Aluminosilicate Nanocomposite Materials. Poly(ethylene glycol)−Kaolinite Intercalates

James J. Tunney and Christian Detellier*

Ottawa-Carleton Chemistry Institute, Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

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This paper reports the first example of the direct intercalation of an organic polymer into the interlamellar spaces of kaolinite. Poly(ethylene glycols) (PEG 3400 and PEG 1000) were intercalated into kaolinite by displacing dimethyl sulfoxide (DMSO) from the DMSO−kaolinite intercalate (Kao−DMSO). This was done directly from the polymer melt at temperatures between 150 and 200 °C. XRD showed that the intercalated oxyethylene units were arranged in flattened monolayer arrangements, such that the interlayer expansion was 4.0 Å. Infrared analysis of Kao−PEG 3400 supported the assignment of a trans conformation to at least a portion of the ($O-CH_2CH_2-O$) groups of the PEG polymer while ^{13}C CP and DD/MAS NMR indicated that the polymer was intercalated intact and was more constrained in the interlamellar spaces of kaolinite than it was in its bulk form. TGA/DSC analysis revealed that the complete decomposition of the organic component of the oxyethylene-based organokaolinites did not occur until greater than 1000 °C. The formulas were estimated to be $Al_2Si_2O_5(OH)_4(-OCH_2CH_2-)_{0.77}(DMSO)_{0.27}$ and $Al_2Si_2O_5(OH)_4(-OCH_2CH_2-)_{0.99}(DMSO)_{0.17}$, respectively for the cases of PEG 1000 and PEG 3400. The calculated formulas for both samples are consistent with one unit of oxyethylene or DMSO per $Al_2Si_2O_5(OH)_4$ unit. Given the known density of hydroxyl groups on the aluminol surface, a polymer conformation where ethyleneoxy groups repeat every 2.8 Å with the oxygens all facing toward the hydroxyl surface should be favored. It is suggested that the polymer adopts a conformation $TG_2T'G_2'$, in which the repeat unit per ethyleneoxy group is 2.94 Å, and all the oxygens are lined up on one side of the chain. The tension resulting from the imperfect fit could be relaxed by a certain degree of trans conformations.

Introduction

Over the past few years, there has been considerable interest in the intercalation of poly(ethylene oxide) (PEO) and other polymers in layered structures.[1−19] The two-dimensional confinement of PEO in an inorganic lattice can lead to certain desirable anisotropic ionic conduction properties. Some of the layered materials which have been intercalated with PEO, or its smaller molecular weight analogue poly(ethylene glycol) (PEG), include zirconium phosphate,[11,12] V_2O_5,[13] MPS_3 (M = Mn, Cd),[8] MoS_2,[3,9] and smectite clays.[2,4−7,10] The conformations that PEO adopts in the confined spaces of these inorganic matrixes are quite variable. For example, PEO intercalated in V_2O_5 is thought to be in a straight-chain conformation,[13] whereas in MPS_3[8] and MoS_2[3,9] the PEO chains are thought to adopt a bilayer arrangement. Finally, in some smectite clays, the PEO was hypothesized to form helixes, in which the interlayer cation is found within the helix.[4]

The preparation of two-dimensional inorganic−polymer nanocomposites generally involves either polymer intercalation from solution or intercalation of a suitable monomer and its subsequent polymerization. Workers at Toyota, for example, have prepared a number of nanoscale polymer−clay hybrid composites using these techniques.[14−17] Many of these composite hybrids were found to exhibit much improved mechanical and thermal properties. Recently, workers have started looking at alternate preparation methods, where the polymer is inserted directly into the layered material without the use of a solvent. Giannelis and co-workers have prepared a series of two-dimensional nanostructures

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based on the direct polymer melt intercalation of organically modified smectites.[10a,b] A PEO−smectite nanocomposite with a XRD pattern identical with the PEO−smectite materials prepared via the solution intercalation method[4] was one of the materials prepared. Very recently, hectorite was hydrothermally crystallized in the presence of a polymer solution,[10c,d] yielding a polymer−clay nanocomposite. Clay-reinforced epoxy nanocomposites were prepared, forming exfoliated nanocomposites, with well-separated clay layers in a continuous polymer matrix.[10e,f]

The direct incorporation of PEO or any other polymer into the structure of kaolinite has never been reported in the literature. Sugahara et al. have nonetheless succeeded in preparing kaolinite−polyacrylonitrile[18] and kaolinite−polyacrylamide[19] nanocomposites by first intercalating the appropriate monomer into the interlayers and then inducing polymerization by thermal treatment.

