Sequential and Simultaneous Melt Intercalation of Poly(ethylene oxide) and Poly(methyl methacrylate) into Layered Silicates

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ABSTRACT: Both poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) were melt intercalated in a sequential or simultaneous (blend) manner into two layered silicates, a sodium montmorillonite (MMT) and an organically modified bentonite (B34). The B34 nanoclay, which was already pre-intercalated to the point of saturation by PEO, was found able to take up additional PMMA. The converse was also found to be true where, despite the silicate galleries being saturated by PMMA, additional PEO was able to be incorporated. This implies that the packing density of the mixed PEO and PMMA phase in the gallery of B34 is greater than that of either polymer alone in the gallery. The intercalation of a miscible PEO/PMMA blend into B34 results in a greater increase in the spacing between layers than by either for a PEO-B34 hybrid or for a saturated PMMA−B34 hybrid. However, the intercalation of a PEO/PMMA blend into MMT results in the same gallery size increase as for the PEO−MMT hybrid. The organically modified bentonite is thus able to host a higher concentration of macromolecular chains from a miscible blend than from either polymer alone. The presence of PEO, which has a lower intercalation temperature than PMMA, thus encourages reptation of the PMMA into the silicate galleries at temperatures below that it could move in alone.

Introduction

Melt intercalation has been demonstrated to be a successful method for production of polymer-layered silicate nanocomposites.[1] Compared to the other two main methods of nanocomposite formation, polymerization and polymer solution intercalation, the advantages of melt intercalation are considerable. Melt intercalation allows greater possibilities for producing hybrids which are not readily attainable by other methods. Importantly, melt intercalation can be processed by current industrial polymer processing techniques such as extrusion, where thermodynamics, kinetics, and processing factors influence the degree of intercalation and delamination of the platelets. More importantly, the absence of a solvent makes melt intercalation an environmentally friendly and economically beneficial method. A wide range of polymers have been reported to be able to be intercalated into layered silicates via the melt intercalation process.[2−5]

Most materials that have been intercalated have been homopolymers. Some copolymers have also been reported to form nanocomposites with layered structures, such as layered silicates[4] and maghemite (γ-Fe_2O_3).[5] These include copolymers of MMA with QD1 or QD4,[6] polystyrene−poly(vinylphenol) copolymers,[7] diblock copolymers of P(S-*b*-PBMA),[5] PMMA−PEO, PEO−PS, and PMMA−PMAA block copolymers,[8] poly(styrene-*b*-butadience) copolymers (SBS),[9] styrene−acrylonitrile copolymer,[4] and copolymers of methyl methacrylate (MMA)/*n*-dodecyl methacrylate (LMA).[10] Relatively few studies have involved melt intercalation of two polymeric components (effectively ternary systems, including the layered silicate). Of the possible blend systems that have been examined to date in terms of nanocomposite formation, PEO and PMMA, in which both components (PEO and PMMA) are themselves miscible have begun to attract interest.[11] In that work, organically modified montmorillonite (OMMT) was intercalated into the PEO/PMMA blend using dichloromethane as the cosolvent at room temperature. The specific interaction between the components was quantified by the Flory−Higgins interaction parameters, B, in pairs, determined by combination of melting point depression and the binary interaction model. It was found that the B value for the PMMA/OMMT pair was smaller than that measured for the PEO/OMMT pair, suggesting that PMMA had a greater affinity for OMMT than PEO. PEO−PMMA (1:9) blends have also recently been intercalated into montmorillonite in order to increase the ionic conductivity at room temperature.[12] It was found that PMMA in the molten PEO could intercalate into silicate layers together with PEO chains, the PMMA having a modifying effect on PEO, which was beneficial to increased ionic transport in the interlayers. Intercalation of another blend system of a nanocomposite and ethylene−vinyl alcohol copolymers (EVOH), containing about 32 mol % ethylene, has also recently been reported[13] in which permeability to methanol as a function of composition was explored. PA-6 and EVOH are miscible blends, and it was found that although the clay was fully exfoliated in PA-6, this decreased upon addition of EVOH to the point that the 75 wt % of EVOH showed little or no exfoliation. (Nanocomposites of EVOH itself were not able to be made.) This appears to be the limit of ternary work (two thermoplastics and nanoclay) reported to date.

We have previously reported the individual melt intercalation of PEO and PMMA into layered silicates, such as MMT or B34, or into a mixture of MMT and B34 to allow investigation of the melt intercalation process,[14,15] the characteristics of the intercalated hy-

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Table 1. Samples of Melt Intercalation of a Polymer into a Pre-intercalated Polymer/Layered Silicate Hybrid

sample ID	sample process and compositions
E(MB15)15	PEO: (PMMA:B34 = 15:85, 160 °C, 8 h) = 15:85, 85 °C, 8 h
E(MB15)30	PEO: (PMMA:B34 = 15:85, 160 °C, 8 h) = 30:70, 85 °C, 8 h
E(MB30)15	PEO: (PMMA:B34 = 30:70, 160 °C, 8 h) = 15:85, 85 °C, 8 h
E(MB30)30	PEO: (PMMA:B34 = 30:70, 160 °C, 8 h) = 30:70, 85 °C, 8 h
M(EB15)15	PMMA: (PEO:B34 = 15:85, 85 °C, 8 h) = 15:85, 160 °C, 8 h
M(EB15)25	PMMA: (PEO:B34 = 15:85, 85 °C, 8 h) = 25:75, 160 °C, 8 h
M(EM15)15	PMMA:(PEO:MMT = 15:85, 85 °C, 8 h) = 15:85, 160 °C, 8 h

brids,[16,17] and the saturation ratio of polymer to silicate with regard to intercalation.[16,18] PEO was found to be able to melt intercalate into both MMT and B34, while PMMA was only able to melt intercalate into B34.[18] In this work, the effect of a pre-intercalated polymer on the subsequent, sequential intercalation of another polymer is presented for the first time. This is compared with the simultaneous melt intercalation of a miscible blend of the same two components. All materials are introduced into a majority-clay system, so that the effect on expansion of the clay layers by the various possible combinations can be readily studied, particularly by observing changes in interlayer d spacing by X-ray diffraction. It should be noted, in order to do these measurements, clay-rich compositions are used, and the ingress of polymer chains occurs in a quiescent state, thermodynamic factors driving the reptation of chains into the clay galleries. In other nanocomposites in which the polymer melt is the majority phase, shear also plays a role, but such nanocomposites are outside the scope of this work.

