Preferential Intercalation in Polymer-Clay Nanocomposites

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Received: April 23, 2004

When polymer-clay nanocomposites are prepared from a polymer of broad molecular mass distribution, the question arises whether the clay scavenges the low molecular mass fractions or prefers to receive the larger molecules which might provide bridges between nanoparticles. This is the first report of competitive sorption experiments for molecular mass in polymer-clay nanocomposites and shows that high molecular mass fractions of polymer intercalate preferentially into a smectite clay during solution preparation. Poly(ethylene glycol)s (PEGs) with different monomodal molecular mass distributions were mixed and added to montmorillonite in aqueous suspension. After centrifuging, excess PEG in the supernatant was analyzed gravimetrically and by gel permeation chromatography (GPC). The montmorillonite preferentially absorbed the higher mass fractions. X-ray diffraction confirmed intercalation. Sodium-treated montmorillonite also showed this preference. A heat-treated montmorillonite with collapsed layers was used as an experimental control to distinguish surface adsorption and gallery intercalation.

Introduction

A 'nanocomposite' is defined as a particle-filled matrix in which at least one dimension of the dispersed phase is in the nanometer scale.[1] In the case of polymer-clay nanocomposites, intercalation or exfoliation results in separation of the silicate layers that have thicknesses of ~1 nm and aspect ratios of 30 ~ 2000. Recent interest is partly due to better properties but also to the rapid commercialization by the Toyota Group.[2–4] Property enhancement is achieved at lower volume fractions (1 ~ 10 vol %) of reinforcement than in conventional composites (20 ~ 40 vol %). Nanocomposites can be processed by the same techniques as the polymer matrix. The clay is abundant, so the cost of materials is low compared to composites relying on fibers for a high aspect ratio; yet the filler aspect ratio is similar or even higher.

Polymer-clay nanocomposites take advantage of smectite clays because of their swelling properties, high cation exchange capacities, high aspect ratio, and large surface areas.[5,6] Montmorillonite (MMT), one of the most common smectite clays, is composed of units made up of two silica tetrahedral sheets centered with an alumina octahedral sheet. Its layers are stacked by weak dipolar or van der Waals forces, leading to the intercalation of water or polar organic molecules and causing the crystal lattice to expand in the *c* direction.[7,8] Therefore, not only adsorption on the external surface but also absorption (intercalation) in the galleries can occur. When MMT is heated (typically ≥ 600 °C), the interlayer water and lattice hydroxyls are removed, causing both the structure to be disrupted and the platelets to stack together.[7] In this case, only adsorption on the external surface takes place; hence, the heat-treated MMT provides a control, enabling adsorption and absorption to be distinguished.

There are three principal methods for synthesis of such nanocomposites: in situ polymerization,[9–12] solvent methods,[13–18] and polymer melt intercalation.[8,19–21] In the first, polymerization of monomers or oligomers takes place within the galleries,

possibly catalyzed at cation sites.[1] In solvent and melt intercalation, diffusion into the galleries occurs from a solvent or the melt, respectively. This work uses the solvent method.

Three types of composite are possible. In a 'conventional' composite, polymer does not enter the galleries. If diffusion into the galleries occurs and the layers remain stacked, an 'intercalated' composite is formed. If interplanar attraction is overcome and the silicate layers are separated, the composite is 'exfoliated'.

Attempts to investigate the reinforcement mechanism of clay filler in polymers mostly consider the formation of chemical bonds between polymer and clay.[2] Most commercial polymers have wide, and sometimes multimodal, molecular mass distributions. If clay shows preferential intercalation of either low or high fractions, technical benefits for the reinforcement mechanism may result. If low is preferred, the clay could be used to scavenge the fractions that can lead to low strength in semicrystalline polymers, whereby syneresis rejects smaller molecules to spherulite boundaries. On the other hand, if high fractions are preferred, there is more scope for a tie chain network to develop; indeed, intercalation followed by subsequent recovery might be used for fractionation.

Natural Wyoming sodium montmorillonite was chosen because of its wide availability and popularity in this context. In some experiments, the natural clay was sodium saturated to replace other cations. Poly(ethylene glycol) (PEG) has been the subject of many intercalation studies[14–17,22–30] and is available in a wide range of molecular masses with reasonably symmetrical distributions.