For kaolinite, it has been shown that it is possible to prepare two distinct ethylene glycol phases of kaolinite, Kao−EG 9.4 Å and Kao−EG 10.8 Å.[20] The Kao−EG 10.8 Å phase was the more weakly bound intercalated phase, while the Kao−EG 9.4 Å phase was attributed to an EG unit covalently bound to interlayer aluminol surface of kaolinite. A polytype of kaolinite, halloysite, was also reported to intercalate not only EG but also diethylene glycol (DiEG) and triethylene glycol (TriEG).[21] From these data, it was logical to assume that larger molecules based on the oxyethylene unit, of which EG was the simplest unit, may also intercalate into the structure of kaolinite. With this idea in mind, it was attempted to intercalate larger oxyethylene-based molecules into kaolinite. In this paper, the preparation and characterization of two oxyethylene-based organokaolinites are reported, kaolinite PEG−1000 (Kao−PEG 1000) and Kao−PEG 3400. This is the first example of the direct intercalation of a polymer into kaolinite.

Experimental Section

Chemicals. All chemicals used were of reagent-grade quality and were not further purified unless otherwise specified. Well-crystallized kaolinite from Georgia (labeled KGa-1) was obtained from the Source Clay Repository of the Clay Mineral Society (Department of Geology, University of Missouri). This was purified based on previously reported sedimentation techniques,[22−25] and the <2 μm size fraction was used.

Instrumentation. Infrared spectra were obtained on a Bomem Michelson MB 100 FTIR spectrometer using 30−50 averaged scans at 4 cm^{-1} resolution. The samples were prepared as KBr pellets (0.25−0.50 wt % in KBr). XRD powder patterns were performed on a Philips PW 3710 diffractometer using a generator voltage of 45 kV and a generator current of 40 mA. A step size of 0.04° 2θ was used with a dwell time of 0.5 s/step. Samples were prepared on a circular glass disk by dispersing 20−30 mg of sample with 1 mL of methanol, followed by sonication for 10 s and application and drying on a glass slide. All thermal analysis (TGA and DSC) runs were done on a Polymer Labs 1500H under either flowing nitrogen or air (20−90 cm^3/min) and a heating rate of 10−20 °C/min. Approximately 10 mg of sample was used for each run using alumina sample and reference pans. Calibration of the thermocouple was performed by using the known endothermic melting transitions of lead, zinc, and gold. ^{13}C CP/MAS and DD/MAS experiments were performed on a Bruker ASX-200 (50.32 MHz) using spinning rates ranging from 3 to 5 kHz, and a contact time of 0.2 ms. All ^{13}C CP/MAS spectra were referenced to hexamethylbenzene at 14.9 ppm.