Materials and Experimental Methods

The layered silicate materials used were a sodium montmorillonite (MMT) (Source Clay Minerals Repository) and an organically modified bentonite, the organo-ion being tetraallkylditallow ammonium bentonite (B34) (Rheox). MMT was used after being dried at 250 °C for 300 min to reduce the amount of intercalated water. The polymers used were isotactic PMMA (M_n = 40 887, PD = 1.95) and PEO (M_n = 172 700, PD = 2.58) (Aldrich Chemical Co.). They are the same PEO or PMMA samples that we have been previously intercalated individually into these clays by the melt intercalation technique. The intercalation process involves heating a hydraulically compressed disk ("biscuit") of the appropriate mixed powders of polymer and clay to a temperature higher than the melting point of PEO or T_g of PMMA for sufficiently long times. To investigate the effect of interaction between polymers on melt intercalation, both sequentially and simultaneously, two series of experiments were designed as described below.

Melt Intercalation of an Additional Polymer into an Already Melt Intercalated Polymer/Layered Silicate Hybrid. The first set of experiments involved sequential intercalation of a second polymer into a hybrid, which had already been intercalated with one polymer, both via melt intercalation. The aim of this experiment was to investigate whether the pre-intercalation of a polymer with which the second polymer has an affinity would improve the subsequent degree of such melt intercalation of the second polymer. For example, PMMA and B34 were mixed at a weight ratio of 15:85, compressed into pellets at 70 MPa, and then annealed at 160 °C for 8 h. The ground powder of this pre-intercalated PMMA−B34 hybrid was then mixed with PEO at a ratio of PEO:hybrid = 15:85. Pellets were again pressed at 70 MPa and annealed at 85 °C for 8 h. A designation of "PEO: (PMMA:B34 = 15:85, 160 °C, 8 h) = 15:85, 85 °C, 8 h" thus indicates the compositions and process described above. The samples made are summarized in Table 1 using the above description and their annotated sample ID.

Melt Intercalation of Miscible PEO/PMMA Blends into Layered Silicates. PEO/PMMA blends were made via solution blending in chloroform ($CHCl_3$) prior to intercalation. Blends of PEO and PMMA were cast from solution and dried under vacuum at 70 °C for 72 h to remove the residual solvent, the weight ratios of PEO to PMMA being 25:75, 50:50, and 75:25, identified by abbreviating Blend25, Blend50, and Blend75, respectively, where the number corresponds to the weight concentration of PEO. The range of blends was made to demonstrate the full miscibility of PEO and PMMA blends produced by this method. After formation and prior to intercalation, the samples were stored in a desiccator to prevent moisture uptake. The PEO/PMMA blends made were ground into fine powders using a disk mill, and the powder was physically mixed with B34 or MMT, using the same procedure of melt intercalation as for a single polymer mixed with a clay powder described above. One of the blends, Blend50, was combined with MMT and B34 in the ratios of Blend50 to MMT or B34 of 50:50, 40:60, 30:70, 20:80, and 10:90 and is annotated as BM50, BM40, BM30, BM20, and BM10, or BB50, BB40, BB30, BB20, and BB10, respectively. Nanocomposite disks (biscuit) were made under a pressure of 70 MPa and annealed at 85 °C for 8 h.

Powder X-ray Diffraction of Nanocomposites. X-ray diffraction patterns were collected on a Rigaku-Geigerflex X-ray diffractometer using Ni-filtered Cu Kα radiation from 1.5° to 30°, the scanning speed being 1°/min with a step of 0.05°. Powder samples were packed in horizontally held trays. The changes in the XRD peak positions reflect the intercalation of the polymer into layered silicates. The gallery sizes in intercalated hybrids were deduced from XRD peak positions of (001) of the hybrids.

Thermal Analyses. Differential scanning calorimetry (DSC) data were obtained on a Perkin-Elmer differential scanning calorimeter DSC 7. Samples, approximately 10 mg in mass, were loaded into an aluminum cups, and both the sample chamber and the reference chamber (empty chamber) were heated at 10 °C/min. Thermogravimetric analysis (TGA) was performed on a SETARAM TG-DTA 92 from 50 to 1000 °C at a heating rate of 10 °C/min under an air or a nitrogen gas blanket, the mass of each specimen being around 20 mg. Dynamic mechanical thermal analysis (DMTA) was carried out using a Perkin-Elmer DMA7 using a penetration probe geometry on a sample with helium flushed through the chamber at a rate of 40 mL/min. The temperature was scanned from 20 to 150 °C at a rate of 5 °C/min, and the applied frequency was 1 Hz, the sample dimension being approximately a 3−4 mm cube. The glass transition measured by DMTA was defined as the peak temperature of the loss modulus plot.

Results and Discussion

1. Intercalation of PEO or PMMA Alone into Layered Silicates. Before discussing the results of more complex PEO/PMMA blend intercalation, the results of intercalation of the individual polymers are presented. The manner in which the intercalation of the homopolymer into the clay in the PEO/B34, PEO/MMT, and PMMA/B34 systems occurs has been reported previously.[16,18] The difference in behavior of the PEO/B34 intercalated hybrid compared to the PMMA/B34 intercalated hybrid, as observed from XRD patterns, is summarized and contrasted below.