Experimental Section

Materials. The montmorillonite (type: BH natural) generously supplied by Black Hills Bentonite, LLC (Wyoming, United States) is a natural unaltered sodium MMT (<200 mesh) with a density of 2600 kg/m³, received in the dried and ground condition. This clay has a similar composition to Wyoming sodium-rich MMT (SWy-2) from the Source Clays Repository of The Clay Minerals Society as shown in Table 1. Some MMT (6 g) was dispersed in 400 mL aqueous acetone solution (1:1 by volume) and then treated with 600 mL aqueous sodium

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TABLE 1: Chemical Analysis of the Montmorillonite Used in This Work* Compared with that from the Source Clays Repository of the Clay Minerals Society[31]

clay	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	TiO_2	others
BH	71.71	17.13	3.54	1.57	2.31	0.49	2.58	0.15	0.52
SWy-2	68.47	20.16	4.13	2.77	1.77	0.69	1.70	0.16	0.15

*As determined using an ARL 9400 X-ray fluorescence spectrometer according to BS EN ISO 12677 method at CERAM (Stoke-on-Trent, United Kingdom).

chloride solution (100mM) (BDH Laboratory Supplies, Dorset, United Kingdom) at 50 °C for 24 h according to the literature method[32] to yield sodium-treated montmorillonite (Na−MMT) to extinguish the effect of other cations. After repeated washing by filtration, the clay was dried at 80 °C for 24 h, ground to a fine powder, dried again at 120 °C for a further 24 h, and stored in a desiccator. To collapse the layers and thus control for surface adsorption, some MMT and Na−MMT were heated at 800 °C for 3 h in a furnace (Lenton Thermal Design Ltd. Sheffield, United Kingdom).

Reagent-grade PEG with a nominal average molecular mass of 4000 (denoted PEG 4000) from BDH Laboratory Supplies (Dorset, United Kingdom) and a similar grade denoted PEG 35 000 with 2-*tert*-butyl-4-methoxyphenol as stabilizer from Merck Eurolab (Germany) were used. Next, 5 g clay was added to 100 mL distilled water and agitated for 5 h on a roller table. In the next step, 1.5 g of PEG 4000 and 1.5 g PEG 35 000 were added together to the suspension, which was mixed for a further 5 h, a period typically used in preparing such composites.[14,33,34] Samples were centrifuged (Centaur 2, DJB Labcare, Bucks, United Kingdom) at 4200 rpm for 36 h until a clear supernatant was left. Sediment and supernatant were dried separately at 60 °C for 24 h. The amount of free polymer in the supernatant was weighed using a four-place balance. This procedure was applied to natural MMT, heat-treated montmorillonite, Na−MMT, and heat-treated Na−MMT.

A Siemens D5000 X-ray diffractometer (40 kV, 40 mA) with CuKα radiation ($\lambda = 0.154$ nm) was used for X-ray diffraction (XRD) of the clay powders. The aperture slits were set as 0.1° and the scanning step was 0.02°, with a scan time of 2.5 s per step. Fourier transform infrared spectroscopy (FT−IR) was carried out on a Perkin-Elmer 1720X spectrometer. The scanning number was 32 times and the resolution was 4 cm^{-1}. Specific surface areas (SSA) of the clays were measured by nitrogen adsorption on Gemini 2370 B.E.T. equipment (Micromeritics Instrument Corporation, Norcross, United States) after degassing in a Flowprep 060 degasser under a nitrogen flow. The analysis mode was equilibration and the equilibration time was 5 s, with an evacuation rate of 667Pa.s^{-1} and evacuation time of 60s.