Kao−PEG 1000 (1). Poly(ethylene glycol) 1000 (10 g, Aldrich) was heated to 155 °C in a 50 mL round-bottom flask placed in a silicone oil bath. To this viscous melt, 2.0 g of Kao−DMSO[20a,b] was added at once, and the reaction was allowed to proceed for a total of 216 h (9 days). At selected times during the reaction, small aliquots were removed with a pipet, quenched by cooling, and worked up by repeatedly washing with methanol to remove excess poly(ethylene glycol). Typically, after workup, each aliquot yielded 40−60 mg of product. FTIR spectra and XRD patterns were taken for these aliquots in order to monitor the extent of reaction. The remaining final product was worked up by washing/centrifuging in methanol three times, followed by air-drying at 25 °C and then drying in an oven at 100 °C for 3 days. This yielded an off-white powder (**1**). XRD: d spacing = 11.12 ± 0.04 Å, intercalation ratio = 0.95. FTIR (in cm^{-1}): ν(OH) 3695 (m), 3650 (m), 3633 (m), 3621 (m), 3600−3300 (m, br); ν(C−H) 3020 (v w), 2959 (w, sh), 2924 (w), 2878 (w); δ(HOH) 1645 (w); δ(C−H): 1461 (w), 1407 (w), 1356 (w), 1318 (w), 1268 (w), 1249 (w); Si−O vibrations 1124 (s), 1087 (s), 1049 (vs), 1026 (vs); δ(Al−OH) 955 (w), 939 (w), 911 (s); other bands 852 (w), 838 (w), 815 (w), 798 (w), 748 (w), 685 (m), 542 (s), 472 (s), 430 (s). Calcination weight loss (3 h at 1100 °C in air atmosphere): 29.1%. ^{13}C CP/MAS: CH$_2$ ether: 70 ppm, $\nu_{1/2}$ = 415 Hz; CH$_3$ DMSO: 42 ppm, $\nu_{1/2}$ = 115 Hz. Elemental analysis: carbon 7.90%; hydrogen 2.63%.

Kao−PEG 1000 (2). When the *N*-methylformamide intercalate of kaolinite (Kao−NMF) was used as the starting material for the reaction with PEG 1000, it was found that at 155 °C structural collapse to unexpanded kaolinite would occur since Kao−NMF is not as thermally stable as Kao−DMSO and is subject to thermal decomposition at lower temperatures than Kao−DMSO.[26,27] It was therefore decided to gently ramp up the reaction temperature in order to allow reaction with PEG 1000 to occur before the structural collapse of Kao−NMF might occur. Poly(ethylene glycol) 1000 (10 g) was allowed to melt in a 50 mL round-bottom flask by placing the flask and its contents in a silicone oil bath at 70 °C. Kao−NMF (1.5 g) was added at once, with vigorous stirring maintained. The reaction mixture was maintained at 70 °C for 6 days followed by slowly increasing the reaction temperature to 160 °C over the course of an additional 4 days. Finally the reaction mixture was maintained at 160 °C for 3 more days. Aliquots were removed and analyzed at various times to monitor the extent of reaction as was previously described for **1**. The remaining final product was collected and worked up after a total reaction time of 312 h to yield an off-white powder (**2**). XRD: d spacing = 11.01 ± 0.05 Å; intercalation ratio = 0.78. FTIR (in cm^{-1}): ν(OH) 3698 (m), 3651 (m, sh), 3623 (m), 3600−3300 (m, br), 3412 (w); ν(C−H) 2929 (w, sh), 2882 (w); ν(C=O) 1661 (w); δ(C−H) 1463 (w), 1417 (vw), 1377 (vw), 1358 (w), 1315 (w), 1247 (w); Si−O vibrations 1121 (s), 1087 (s), 1044 (vs), 1026 (vs), 1012 (vs); δ(Al−OH) 913 (s); other bands 797 (w), 751 (w), 687 (m), 541 (s), 470 (s), 428 (s). Calcination weight loss (3 h at 1100 °C in air atmosphere): 23.5%.

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Table 1. Summary of the Product Codes, Reaction Conditions, and Preliminary Characterizations for Kao−PEG 1000 and Kao−PEG 3400 Prepared in This Study[a]

product		reaction conditions						product characterization		
name	code	starting material (SM)	reaction media (RM)	(RM)/(SM) (g/g)	T_{rxn} (°C)	t_{rxn} (h)	*d*[b] (Å)	I.R.[c]	calcination wt loss[d] (wt %)
Kao−EG 10.8 Å[e]		Kao−DMSO	EG/H_2O (95/5)	50	185	20	10.85	0.95	
Kao−PEG 1000	**1**	Kao−DMSO	PEG 1000	5	155	216	11.12	0.95	29.1
Kao−PEG 1000	**2**	Kao−NMF	PEG 1000	7	[f]	312	11.01	0.78	23.5
Kao−PEG 1000	**3**	kaolinite	PEG 1000	8	200	144	7.16	0	
Kao−PEG 1000	**4**	Kao−NMF	PEG 1000/diox	[g]	100	162	7.16	0	
Kao−PEG 1000	**5**	Kao−NMF	PEG 3400/H_2O	[g]	100	162	7.16	0	
Kao−PEG 3400	**6**	Kao−DMSO	PEG 3400	5	155	216	11.16	0.96	29.4
Kao−PEG 3400	**7**	Kao−DMSO	PEG 3400	4	195	116	11.19	0.97	30.4
Kao−PEG 3400	**8**	kaolinite	PEG 3400	8	200	144	7.16	0	