Figure 1 shows the XRD patterns of samples in the PEO/B34 and PMMA/B34 systems. The XRD pattern

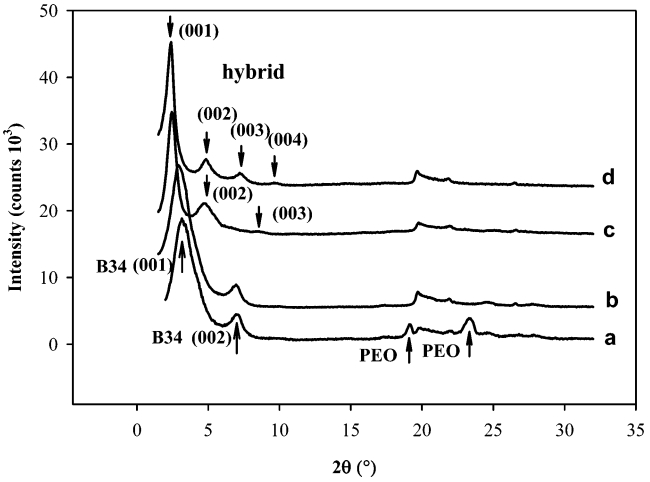

Figure 1. XRD patterns for the PEO/B34 and PMMA/B34 systems: (a) physical mixture of PEO:B34 = 20:80, (b) physical mixture of PMMA:B34 = 30:70, (c) PEO:B34 = 15:85, after being heated at 85 °C for 8 h, and (d) PMMA:B34 = 25:75, after being heated at 160 °C for 8 h.

Table 2. *d* Spacing Values in Å of the (00*l*) Peaks in the PEO/B34 and PMMA/B34 Systems, the B34 Alone Having a (001) *d* Spacing of 30 Å

polymer/silicate system	$d_{(001)}$	$d_{(002)}$	$d_{(003)}$	$d_{(004)}$
PEO:B34 = 15:85	36.8	18.8	11.4	
PMMA:B34 = 30:70	36.8	18.2	12.3	9.1

of a mixture of PEO and B34 before heat treatment or intercalation (Figure 1a) shows both the order of B34 and the crystalline portion of PEO. The two left-most arrows indicate (001) and (002) peak of B34, respectively, with the (001) peak involving a *d* spacing of 30 Å. The other two upward-pointing arrows indicate the PEO peaks. The state of intercalation of PEO into B34 as judged by XRD can thus be seen both by any changes of clay *d* spacing and any peaks present due to PEO crystallites. This latter aspect is particularly useful in that the absence of any PEO crystal peaks has been shown to indicate the lack of any residual PEO outside of the galleries.[15]

In contrast, the XRD pattern of a mixture of PMMA and B34 shows only peaks of crystalline B34 since PMMA is amorphous (Figure 1b). It is thus difficult to judge by XRD alone whether there is any residual PMMA in a composite after annealing. Parts c and d of Figure 1 show the XRD pattern of heated samples (intercalated samples) of PEO:B34 = 15:85 and PMMA:B34 = 30:70, respectively. A major difference between these two patterns is the different numbers of higher order peaks that can be observed due to clay layer spacing. Three peaks of the (00*l*) series have been observed for samples in the PEO/B34 system, while four peaks related to the (00*l*) series are visible in the PMMA/B34 system. The enhanced appearance of sharper, higher order peaks in intercalated samples (compared to clays) is indicative of a greater degree of layer order and coherency, which leads to the weaker and broader higher order peaks becoming more apparent. The positions of the (00*l*) peaks are also slightly different between these two systems; their values are summarized in Table 2. It is important to note (perhaps coincidentally) that the primary *d* spacing relating to the (001) peaks in the two XRD patterns are both similar, some 36.8 Å.

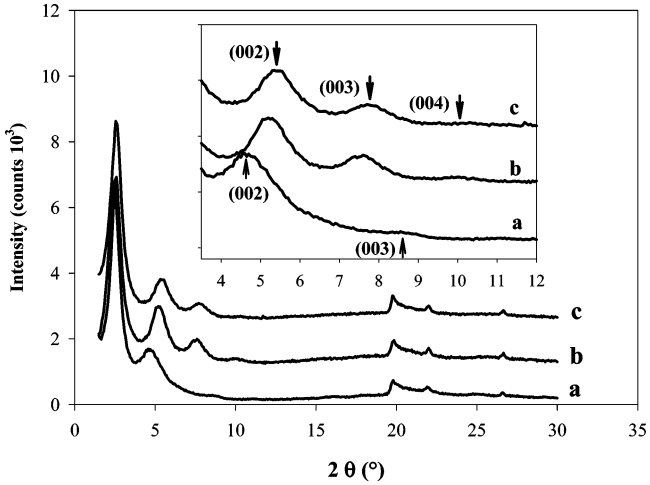

Figure 2. XRD patterns for sequential intercalation of PMMA into PEO/B34 pre-intercalated hybrid: (a) hybrid of PEO:B34 = 15:85 (referred to as X); (b) PMMA:X = 15:85, and (c) PMMA:X = 25:75; all intercalated hybrids have been annealed at 160 °C for 8 h.

Table 3. Values of *d* Spacing in Å of (00*l*) Peaks for Sequential Intercalation Samples of PMMA into the PEO/B34 Pre-intercalated Hybrids Shown in Figure 2

polymer/silicate system[a]	$d_{(001)}$	$d_{(002)}$	$d_{(003)}$	$d_{(004)}$
PEO:B34 = 15:85 in (a)	36.8	18.8	11.4	
M(EB15)15 in (b)	36.8	18.3	12.3	9.1
M(EB15)25 in (c)	36.8	18.2	12.3	9.1

[a] a, b, and c stands for the XRD patterns of Figure 2a, b, and c, respectively.

The maximum amount of a polymer able to be intercalated into a clay has been defined to be the "saturation ratio", and this saturation ratio of PEO/B34 or PMMA/B34 systems has been determined to be 15:85[17] or 25:75.[18] Note also that the temperature used for intercalation of PMMA is somewhat higher (160 °C) than that for PEO (85 °C).