The molecular-mass distributions of PEG were analyzed using gel permeation chromatography (GPC), employing tetrahydrofuran with antioxidant as the solvent and columns of PLgel 2 x mixed bed-D (30 cm, 5 μm). The nominal flowrate was 1.0 mL/min. Two sampling methods were used: (a) dissolve the entire sample and introduce an aliquot into the instrument (to eliminate possible molecular mass segregation during drying) and (b) abstract and dissolve a sample from the solid. Consistent results were obtained from both. The dried solutions of PEG with and without centrifuging gave the same molecular-mass distribution, indicating that 36 h centrifuging did not affect the distribution. The system was calibrated with narrow molecular mass distribution PEG calibrants and the data were collected and analyzed using Viscotek 'Trisec 2000' and 'Trisec 3.0' software at Rapra Technical Limited (Shrewsbury, United Kingdom). All the samples were run in duplicate.
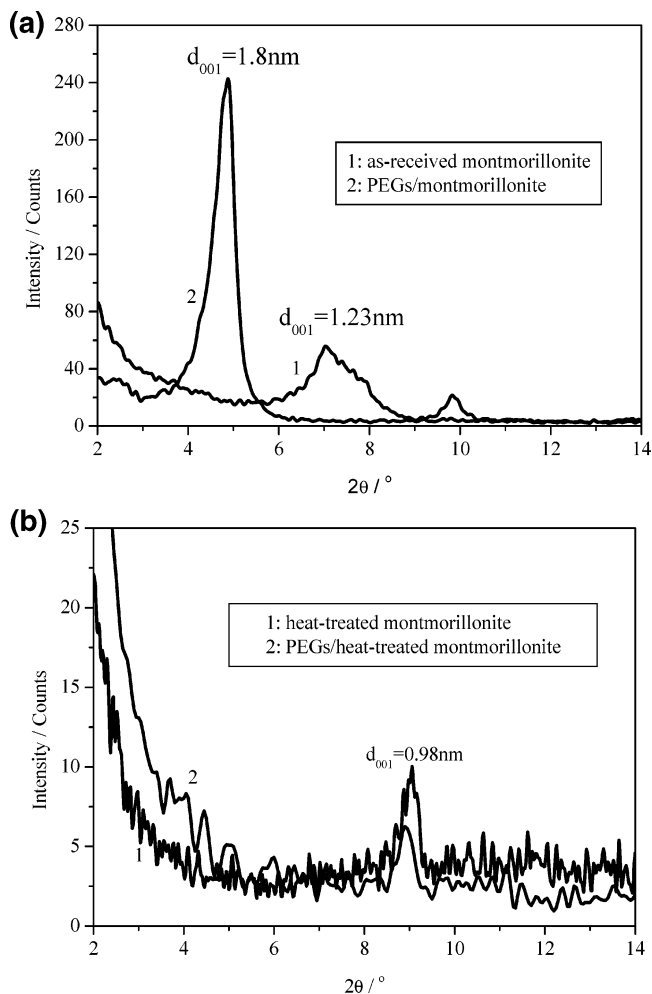
Figure 1. XRD patterns for the montmorillonites and their PEG nanocomposites.

Results and Discussion

Figure 1a presents the XRD trace for the as-received MMT intercalated with the mixture of PEGs. Its 001 reflection was located at the same 2θ position (the basal plane spacing, d_{001} = 1.8 nm) as reported for a monomodal PEG, consistent with the finding that d_{001} of clay is independent of PEG molecular mass when it is higher than 1000.[15,23] The shift of the 001 peak of clay after treatment confirms the intercalation of the PEGs, although XRD alone cannot be used to indicate the extent of intercalation.

The XRD patterns for the heat-treated MMT and its composites are shown in Figure 1b. The value of d_{001} of the MMT was reduced from 1.23 nm to the thickness of platelets (~0.96 nm) after heat treatment at 800 °C for 3 h as found by MacEwan.[35] Longer scans on the as-received and heat-treated MMT (5 ~ 120°) showed that they retained most reflections and intensities, in agreement with Grim's findings.[7] Furthermore, the differential scanning calorimetry trace on the as-received clay showed that at 800 °C the third endotherm had only just begun. Grim[7] shows that the clay differentiates on completion of this endotherm. Not only adsorbed moisture, but also the interlayer water, was expelled from the clay; only the loss of interlayer water changes the *c* direction spacing. The loss of interlayer water and lattice hydroxyls is confirmed by the FT−IR spectra shown in Figure 2. The absorptions at 3620 cm^{-1} and 1632 cm^{-1}, representing the hydroxyls[36] and free water respectively, disappeared on drying in agreement with previous work[7] indicating that rapid loss of lattice hydroxyls begins at
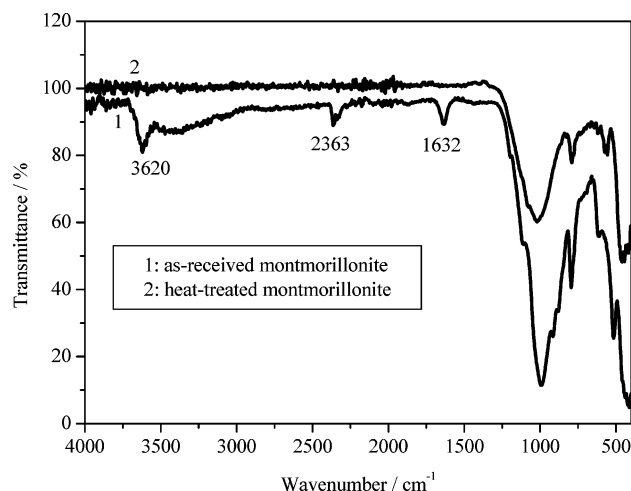
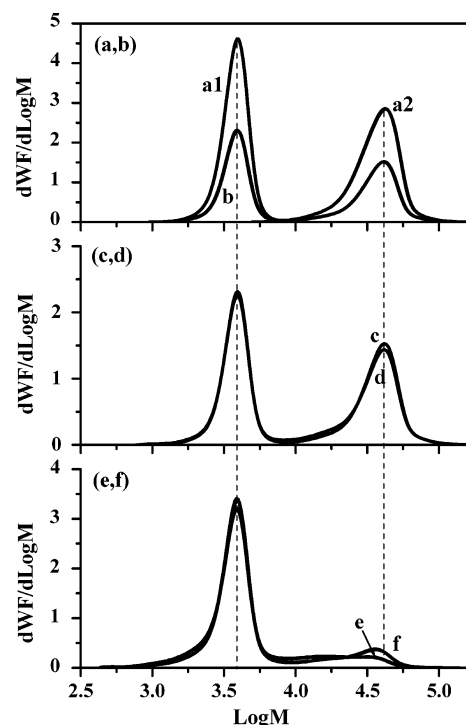**Figure 2.** FT−IR spectra for the montmorillonites.

