecular weight PEO (5 000 000) was not completely intercalated in some cases (Mo1–Mo4), even when heated for 15 h at 75 °C, which is above the melting point of this polymer (Figure 2c). PEO with very long chains forms high-viscosity melts even at temperatures much higher than its melting point.[27] Such a high viscosity could hinder the intercalation of the

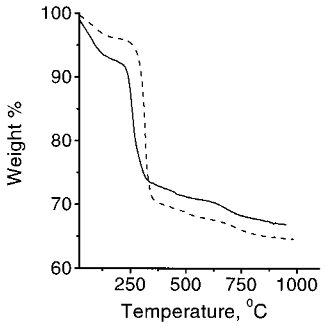

Figure 3. Thermogravimetric analysis of Mo1−PEO (solid line) and Mo5−PEO (dashed line).

polymer into the interlayer spaces of the inorganic host.

The trends observed above (Figure 2) could be summarized as follows. A mixed-layer structure containing a polymer intercalated phase corresponding to roughly two polymer layers and a phase with lower spacing (one layer of PEO chains and/or a nonintercalated phase) is formed in the high-charge silicates. A more uniform interlayer structure is present as the layer charge decreases. Additionally, the *d* spacing increases with decreasing layer charge.

TGA was used to quantify the amount of intercalated PEO and water present in the nanocomposites. Aranda and Ruiz-Hitzky[4] found very good agreement between the amounts of PEO adsorbed on layered silicates determined by TGA and organic content microanalysis. For these measurements samples prepared via solution intercalation were used.

PEO decomposes at temperatures above 300 °C, forming monomers, small oligomers, and other decomposition products.[28] Thermal decomposition of PEO nanocomposites proceeds as a multiple-step process: (1) weight loss due to the release of water (<225 °C); (2) decomposition of the polymer (225−400 °C); (3) dehydroxylation of montmorillonite at about 700 °C. Representative TGA traces of two nanocomposites, PEO−Mo1 (solid line) and PEO−Mo5 (dashed line), are shown in Figure 3. Both the release of water and the decomposition of the polymer shift to higher temperature for the Mo5-containing sample. Judging from the weight losses, the Mo5−PEO hybrid contains less water but more polymer compared to the corresponding Mo1 hybrid.

Figure 4 shows the amount of water and PEO as a function of the layer charge or CEC. The amount of PEO initially increases with CEC, but it reaches a maximum. On the other hand, the amount of adsorbed water continuously increases with CEC but does not exceed 10% of the total weight. Normally the amount of water in the silicate before polymer intercalation can be as high as 20%. This suggests that PEO, when adsorbed on the silicate surface, replaces water in agreement with previous observations.[3,6,7,12] Low contents of PEO and water in the Mo7 and Mo8 samples could be explained by the presence of collapsed interlayers, in which less surface area is accessible for intercalation.

The increase of the water content in PEO−RCMs with CEC indicates that water remaining after polymer intercalation is mainly associated with the exchangeable cations and is part of their hydration shells. Therefore, PEO does not coordinate directly with the exchangeable cations. If complexation with the cations is necessary for PEO intercalation, then the decrease of the layer charge, or CEC, would lead to less intercalated polymer. The opposite was observed for fully expanded RCMs (Mo1−Mo5). Reducing the number of hydrated cations frees up more silicate surface, allowing more polymer to be intercalated. In contrast, in high CEC silicates, the amount of hydrated cations hinders polymer intercalation. Exchangeable cations are in fact the only strongly hydrophilic sites on the silicate surface,[29] and the water bound to these cations is released only at relatively high temperatures. On the other hand, basal Si−O groups in the spaces between hydrated cations in the interlayers are relatively hydrophobic. PEO is more hydrophobic than water and is preferentially adsorbed on these sites. It does not require replacement of the water from the hydration shell of the cations. The existence of two kinds of water and their different contents in RCMs are supported by differential thermogravimetry (DTG) (Figure 5). Water was released from the RCMs in two steps with increasing temperature as shown by two representative examples (Mo1, Mo5). The amount of relatively weakly bound water (released below 100 °C) was higher in Mo5 (about 16.5% compared to 12% in Mo1). In contrast Mo1 contained relatively more water coordinated to the cations than Mo5 (about 6% and 3%, respectively). This water was released at temperatures above 100 °C.