2. Melt Intercalation of an Additional Polymer into an Already Melt Intercalated Polymer/Layered Silicate Hybrid. The ability of an additional polymer to intercalate an already pre-intercalated hybrid is demonstrated here, using PEO and PMMA. The hybrid of the first polymer and B34 is referred as X. The second polymer is mixed with the hybrid X at the stated ratio to simplify the description. Note that X can refer to different hybrids, involving different materials and ratios.

Figure 2 shows the XRD patterns for the melt intercalation of different amounts of PMMA at 160 °C for 8 h into the PEO pre-intercalated B34 hybrid. The ratio of the pre-intercalated PEO-B34 hybrid is 15:85, and this can be considered to have filled the gallery, it being the concentration of the saturation ratio of the PEO/B34 system.[16] Upon addition of further PMMA, the (001) peak remains unchanged. However, the higher order (00*l*) peaks change from three peaks for sample of PEO-B34 hybrid in Figure 2a to four peaks for samples of PMMA intercalation into the PEO-B34 hybrid in Figure 2b,c. The *d* spacing of the (00*l*) series is summarized in Table 3. PMMA thus appears able to intercalate into PEO pre-intercalated B34 hybrid, even though the PEO content is already at its previously determined saturation level. Stricly, it is possible that some PEO is also removed by exposure to the PMMA,

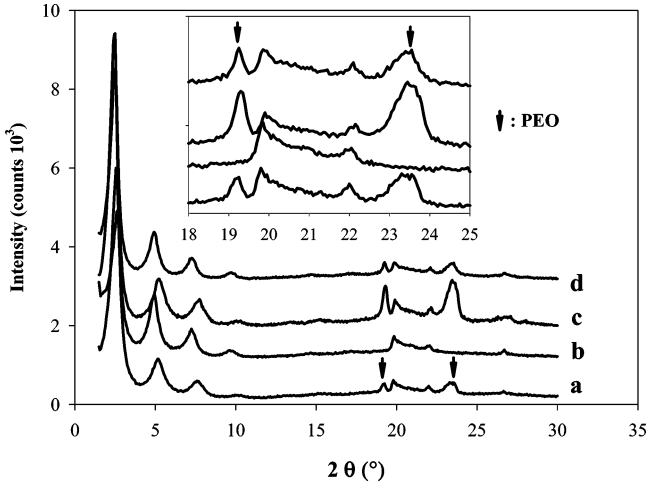

Figure 3. XRD patterns for sequential intercalation of PEO into a PMMA/B34 (15:85) pre-intercalated hybrid: (a) a unheated mixture of pre-intercalated PMMA:B34 = 15:85 (referred to as X) and PEO at PEO:X = 15:85, (b) PEO:X = 15:85, heated at 85 °C for 8 h, (c) a mixture of PEO:X = 30:70 before heating, and (d) PEO:X = 30:70; all intercalated hybrids have been annealed at 85 °C for 8 h.

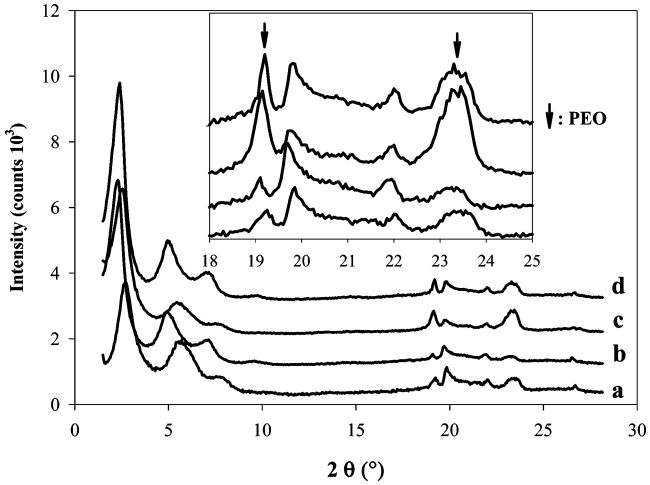

Figure 4. XRD patterns for sequential intercalation of PEO into a PMMA/B34 (30:70) pre-intercalated hybrid (referred to as X): (a) PEO:X = 15:85, mixture prior to heat treatment, (b) PEO:X = 15:85, annealed at 85 °C for 8 h, (c) PEO:X = 30:70, mixture prior to heat treatment, and (d) PEO:X = 30:70; all intercalated hybrids have been annealed at 85 °C for 8 h.

Table 4. Values of *d* Spacing in Å of (00*l*) Peaks in Sequential Intercalation of PEO into a PMMA/B34 (15:85) Pre-intercalated Hybrid Samples Shown in Figure 3

polymer/silicate system[a]	$d_{(001)}$	$d_{(002)}$	$d_{(003)}$	$d_{(004)}$
PMMA:B34 = 15:85 in (a)	35.3	17.9	12.2	9.1
P(MB15)15 in (b)	36.8	17.9	12.4	9.1
mixture of P(MB15)30 in (c)	35.3	17.9	12.2	9.1
P(MB15)30 in (d)	36.8	17.9	12.4	9.1

[a] a, b, c, and d stands for Figure 3a, b, c, and d, respectively.

but there is clearly a net increase in amount of PMMA in between the clay layers, as indicated by the appearance of the higher order peaks typical of PMMA. The PEO in the hybrid gallery should remain in the gallery during PMMA intercalation, since the onset of the weight loss of PEO from the gallery in this system has been shown to commence only at about 190 °C.[15] It appears that PMMA is able to reptate into the PEO preoccupied gallery and associate with the PEO chains for which there would be favorable interactions and/or with the organic cations, in the manner described in the structural model of the PMMA/B34 system.[17] By contrast, addition of more than 15 wt % PEO into B34 clearly shows PEO crystalline peaks in XRD and indicates that excess PEO remains outside of gallery.