[a] Reaction details of the various reactions are given in the Experimental Section. [b] The specified interlayer distance (*d*) is that of the principal product phase calculated using (00*l*) reflections (see text). [c] The modification or intercalation ratio (I.R.) is the ratio of the intensities of the *d*(001) reflection of the modified phase over the sum total of all the *d*(001) reflections of the modified phase(s) and residual unexpanded kaolinite. [d] Based on the weight after calcination in air at 1100 °C. [e] Taken from ref 20b. [f] Temperature was ramped from 70 to 160 °C. [g] See Experimental Section for details.

Kao−PEG 1000 (3). The control experiment involved placing 5 g of PEG 1000 in a 50 mL round-bottom flask, heating to 200 °C, adding 0.6 g of kaolinite, and stirring the mixture under nitrogen atmosphere at this temperature for a total of 6 days. Workup consisted of washing with methanol to remove excess PEG 1000, followed by air-drying to yield product **3**, which was then characterized by XRD and FTIR. This showed that there was no detectable change in the nature of the unexpanded kaolinite starting material.

Kao−PEG 1000 (4). Kao−NMF (1.0 g, intercalation ratio, I.R. = 0.91) was mixed with a solution consisting of 4.0 g of PEG 1000 dissolved in 40 mL of 1,4-dioxane. This was refluxed for 162 h in open atmosphere. After filtering, washing with 1,4-dioxane and air-drying, 0.81 g of off-white powder **4** was collected. The FTIR spectrum of this product showed that no polymer incorporation had been achieved, and instead one observed a pattern consistent with a partially collapsed Kao−NMF (ν(N−H) = 3419 cm^{-1}, ν(C=O) = 1688 cm^{-1}).

Kao−PEG 1000 (5). Kao−NMF (1.0 g, I.R. = 0.91) was mixed with a solution consisting of 4.0 g of PEG 1000 dissolved in 40 mL of water. This was refluxed for 162 h in open atmosphere. After filtering, washing with 1,4-dioxane and air-drying, 0.87 g of off-white powder **5** was collected. The FTIR spectrum of this product was consistent with a fully collapsed kaolinite.

Kao−PEG 3400 (6). Poly(ethylene glycol) 3400 (10 g, Aldrich) was heated to 155 °C in a 50 mL round-bottom flask placed in a silicone oil bath to which 2.0 g of Kao−DMSO was added at once. This reaction was treated in exactly the same way as described for **1**, removing aliquots periodically to assess the extent of reaction. This yielded off-white powder **6**. XRD: *d* spacing = 11.16 ± 0.04 Å; intercalation ratio = 0.96. FTIR (in cm^{-1}): ν(OH) 3696 (m), 3650 (m, sh), 3636 (m), 3620 (m), 3600−3300 (m, br); ν(C−H) 3022 (v w), 2956 (w, sh), 2930 (w), 2880 (w); δ(HOH) 1640 (w); δ(C−H) 1465 (w), 1400 (w), 1359 (w), 1318 (w), 1268 (w, sh), 1248 (w); Si−O vibrations 1124 (s), 1086 (s), 1050 (vs), 1026 (vs); δ(Al−OH) 955 (w), 938 (w), 911 (s); other bands 852 (w), 797 (w), 747 (w), 684 (m), 545 (s), 470 (s), 430 (s). Calcination weight loss (3 h at 1100 °C in air atmosphere): 29.4%. ^{13}C CP/MAS: CH_2 ether: 70 ppm, $\nu_{1/2}$ = 450 Hz; CH_3 DMSO: 42 ppm, $\nu_{1/2}$ = 150 Hz. Elemental analysis: carbon 8.09%; hydrogen 2.73%.