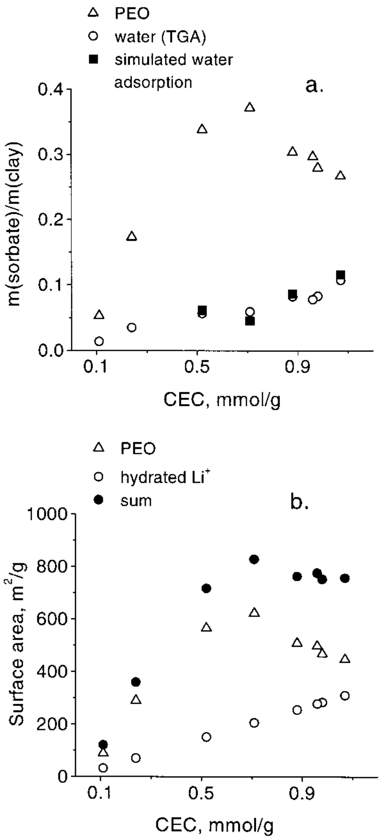

Figure 4. Relationships between the amounts of water and PEO adsorbed from water dispersions and the cation exchange capacity of montmorillonite: (a) weights of adsorbed PEO and water; (b) surface areas occupied by PEO and hydrated Li^+ cations.

The CEC values and experimentally measured amounts of PEO were used to estimate the surface area

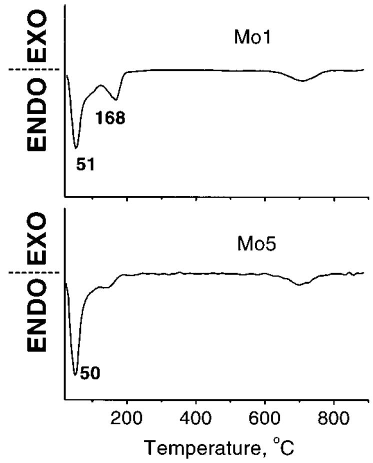

Figure 5. Differential thermogravimetry of Mo1 and Mo5 samples.

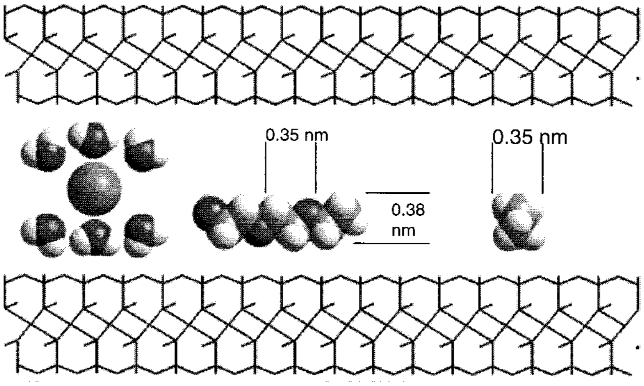

Figure 6. Schematic showing coordination of Li^+ by water molecules (left), the length (0.35 nm) of an all-trans PEO monomer (center), and the width (0.38 nm) of an all-trans PEO chain (right).

Table 2. Amounts of PEO and Water Adsorbed from Water Solution on Smectites, As Determined by Thermogravimetry

smectite	water amount (%)	PEO amount (%)	Smectite	water amount (%)	PEO amount (%)
FH	5.1	0.0	SWa-1	2.5	16.2
ST	8.8	11.4	JP	5.4	19.2
SAz-1	9.9	11.4	M40A	4.2	22.2
HD	7.3	13.3	saponite	4.2	22.1

occupied with hydrated Li^+ cations and polymer chains, respectively. For each Li^+ cation, an octahedral complex with the plane of three water molecules parallel to the silicate surface was considered (Figure 6). Such a complex would occupy 0.48 nm^2 (0.24 nm^2 for each layer).[29]