The reciprocal experiment was also performed with samples of varing concentrations of PEO, intercalated into a pre-intercalated PMMA/B34 hybrid, the ratio of PMMA to B34 being 15:85 and 30:70. The XRD patterns of PEO and pre-intercalated PMMA/B34 hybrid (PMMA:B34 = 15:85) are shown in Figure 3. The *d* spacing of the (00*l*) peaks in the samples shown in Figure 3 is summarized in Table 4. The combination of PEO and PMMA−B34 hybrid (PMMA:B34 = 15:85, in this case referred to as X) at a ratio of PEO:X = 15:85 is shown in Figure 3a, and its subsequently annealed sample is shown in Figure 3b. The peaks of crystalline PEO can be seen to disappear after heating at 85 °C for 8 h, indicating ingression of PEO into the PMMA-filled galleries. The *d* spacing of the (001) peak of pre-intercalated PMMA/B34 hybrid is 35.3 Å (Figure 3a) and found to increase to 36.8 Å after annealing at 85 °C for 8 h (Figure 3b). A similar result occurs in the case of PEO:X = 30:70, except that the XRD peaks of crystalline PEO are also seen in samples both before (Figure 3c) and after annealing (Figure 3d). However, the relative intensity of the PEO peaks in XRD pattern in the sample is reduced after annealing. From quantitative XRD analysis, the relative intensity of the peaks of crystalline PEO in heated samples (Figure 3d) is about half of that in the sample mixture prior to annealing (Figure 3c). This indicates some fraction of the available 30% PEO is able to intercalate into a PMMA pre-intercalated B34 hybrid, with some remaining outside the galleries.

It is thus clear that PEO can also intercalate into the pre-intercalated PMMA−B34 hybrid at a ratio of PEO to hybrid of 15:85. The gallery size increases from 5.3 Å if only PMMA is intercalated to 6.8 Å after PEO is subsequently intercalated. The PMMA−B34 pre-intercalated hybrid with 15% PMMA already within the galleries can thus take up a further 15% PEO into the gallery. The total ratio of both polymers to the layered silicate in this composite (extra 15% PEO) is deduced to be about 28:72. Note that in this case (as opposed to the previous, converse set of experiments) due to the temperatures used, the PMMA inside the galleries is much less mobile than the incoming PEO (whereas previously the pre-intercalated PEO was mobile, as PMMA reptated into the hybrid).

In the next experiment, the ratio of PMMA to B34 in the pre-intercalation sample was selected as 30:70, greater than the saturation ratio of PMMA to B34, to investigate whether already saturated PMMA−B34 hybrid would allow the intercalation of additional PEO (the excess PMMA outside the galleries at 85 °C being in the glassy state). The XRD patterns of PEO intercalation into the 30:70 PMMA/B34 hybrid are shown in Figure 4, and the PMMA−B34 intercalated hybrid of 30:70 is now denoted X. Parts a and b of Figure 4 show the sample of PEO:X = 15:85 before and after annealing at 85 °C for 8 h, respectively. Similarly, parts c and d of Figure 4 show the sample of PEO:X = 30:70 before and after annealing at 85 °C for 8 h, respectively. The changes of the XRD peaks of crystalline PEO in these samples can be examined. Even though the peaks

Table 5. Relative XRD Peak Intensity Ratios of PEO to That of Hybrid for Sequential Intercalation of PEO into a PMMA/B34 (30:70) Pre-intercalated Hybrid Samples Shown in Figure 4

sample ID[a]	P(MB30)15 mixture (a)	P(MB30)15 heated (b)	P(MB30)30 mixture (c)	P(MB30)30 heated (d)
$I_{(PEO)}$ (counts)	628	396	2389	1630
$I_{(hybrid)}$ (counts)	2073	3266	1099	2720
ratio of $I_{(PEO)}$ to $I_{(hybrid)}$	0.30	0.12	2.17	0.60

[a] a, b, c, and d refer to Figure 4a, b, c, and d, respectively.

Table 6. T_g (Glass Transition Temperature), T_m (Melting Point), and ΔH_m of Solution Blends of PEO and PMMA

sample ID	Blend 2575	Blend 50	Blend 7525
PEO:PMMA in a blend	25:75	50:50	75:25
T_m from DSC (°C)	60	63	65
ΔH_m (J/g)	29.4	71.1	116.2
crystallinity of PEO in blend (%)	14.9	36.1	59.0
amorphous PEO in blend (%)	10.1	13.9	16
ratio of amorphous PEO:PMMA	12:88	22:88	39:61
experimental T_g from DMTA (°C)	75	65	55
calculated Flory−Fox T_g (°C)	88	67	37

persist in all four samples, the relative intensity of PEO to the hybrid changes before and after heat treatment. The relative intensity ratios of the PEO peak, $I_{(PEO)}$, at $2\theta = 19.1°$ ($d = 4.7$ Å) to that of the unchanged peak of the hybrid, $I_{(hybrid)}$, at $2\theta = 19.8°$ ($d = 4.5$ Å) are summarized for these samples in Table 5.

It is clear that the PEO chains are able to intercalate into the galleries of the hybrid, despite there being excess PMMA present. It is difficult for the XRD results to be quantitative since the XRD peak intensity ratios in Table 5 are not necessarily proportional to the mass change in the sample, and both PEO and intercalated hybrid change their amount during the process. However, it does appear clear that an oversaturated PMMA−B34 hybrid can host more PEO into its galleries. In addition, the (001) d spacing of the PMMA−B34 hybrid does not change after PEO intercalation. This suggests that the packing of the two polymers in the gallery may well be denser than either polymer alone since the layers not significantly pushed further apart. However, it is also possible that the extra PMMA chains lie laterally in between the layers and perhaps only partly overlap with the PEO chains in the gallery.

In summary, PMMA can intercalate into PEO pre-intercalated B34 hybrids, and PEO can also intercalate into PMMA pre-intercalated B34 hybrids. In the both cases, the second polymer is able to further intercalate into a saturated, pre-intercalated hybrid system. The gallery size, reflected by the (001) d spacing of hybrid and un-intercalated clay, however, remains the same (6.8 Å) as for nanocomposites of either single polymer. B34 can thus host greater amounts of mixtures of two polymers compared to that of any single polymer, even if the first intercalated polymer is in excess of that required to fill the space between layers.