Kao−PEG 3400 (7). Poly(ethylene glycol) 3400 (10 g, Aldrich) was heated to 195 °C in a 50 mL round-bottom flask placed in a silicone oil bath. Kao−DMSO (2.5 g) was added at once to the melt, and the reaction was allowed to proceed for a total of 116 h. Small aliquots were removed at given times during the course of reaction to monitor product formation. After 116 h reaction time, the final product **7** was an off-white powder. XRD: *d* spacing = 11.19 ± 0.04 Å; intercalation ratio = 0.97. FTIR: essentially identical to **6**. Calcination weight loss (3 h at 1100 °C in air atmosphere): 30.4%.

Kao−PEG 3400 (8). The control experiment was done in exactly the same way as described for **3** with the exception that PEG 3400 was used instead of PEG 1000. The final product **8** was characterized by XRD and FTIR, which showed that the kaolinite starting material remained unexpanded.

Results and Discussion

Preparation. The organoclays were typically prepared by first preparing the dimethyl sulfoxide (DMSO) or *N*-methylformamide (NMF) intercalate of kaolinite[20] and then reacting this directly with the polymer. Typically, 1−2 g of either Kao−DMSO or Kao−NMF intercalate were mixed with an excess of either PEG 1000 or PEG 3400. This was done directly in the melt of the appropriate organic reagent, without the use of a solvent. The mixture was maintained at a given temperature for a given period of time followed by the reaction workup. The reaction details for the individual reactions are given in the Experimental Section and are summarized in Table 1. The product codes and reaction conditions are given along with the interlayer *d* spacing, intercalation ratio, and calcined weight loss of the products. The interlayer or *d* spacings were calculated from the first 5 or 6 d_{00l} reflections of the principal phase.

The interlayer expansion for these materials was comparable. Basal spacings ranged from 10.85 Å for Kao−EG to 11.19 Å for Kao−PEG 3400 (**7**). After subtracting for the 7.14 Å basal spacing of kaolinite, this corresponds to a clearance space of approximately 3.7−4.1 Å which is roughly what one might expect, based on CPK models for an oxyethylene unit sandwiched between two clay layers or for a flattened monolayer arrangement of the polymer chains in the interlamellar space. Comparable values for the interlayer expansion of other layered materials due to the monolayer intercalation of molecules based on the oxyethylene unit can be found.[7,12,13,21,28−32] For example, interlayer expansions of 3.7 Å for ethylene glycol intercalated into vermiculite,[28] 4.0 Å for 15-crown-5 intercalated into

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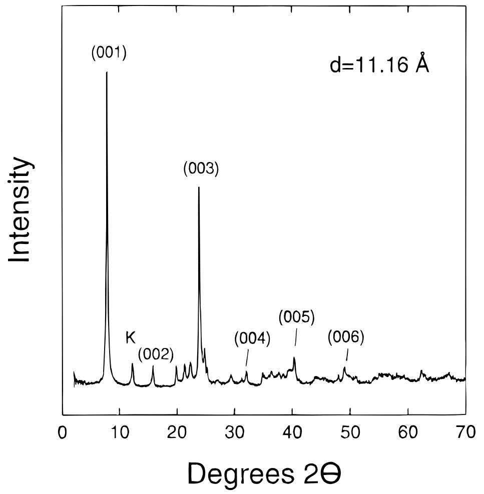

Figure 1. XRD pattern (2−70° 2θ) of Kao−PEG 3400 (**6**) dried at 100 °C for 3 h. (00*l*) peaks are indicated along with the residual (001) unexpanded kaolinite peak (K).