The dimensions of zigzag chains of PEO containing only trans bonds are 0.38 and 0.35 nm, respectively, while the length of the monomeric unit $-C_2H_4-O-$ is 0.35 nm (Figure 6). Also recall that the observed *d* spacing corresponds to two layers of polymer chains. Therefore, each monomeric unit of adsorbed PEO occupies only one of two layers, and the area is $(0.35\ nm)^2 = 0.12\ nm^2$. The presence of gauche conformations would affect the value of the surface occupied by the polymer, but not significantly. Therefore, this arrangement was neglected. In the calculations we assumed that all the water molecules are associated with Li^+ ions and that water molecules are not shared between Li^+ ions. We also assumed that all the cations and the polymer reside in the galleries and not on particle edges. The calculated surface area occupied by hydrated Li^+ cations and polymer chains, with respect to the CEC and the amount of adsorbed polymer, is presented in Figure 4b. The area occupied by hydrated Li^+ ions increases with CEC and is about 300 m^2/g for the highest charge samples. On the other hand, the area covered by polymer chains is always higher than that covered by the cations and their hydration shells, and it goes through a maximum. While this difference is not as large in the case of PEO−Mo1, the area covered by the polymer increases (for fully expandable RCMs) and that of hydrated cations decreases with decreasing CEC. In the case of Mo5−Mo7 the surface covered with polymer is more than 3 times that occupied by hydrated cations. That this model provides a good estimate despite its simplicity is evidenced by the excellent agreement between the overall surface (near 800 m^2/g) of the expandable RCMs (Mo1−Mo6) and that calculated from the unit-cell dimensions and determined by other methods.[30]

The trends observed in the RCMs were confirmed using Na-smectites of different composition and layer charge. The layer charge of these silicates, determined by the alkylammonium method, decreases in the order ST ≈ SAz-1 > HD > SWa-1 > JP > M40A.[17,18] The amounts of PEO and water present (Table 2) were compared together with those of two reference samples, very-high-charge, synthetic fluorohectorite and low-charge trioctahedral smectite−saponite. No PEO was intercalated on FH, or if it was, it was subsequently washed away with water, suggesting a very weak adsorption. The amount of adsorbed water was also relatively low (5.1%). Due to the very high cation density on FH, hydrated exchangeable cations occupy the majority of the surface and, hence, hinder PEO intercalation. The small amount of water present could be due to lower expandability of this silicate, which is common for high-charge smectites[31] and/or the high cation density. The hydration shells of some neighboring cations may not be fully saturated and may share water molecules. High-charge SAz-1 and ST intercalated a relatively small amount of PEO (about 11.5%) and retained a high amount of water (10% and 8.9%, respectively). Lowest charge montmorillonite M40A and low-charge saponite contained the highest amount of PEO. However, the amount of water remaining on the clay surface depends not only on the layer charge of smectite and the number of exchangeable cations, but also on the layer charge location, controlling the expandability of the smectite.[31] Relatively lower water amounts were observed for the tetrahedrally charged silicates (ST vs SAz-1; SWa-1 vs JP).

The amount of water present on PEO−RCMs calculated by computer simulations agrees well with the experimental values and trends, confirming the accuracy of the force field (Figure 4). The simulations also show that the intercalated polymer chains form two discrete layers, but the polymer retains a disordered, liquidlike structure.[32] This layering of molecules in confinement has been observed previously both experimentally[33] and in computer simulations.[34]

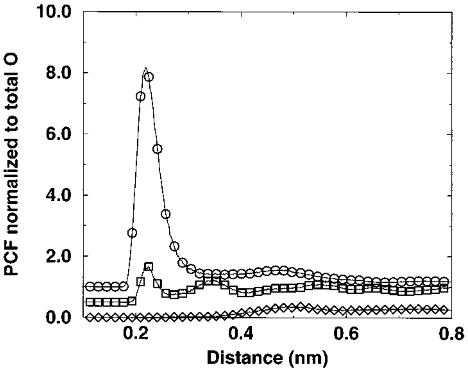

Figure 7. Radial pair correlation functions for oxygen atoms in the silicate/PEO nanocomposite (CEC = 1.05 mmol/g): (circles) water oxygen atoms, shifted up 1.0 for clarity, coordination number (CN) = 5.47; (squares) silicate surface oxygen atoms, shifted up 0.5 for clarity, CN = 1.10; (diamonds) PEO oxygen atoms, CN = 0.05. The overall CN (6.2) is equal to the sum of of CNs of water, PEO, and silicate oxygen atoms.