3. Melt Intercalation of Miscible PEO/PMMA Blends into Layered Silicates. The second set of experiments involves intercalation of a miscible blend of the two polymers into clay. PEO and PMMA have been reported to be miscible at the molecular level; concentration-dependent intermediate glass transition temperatures have been reported over the whole PEO/PMMA composition range.[19−21] Table 6 summarizes the T_g, T_m, and ΔH_m of the blends of PEO and PMMA at ratios of 25:75, 50:50, and 75:25. The crystallinity of PEO is depressed by the presence of PMMA, and the value of the melting point of crystalline PEO decreases slightly with increasing PMMA content. The appearance of a single T_g for each blend was confirmed by DMTA measurement. The decomposition temperatures of the blends, as measured by TGA, also increase slightly with increasing PMMA content but are similar to those of either PEO or PMMA.

The melt intercalation of Blend50 into MMT or B34 is investigated using XRD, DSC, and TGA. Note that the comparison of the clays is also potentially very interesting because, as stated earlier, while PEO is able to intercalate MMT and B34 galleries, PMMA intercalates only into the organically modified B34. The annealing temperature used to form the intercalated blend nanocomposites is 85 °C (as used for PEO alone) and well above the T_g of the Blend50 (47 °C from DSC and 67 °C from DMTA) and T_m of Blend50 (63 °C), and the annealing process involves a time scale of 8 h in most cases. Note that, nonetheless, the temperature is well below that which would be required for the PMMA alone.

3.1. XRD Results for Blend Melt Intercalation. Figure 5 and Figure 6 show the XRD patterns of the Blend50/MMT and Blend50/B34 systems with different ratios of Blend50 to MMT and B34. In a physical mixture of Blend50 and MMT or B34, the XRD peaks of crystalline PEO in the blend are clearly seen, as shown in Figures 5a and 6a, respectively. The crystalline PEO peaks are not observed in samples annealed at 85 °C for 8 h containing less than 40% of Blend50 in both systems, as shown in Figures 5b−e and 6b−e, respectively. When the Blend50 content reaches 50%, these crystalline PEO peaks appear again in the annealed samples, as shown in Figures 5f and 6f. However, the intensities of crystalline PEO are very weak, especially in the Blend50/B34 system. To observe the crystalline PEO peaks more clearly, an enlargement of

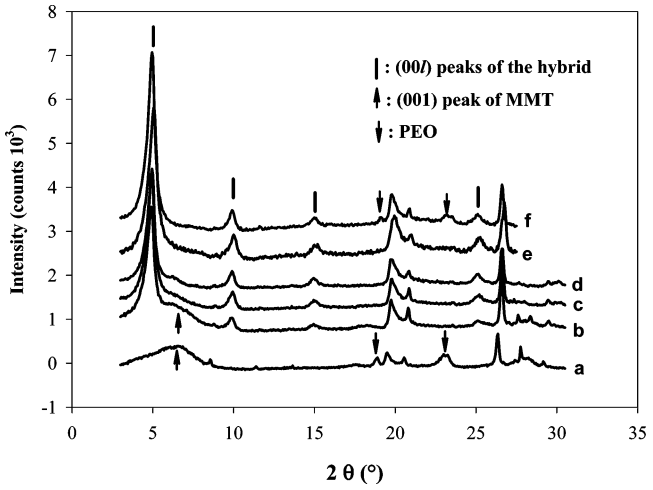

Figure 5. XRD patterns for the Blend50/MMT system: (a) Blend50:MMT = 40:60, physical mixture before annealing, (b−f) samples after annealing at 85 °C for 8 h: (b) Blend50:MMT = 10:90, (c) Blend50:MMT = 20:80, (d) Blend50:MMT = 30:70, (e) Blend50:MMT = 40:60, and (f) Blend50:MMT = 50:50.

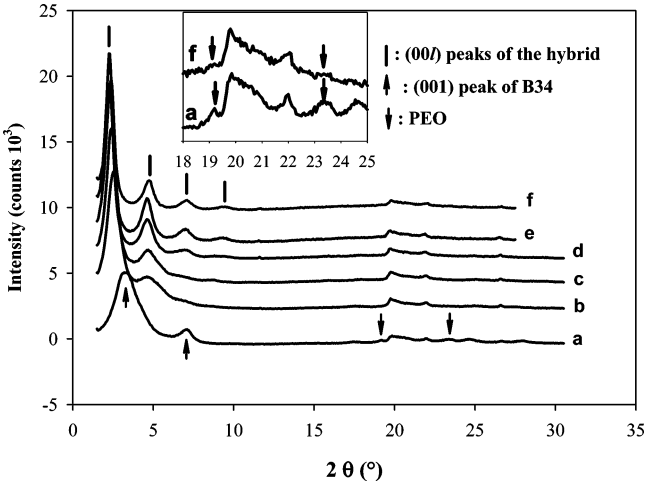

Figure 6. XRD patterns for the Blend50/B34 system: (a) Blend50:B34 = 20:80, physical mixture before annealing; (b–f) samples after annealing at 85 °C for 8 h: (b) Blend50:B34 = 10:90, (c) Blend50:B34 = 20:80, (d) Blend50:B34 = 30:70, (e) Blend50:B34 = 40:60, and (f) Blend50:B34 = 50:50.

Table 7. *d* Spacing Values in Å of the (00*l*) Peaks and Unchanged (100) Peak in the Blend50/MMT System with Different Polymer/Silicate Ratios and Annealed at 85 °C for 8 h

blend50/MMT	20:80	30:70	40:60	50:50	pure MMT
(001) *d* spacing	17.9	17.9	17.5	17.9	9.6
(002) *d* spacing	8.9	8.9	8.9	8.9	*a*
(003) *d* spacing	5.9	5.9	5.9	5.9	*a*
(100) *d* spacing	4.5	4.5	4.5	4.5	4.5

[a] Indicates no such peak can be observed.