Na$^+$-montmorillonite,[29,32] 3.9 Å for 18-crown-6 intercalated into Ba^{2+}-montmorillonite,[29,32] 2.8 Å for PEG intercalated into layered α-zirconium phosphate,[12] and 4.5 Å for poly(ethylene oxide) intercalated into V$_2$O$_5$.[13] The XRD pattern of Kao−PEG 3400 (**6**) from 2 to 70° 2θ is shown in Figure 1 showing 6 (00*l*) reflections. XRD patterns of the other Kao−PEG materials are similar to this, and in all cases at least four (00*l*) reflections could be indexed.

It is noteworthy that preliminary attempts at intercalation of PEG which were not done using the PEG melt method but instead were done using PEG 1000 dissolved in either water (**5**) or 1,4-dioxane (**4**) solvent were unsuccessful. The success of the intercalation by the melt method could be due to a strong concentration effect of the polymer in the melt compared to the dioxane or water solutions, coupled with a possible lower stabilization energy of each polymer unit in the melt and with a competition of the interlamellar hydrogen bonding sites of kaolinite by the solvent molecules. Regarding this last point, for example, we have recently shown that an 8.4 Å hydrated form of kaolinite could be prepared from Kao−DMSO.[20c]

IR Analysis. Kaolinite is characterized by a diagnostic, signature O−H stretching pattern consisting of four bands at 3694, 3669, 3653, and 3621 cm^{-1} (Figure 2a). The attribution of these bands has been the subject of extensive study.[33−38] The band at 3621 cm^{-1} has been unambiguously assigned to the stretching frequency of the internal hydroxyl group of kaolinite. This hydroxyl group is believed to be oriented almost parallel to the direction of the (00*l*) layers, pointing in the direction of the unoccupied octahedral hole.[39,40] The inner-surface hydroxyl groups associated with the remaining bands (3694, 3669, and 3653 cm^{-1}) are believed to make an angle of 60−73° with the (001) plane.[39]

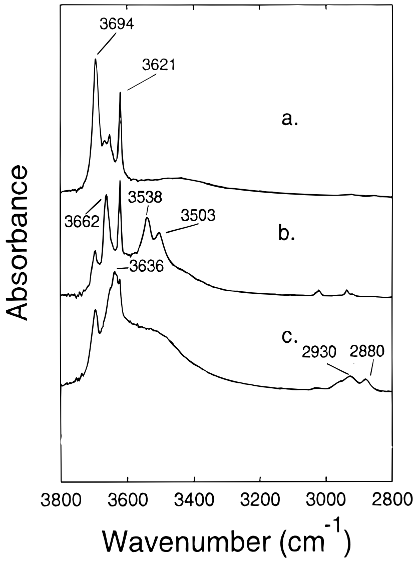

Figure 2. FTIR spectra (3800−2800 cm^{-1}) of kaolinite (a), Kao−DMSO (b), and Kao−PEG 3400 (**6**) (c).

The inner hydroxyl stretching band at 3621 cm^{-1} is not usually influenced very much by interlamellar modification reactions since it is removed from the interlamellar surface. In contrast, the three inner-surface hydroxyl stretching bands are very much influenced by interlamellar modifications,[41−48] as it can be readily observed for Kao−DMSO (Figure 2b).

The O−H stretching patterns for Kao−PEG 3400 and Kao−PEG 1000 differ significantly from both kaolinite and Kao−DMSO (Figure 2c). The band at 3695 cm^{-1} is reduced in intensity with respect to kaolinite but not with respect to Kao−DMSO. There also appears a band at 3636 cm^{-1} along with a broad ill-defined band centered near 3525 cm^{-1}. The band at 3621 cm^{-1} remains unperturbed.

The C−H stretching bands, associated with the methylene groups of the oxyethylene molecules, are perturbed upon intercalation into the interlayers of kaolinite. Close examination of this region also reveals the presence of residual interlayer DMSO or NMF.