Figure 3. GPC molecular mass distribution for (a1) the as-received PEG4000; (a2) the as-received PEG35000; (b) the dried solution of a mixture of PEG4000 and PEG35000; (c) the dried supernatant after sedimentation of heat-treated montmorillonite; (d) the dried supernatant after sedimentation of heat-treated sodium montmorillonite; (e) the dried supernatant after sedimentation of as-received montmorillonite; and (f) the dried supernatant after sedimentation of sodium montmorillonite. (All curves are in duplicate).

about 500 °C. The CO_2 (absorption peak at 2363 cm^{-1}) from carbonate traces[7] was also removed. The d_{001} spacing of the MMT remained the same, 0.98 nm, after mixing with PEGs, so that only adsorption on external surfaces can take place; ambiguous results were obtained at lower heat treatment temperatures.

Most literature values of SSA of natural montmorillonite measured with B.E.T. nitrogen absorption range from 13.7 to 45 m^2/g.[37−41] The measured values for the MMT with a correlation coefficient of 0.9997, 38.2 ± 0.6 m^2/g, were in the range of 38 ± 1 m^2/g reported in Grim's text[7] and slightly higher than those for the montmorillonite (SWy-2) from the Source Clays Repository of The Clay Minerals Society, 23.1 m^2/g,[42] or 28 m^2/g[43] respectively. This result, together with the comparison of chemical compositions shown in Table 1, clearly shows that the clay used in this work serves as a representative of montmorillonite clays. The value of 38.2 m^2/g represents the outer area of the particles and does not include the effective gallery area, estimated as 620 m^2/g.[40,44] The surface area for the heat-treated MMT was lower at 16.3 m^2/g, with a correlation coefficient of 0.9999.

The total uptakes of PEG by the as-received and heat-treated MMTs calculated from the excess in the supernatants were 0.30 ± 0.035 and 0.04 ± 0.002 g/g clay, respectively. The Na−MMT had the same total uptake of PEGs, 0.30 g/g clay, as that of as-received MMT, indicating the impurity cations (cf. Table 1) that are present in the as-received natural sodium MMT do not significantly affect the intercalation amount under these preparation conditions.

Since the outer surface chemical compositions are similar for the as-received and heat-treated MMT, adsorption on the as-received montmorillonite can be calculated from

$$A_a = A_h \cdot \frac{S_a}{S_h} \qquad (1)$$

where A is adsorption, S is specific outer surface area measured by the B.E.T. nitrogen method, and subscripts a and h refer to as-received and heat-treated montmorillonites, respectively. Adsorption of PEG on the natural montmorillonite was thus 0.04 × 38.2/16.3 = 0.09 g/g clay. Absorption due to intercalation can be obtained by the difference showing that 0.21 g/g clay was intercalated in the MMT.

It is well-known that PEG degrades in air at low temperatures, including conditions used for preparation of nanocomposites.[45−47] It has been shown that PEG with a molecular mass higher than 8000 undergoes degradation when drying at 60 °C for 24 h,

the conditions used here.[48] An experimental control is thus mandatory for degradation.