XRD pattern (f) is shown in Figure 5, and the unannealed sample (Figure 6a) is plotted on the same for comparison.

Table 7 and Table 8 summarize the *d* spacing of the (00*l*) peak series and gallery size in each heated sample for the Blend50-MMT and Blend50-B34 systems, respectively. The *d* spacing values in the Blend50-MMT system are independent of the polymer content, as observed in the PEO/MMT system.[16] The (001) *d* spacing is 17.9 Å in both PEO/MMT and Blend50/MMT systems, and the values of (00*l*) peaks are all the same in both systems. It implies that PEO in the PEO–PMMA blend has simply entered the MMT galleries alone. The presence of PEO moving into MMT appears not sufficient to likewise influence the PMMA molecules to also enter the MMT galleries.

Quite different behavior is observed in the Blend50/B34 system. The *d* spacing value increases with polymer loading until the polymer content reaches 40%. The maximum *d* spacing of the (001) peak of the intercalated hybrid is 38.4 Å, plateauing for samples with polymer concentrations of greater than 40%. Thus, the gallery size of some 8.4 Å is 1.6 Å greater than the common gallery size of 6.8 Å in the individual PEO–B34 and PMMA–B34 hybrids. This value of the gallery size of 8.4 Å is also greater than that of intercalation of sequential PMMA to PEO–B34 hybrid or sequential PEO to saturated PMMA–B34 hybrid (the same as 6.8 Å). Indeed, compared to the values of the PMMA/B34 system,[18] the Blend50/B34 hybrid shows larger (00*l*) *d* spacing values than the PMMA–B34 hybrid with the same polymer content in the sample. For example, the (001) *d* spacing values of the PMMA–B34 hybrid with 20% PMMA is 34.7 Å,[18] while the value for the Blend50/B34 hybrid with 20% polymer blend is 36.8 Å. This suggests that the PEO/PMMA blends can melt intercalate into B34 and extend the gallery size of B34 to 8.4 Å, some 1.6 Å greater than in either the PMMA/B34 or the PEO/B34 system. The saturation level of the polymer blend to intercalate into B34 is around 40%, 15% more than that of PMMA to B34 and 25% more than that of PEO to B34, although only causing a further 1.6 Å increase in interlayer spacing.

This result again raises the possibility (as in the case of sequential intercalation) that the packing density of a PEO/PMMA blend in the galleries of layered silicates is greater than that of a single component in the galleries, although it is possible that the chains coreside in different spatial reasons within the gallery. It should be noted, as is often discussed, that, in miscible polymer blends, the packing density may be greater than that of the components.[22] However, for both polymers to be incorporated into the gallery, the mobility of the PMMA chains at 85 °C need to be facilitated by being a component of a miscible blend with PEO, since PMMA alone would not become intercalated at that annealing temperature. Conversely, it cannot be the PEO alone reptating from the miscible blend, as the resulting *d* spacing is greater than that for PEO alone. For the Blend50–MMT system, on the other hand, only PEO appears to intercalate from the blend can enter into the MMT, resulting in the (00*l*) *d* spacings of Blend50/MMT system being as the similar to those in PEO–MMT hybrid.

3.2. DSC Results for Melt Intercalation of the Blends. Figure 7 and Figure 8 show the DSC results of mixture samples with different Blend50 contents before and after annealing for Blend50/MMT and Blend50/B34 systems, respectively. The results of these DSC results are consistent with the XRD results discussed above.

Parts a, b, and c of Figure 7 show the DSC traces of mixture samples of Blend50 and MMT at a ratio of 50:50, 40:60, and 30:70, namely BM50, BM40, and BM30, respectively. The melting points of PEO are at similar temperatures for all three samples, and do not change with the MMT loading in the mixtures. Parts d, e, and f of Figure 7 are the DSC traces of Blend50 and MMT after melt intercalation at a ratio of 50:50, 40:60, and

Table 8. *d* Spacing Values in Å of the (00*l*) Peaks and Unchanged (100) Peaks in the Blend50-B34 Hybrids Intercalated at Different Polymer/Silicate Ratios and Annealed at 85 °C for 8 h

Blend50–B34 hybrid	20:80	30:70	40:60	50:50	60:40	pure B34
(001) *d* spacing	36.8	37.6	38.4	38.4	38.4	30.0
(002) *d* spacing	18.2	18.6	19.4	19.4	19.4	12.8
(003) *d* spacing	12.4	12.6	12.7	12.7	12.7	*a*
(004) *d* spacing	9.2	9.64	9.4	9.4	9.4	*a*
(100) *d* spacing	4.5	4.5	4.5	4.5	4.5	4.5
increase in the gallery size	6.8	7.6	8.4	8.4	8.4	

[a] Indicates no such peak can be observed.

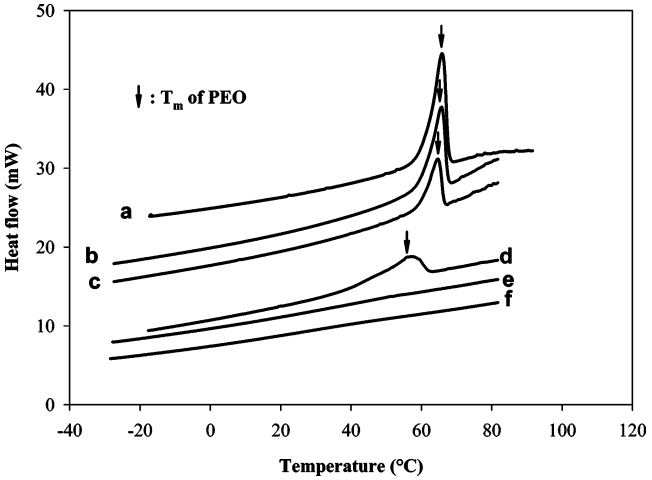

Figure 7. DSC traces for the Blend50/MMT system: mixtures before annealing of (a) Blend50:MMT = 50:50 (BM50), (b) Blend50:MMT = 40:60 (BM40), (c) Blend50:MMT = 30:70 (BM30), samples after annealing at 85 °C for 8 h of (d) BM50, (e) BM40, and (f) BM30.