More detailed information on the interactions of Li^+ cations with oxygen atoms of PEO, water, or the silicate surface is obtained from the radial pair correlation functions (PCFs). The PCF records the average coordination environment of an atom. In the bulk the probability of finding an atom at an arbitrary point is proportional to the density of the medium. By extension, the probability that an atom will be found at distance r from a particular point is proportional to the density of the medium. The PCF of this arbitrary point, normalized to the bulk, would therefore be one for all distances r. If the point represented an atom of finite size, other atoms would be excluded from the space that it occupies. Consequently, the PCF or the probability of finding an atom at distance r from the test atom would be 0 for r less than the sum of the two radii. If other atoms coordinate to the central atom, then the local density in a spherical shell just beyond that atom would be greater than the average density of the medium. The PCF, normalized to the bulk density, at the corresponding r would have a peak with a value greater than 1. Steric ordering around the coordination shell may cause a second, weaker peak approximately one atomic diameter from the first. However, for large r, the effect of the central atom would no longer be felt and the PCF would approach a constant value of 1. In summary, a typical PCF has a value of 0 for r less than one atomic diameter, at least one peak due to coordination and local ordering around the central atom, and a value of 1 at longer distances, due to the normalization against bulk density.

The PCFs in Figure 7 illustrate the degree of association between the Li^+ cations and oxygen atoms from water, PEO, and the silicate surface. The PCFs are normalized against the *total* oxygen atom density in the gallery (excluding the inner layers of the silicate crystal), so that the sum of all PCFs shown in Figure 7 approaches one at large distances, as described above. Since PCFs effectively measure the average local density, they can be integrated to yield the average number of atoms in a sphere around a central atom (Li^+ ion in this case). From the PCFs it is clear that the cations are principally coordinated to water molecules and that the PEO is further away from the cations. In addition, the cations partially associate with the silicate surface while PEO resides outside the coordination shell of the cations. The second peak in the silicate surface oxygen PCF is due to the periodic crystal structure of the montmorillonite.

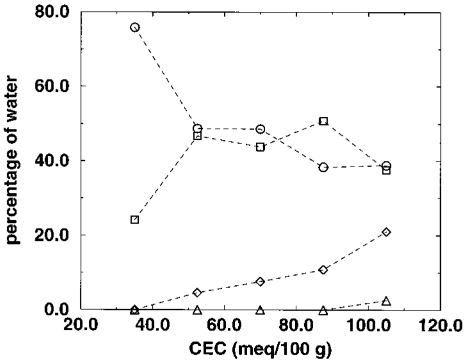

Figure 8. Percentage of absorbed water molecules calculated from computer simulations (accepted MC insertions) which do not coordinate Li ions (circles), or within a distance of 3.5 Å from one (squares), two (diamonds), or three (triangles) Li ions.

From the mass distribution of the GCMC simulations the coordination of the water molecules can be further analyzed (Figure 8). As the CEC increases the amount of water which does not coordinate any Li^+ decreases. The amount, which coordinates a single Li^+ ion, increases at first, leveling out or even falling slightly when it reaches about 50%. At the same time, the amount of water coordinated to two Li^+ ions increases steadily. Only at the highest CEC does any water molecule coordinate with more than two Li^+ ions at the same time. These trends reflect the increased concentration of the Li^+ ions and the need for the water to coordinate to the ions within the constraints of the confined, polymer-filled space.

The computer simulations fully support the model suggested above on the basis of the experimental data. PEO intercalates by replacing predominantly free water molecules in the gallery rather than directly coordinating to the cations, which seem to maintain their hydration shell intact.

Conclusions

Melt or solution intercalation of PEO into layered silicates leads to essentially identical structure in the nanocomposite. Experimental measurements coupled with computer simulations show that polymer chains replace weakly adsorbed water filling the space between hydrated exchangeable cations. No direct association between exchangeable cations and PEO oxygen atoms takes place. The amount of polymer adsorbed is controlled by the layer charge density, i.e., the surface area covered by the hydrated cations vs the surface area covered by weakly adsorbed water. The trends observed in this study may be applied to the intercalation/adsorption of layered silicates with other polymers[35] or organic compounds. For example, the lower expandabil-

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ity of high-charge smectites and vermiculites in organic solvents such as ethylene glycol and glycerol[36] is probably due not only to higher attractive electrostatic forces but also to the high density of hydrated exchangeable cations and the lack of accessible surfaces for adsorption.

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