Figure 3 shows the molecular mass distributions. Each sample has been run at least in duplicate. The first part compares the individual as-received PEGs having molecular masses 4000 and 35 000 (curves a1 and a2) with the dried solution of the 50% mixture of these PEGs (curve b). This mixture was prepared under identical time−temperature conditions as those used for the clay samples. Quadruple runs on this mixture confirm that the PEG 35 000 does not degrade significantly; probably because this polymer contains a stabilizer added by the manufacturer. Curve b provides the clay-free control against which the effect of clay adsorption and absorption should be compared.

Curves c and d in Figure 3 show the control for surface adsorption. These curves are almost coincident and should be compared with curve b. They show that no significant molecular mass preference can be detected for surface adsorption. This is mainly because the total adsorption of polymer by the heat-treated MMTs was very low, 0.04 g/g clay.

Mass distributions for residues from the as-received and sodium-treated montmorillonites (Figure 3, curves e and f) show that the peak location and symmetry for the low molecular mass in the residue were largely unchanged by intercalation. Peaks for the residual high molecular mass PEG have reduced substantially and displaced to lower mass. Comparing curves e with c and f with d shows the extent to which intercalation has abstracted the high molecular mass fraction from solution in the case of both as-received and sodium-treated clays. It appears that slightly more high molecular-mass material was absorbed by the as-received MMT than by the sodium-treated MMT.

The integration limit was placed at 8700, the minimum between the peaks. This enables the specific molecular-mass

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TABLE 2: Molecular Mass Data for PEG

sample (designation as in Figure 3)[a]	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	% peak area for high molecular mass (based on total area under distribution curve)
PEG 4000	3720	3750	1.01	0
PEG 35 000	37 300	33 300	1.12	99.7%
b	20 500	6640	3.1	
b, high	37 300	34 000	1.10	50%
b, low	3770	3740	1.01	50%
c	20 600	6530	3.2	
c, high	38 000	34 100	1.11	50%
c, low	3750	3670	1.02	50%
d	20 000	6460	3.1	
d, high	36 800	32 000	1.15	50%
d, low	3760	3630	1.03	50%
e	6610	3750	1.8	
e, high	22 700	18 700	1.22	16%
e, low	36 200	3270	1.11	84%
f	7860	3930	2.0	
f, high	28 000	23 200	1.21	22%
f, low	3630	3350	1.09	78%

[a] Key: b, dried solution of a mixture of PEG 4000 and PEG 35 000; c, dried supernatant after sedimentation of the heat-treated montmorillonite; d, dried supernatant after sedimentation of the heat-treated sodium montmorillonite; e, dried supernatant after sedimentation of as-received montmorillonite; f, dried supernatant after sedimentation of sodium montmorillonite.

data for high and low residual fractions to be summarized as in Table 2. The residues from the as-received and sodium-treated clays have lower molecular mass, narrower dispersive index ($\bar{M}_w/\bar{M}_n$), and smaller peak area for the high molecular mass fraction. From the peak areas, the uptake of high molecular mass is given by

$$U_h = 0.6 \cdot a_h - a_h{}' (0.6 - U_t) \qquad (2a)$$

The uptake of low molecular mass is given by

$$U_l = U_t - U_h \qquad (2b)$$

where a is area fraction from Table 2, subscript h refers to high molecular mass and prime means after uptake, U_t is the total uptake, and 0.6 g/g clay is the initial amount of PEG. So, for the as-received MMT, $U_h = 0.25$ g/g and $U_l = 0.05$ g/g clay, and for the Na−MMT $U_h = 0.23$ g/g and $U_l = 0.07$ g/g clay. Thus, sodium treatment has a small effect on preferential intercalation.

Since the molecular-mass preference of surface adsorption could not be detected, the adsorption amounts for high and low molecular masses were averaged to give 0.045 g/g for the MMT. After deducting the adsorbed polymer from the total uptake, the intercalated absorptions of high and low molecular masses for the as-received MMT were 0.205 and 0.005 g/g clay, respectively. In preliminary experiments, kaolinite was used as a control because, like the heat-treated montmorillonite, it does not intercalate PEG. The results were similar to those in Figure 3 but it can be argued that kaolinite is sufficiently different structurally and chemically even after correcting for specific surface area to use as a control.