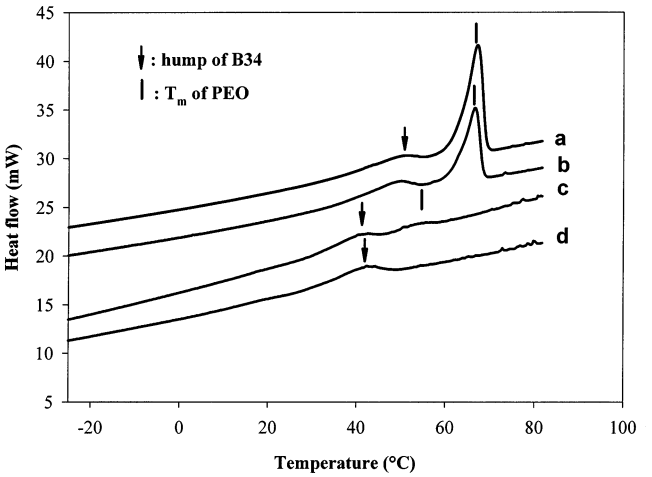

Figure 8. DSC traces for the Blend50/B34 system: mixtures before annealing of (a) Blend50:B34 = 40:60 (BB40) and (b) Blend50:B34 = 30:70 (BB30) and after annealing at 85 °C for 8 h of (c) BB40 and (d) BB30.

30:70, respectively. In Figure 7d, the heated sample of Blend50:MMT = 50:50 shows a peak which appears at a lower temperature than the dry-blended, unannealed sample, and the melting endotherm ΔH_m decreases significantly. This indicates that a significant proportion of PEO enters the gallery, with a small amount of crystalline PEO remaining outside. The decrease in PEO melting point could possibly be due to the crystalline PEO phase outside the gallery becoming smaller and less perfect, with chains being disrupted by extending from inside the galleries to outside between the silicate particles.[15] In a miscible blend system, the melting point may also be influenced by the interaction between the polymers. As mentioned before, since PEO alone wriggles out of the PMMA/PEO blend to enter the galleries of MMT, the decrease in melting point of the Blend/MMT system may be due to the increase of PMMA concentration outside the polymer regions outside of the nanoclay galleries. Two other samples also heated at 85 °C for 8 h with 40% and 30% Blend50 showed no melting transition.

Parts a and b of Figure 8 show the DSC curves of mixture samples of Blend50 and B34 at ratios of 40:60 and 30:70, respectively. The first small broad peak at low temperatures is due to the organo-ions in the B34 galleries. The melting points of PEO in both curves are at the same position. Parts c and d of Figure 8 are the DSC curves for samples of Blend50 and B34 at ratios of 40:60 and 30:70 after annealing at 85 °C for 8 h. The blend:B34 ratio of 40:60 (Figure 8c) appears to indicate the concentration boundary of at which the melting point of PEO no longer occurs.

Generally, crystalline PEO cannot be seen by either XRD or DSC when the Blend50 content is less than 40% in both the Blend50/MMT and Blend50/B34 systems. This does not, however, mean that the saturation ratio of Blend50 to layered silicate is 40:60 for the melt intercalation, as it is not clear whether both PEO and PMMA diffuse into layered silicate at the same rate or one of them prefers to diffuse into the gallery faster. In particular, if PEO diffuses from the melt mixture into silicate gallery at a greater rate and to a greater extent, the indication of crystallinity in PEO outside the hybrid from XRD patterns and DSC traces will disappear once all PEO goes into the silicate gallery, and PMMA may still remain outside the nanoclay. In addition, as reported previously, a PEO/PMMA blend with a PEO content below 20% has been reported to show no evidence of crystallinity.[20] If PEO goes into layered silicate faster than PMMA in the blend, XRD or DSC thus cannot be used as an indicator as to whether crystalline PEO remains outside the hybrid, as low concentrations of PEO and PMMA blends themselves show low crystallinity.

Conclusions

This work has investigated a sequential polymer melt intercalation into pre-intercalated polymer/layered silicate hybrid and the melt intercalation of a solution-blended, miscible PEO/PMMA blend. It is found that PMMA can intercalate into a previously saturated PEO pre-intercalated B34 hybrid. Likewise, PEO is able to intercalate into a PMMA/B34 pre-intercalated saturated hybrid. The resultant gallery sizes are the same for PMMA and PEO individually and remain the same when a second polymer is intercalated into a saturated, pre-intercalated hybrid. This means that the packing density of a combination of PEO and PMMA in the gallery of layered silicates thus appears to be greater than that of any individual polymer in the same galleries.

Melt intercalation of a miscible blend of PEO:PMMA = 50:50 into either MMT or B34 was also investigated by XRD and DSC. The PEO/PMMA blend intercalated hybrid has different features from that of a single polymer, such as different gallery size and resultant thermal behavior. The increase of the gallery size of blend−B34 intercalated hybrids (8.4 Å) is 1.6 Å greater than that of either single polymer intercalated B34 hybrids and that of sequential polymer intercalated saturated hybrids (6.8 Å). A blend of PEO and PMMA seems able to push the layers of B34 slightly further apart than either homopolymer alone. However, the increase of the gallery size of blend−MMT intercalated hybrids remains the same 8.3 Å, as for the PEO/MMT system. It is thus clear that organically modified layered silicates are thus able to host more polymer content, from the blend, than either blend component alone. In the blend/B34 system, PMMA enters into B34, alongside PEO at a temperature as low as 85 °C. In comparison,

for PMMA alone to intercalate into B34 the melt intercalation temperature needs to be higher than 160 °C.

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