This is the first competitive study of molecular mass preference, but preferential intercalation of high-molecular-mass polymer in clay is supported by noncompetitive intercalation isotherms[15,49−53] that show higher-molecular-mass PEG produces a greater uptake and has a higher affinity for clay surfaces than low-molecular-mass material. Preferential surface adsorption of high-molecular-mass polymer from solution on high

energy surfaces is usually found[54−57] and the specific adsorption A is related to molecular mass M by

$$A = KM^{\alpha} \qquad (3)$$

where K is a constant and the index is $0 < \alpha < 0.3$. It is interesting to see if eq 3 can be applied to intercalation as well as to adsorption data. The results of Parfitt and Greenland[49] for equilibrium uptake of different molecular mass PEG in calcium montmorillonite can be plotted to yield $K = 0.08$ and $\alpha = 0.137$, from which the equilibrium uptakes of PEG 4000 and PEG 35 000 can be inferred to be 0.25 and 0.34 g/g. The ratio of uptakes for sodium montmorillonite compared to calcium montmorillonite is about 2.3,[49,58] from which the estimated equilibrium total uptakes of PEG 4000 and PEG 35 000 by sodium montmorillonite are 0.56 and 0.77 g/g, respectively. So, the uptakes in this work are about 40% of the equilibrium value, consistent with the short time scales used to prepare nanocomposites; isothermal equilibrium requires up to170 h.[15,49] Those isotherms did not distinguish gallery absorption and surface adsorption, and the specific uptakes can be different due to different surface conformations,[59] so this calculation is only an estimate and it is preferable to use the heat-treated clay as the control.

Kinetic and thermodynamic arguments can be marshaled to account for these competitive molecular mass preferences. It can be argued that the macromolecule prefers a conformation that allows for maximum segment-surface interaction.[53] For a given mass of polymer, the number of segments is approximately the same. However, the higher mass fraction has fewer molecular chains and can have more conformations per unit mass, yet result in the same total energy. The high molecular mass has the potential to achieve larger segment−surface contact that favors surface adsorption and further intercalation into the clay galleries.

Again, although montmorillonite is generally hydrophilic,[60] the basal Si−O groups in the spaces between hydrated cations in clay interlayers are relatively hydrophobic and PEG is preferentially adsorbed on these sites.[26,41] The low-molecular-mass polymer has a larger number of hydrophilic end groups than the high-molecular-mass one, which should facilitate the preferential intercalation of high molecular mass.

But, there is a difficulty with equilibrium explanations for molecular mass preference. The approach to equilibrium assumes partitioning of solutes of different molecular mass between galleries and solution. Such exchanges are restricted by the long time scales needed for excalation. Indeed, it is reported that PEG with molecular masses above 1500 are not removed from the galleries in the time scales of this experiment; in fact, it is reported that they are effectively not removable by water.[22,58] Perhaps the quest for explanation should pursue kinetic arguments.

It is rather important to recognize that the experimental method used in this work, and by Parfitt and Greenland,[49] does not assume full intercalation; a molecule is assayed as intercalated even if a few segments are occluded by the gallery and the bulk of the molecule remains in solution. If intercalation of the first segment is necessary and sufficient to register the intercalation of the whole molecule, the higher affinity of high molecular-mass material at the particle edge, well-known for adsorption studies, may account for the molecular mass preference. XRD studies of both melt intercalation[61] and in situ polymerization[62] show that a new reflection for the expanded

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basal plane appears at a fixed *d* spacing and its intensity rather than the spacing increases with reaction time, supporting this hypothesis.

From an engineering point of view, these results are significant in two respects. First, it may be that nanocomposites with better mechanical properties could be obtained by controlling molecular-mass distribution to avoid low fractions because these are more likely to reside unattached in interparticle space. Second, this work highlights the possibility that the tie chain network between particles of partially intercalated large molecules may contribute to mechanical properties. Indeed, this idea is appearing in the literature that highlights clays as compatibilizers for polymer blends.

Conclusions

A smectite clay presented with a polymer solution in a good solvent containing different molecular mass fractions of an intercalating polymer, poly(ethylene glycol), preferentially absorbs the high molecular mass fractions. This preference helps to explain the considerable reinforcement of intercalated clay particles in a polymer, focuses on the importance of the tie chain network and raises questions about the effect of lower molecular masses excluded that may provide lower strength if not removed. The heat-treated montmorillonite did not expand; it only adsorbed polymer on its outer surfaces, thus providing an experimental control that allowed adsorption and absorption to be distinguished. Sodium-treated montmorillonite also prefers to intercalate the high-molecular-mass fractions.

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