In the case of Kao−EG 10.8 Å, the intercalated oxyethylene species show distinct asymmetric and symmetric C−H stretching bands at about 2940 and 2880 cm^{-1}, respectively.[20b,c] These frequencies are slightly higher than those of the corresponding bands for the neat liquids (approximately 10−20 cm^{-1} higher) and in the cases of Kao−PEG 3400 and Kao−PEG 1000, the

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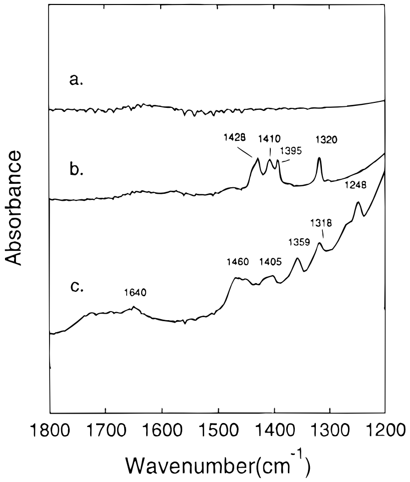

Figure 3. FTIR spectra (1800−1200 cm^{-1}) of kaolinite (a), Kao−DMSO (b), and Kao−PEG 3400 (**6**) (c).

C−H symmetric stretching band is found near 2880 cm^{-1} and the C−H asymmetric stretching band near 2930 cm^{-1} with a shoulder at about 2956 cm^{-1}.

In pure solid PEG 3400, which is most likely a mixture of amorphous and crystalline phases similar to poly(ethylene oxide) (PEO),[49] the symmetric and asymmetric C−H stretching modes are not resolved, and only one broad ill-defined band between 2800 and 3000 cm^{-1} centered at 2887 cm^{-1} is observed. Upon intercalation, one observes the splitting of this broad band at 2887 cm^{-1} into two and possibly three (if one includes the shoulder at 2956 cm^{-1}) distinct bands. Aranda and Ruiz-Hitzky observed a similar phenomenon for various PEO/M^{n+} montmorillonite complexes.[4] They found that upon intercalation, the C−H stretching band of the PEO moiety was resolved into two well-defined bands of moderate intensity at approximately 2910 and 2875 cm^{-1}. They also found that these bands were insensitive to the nature of the interlayer cation of the smectite. Polyether derivatives of zirconium phosphate yielded products which had C−H stretching patterns almost identical to those of Kao−PEG 3400 with bands at 2880, 2920, and 2950 cm^{-1}.[11]

The presence of an ill-defined δ(HOH) band between 1630 and 1650 cm^{-1} for Kao−PEG 3400 and Kao−PEG 1000 suggests that surface adsorbed and co-intercalated water molecules are present to some extent (Figure 3c). In the C−H deformation region (1500−1200 cm^{-1}), one finds a number of bands indicative of various CH deformations originating from the oxyethylene species, or in some instances from residual intercalated DMSO or NMF. Close examination of this region may provide some insights into the structural conformations of interlayer oxyethylene species.

Kao−DMSO shows deformation bands at 1428, 1410, 1395, and 1320 cm^{-1} which have been previously assigned.[44] For Kao−PEG 3400, the C−H deformation bands are near 1460, 1405, 1359, and 1318 cm^{-1}. The broad ill-defined band(s) between 1480 and 1440 cm^{-1} centered about 1460 cm^{-1} can be attributed to CH_2 bending modes of the PEG chain based on literature assignments for PEO.[50] Similarly the band centered near 1405 cm^{-1} may be assigned to the CH_2 wagging mode of the oxyethylene units based on the IR assignment for PEO,[50] although this is complicated by the presence of residual interlayer DMSO. Kao−DMSO has two absorption bands in this region (Figure 3b) which may overlap with the PEG band. The band at 1359 cm^{-1} can be assigned to a combination band made up of CH_2 wagging and C−C stretching modes.[50] A band in this region has also been observed for both crown ethers and PEO intercalated into smectites.[4,51]

The attribution of the band at 1318 cm^{-1} was complicated once again by the fact that Kao−DMSO has an absorption band in this region at 1320 cm^{-1}. The attribution of this band is important since the presence or absence of a band in this region may be indicative of the conformation of the oxyethylene species.[4,52,53] Nonetheless, residual DMSO cannot be the sole contributor to the intensity of this band since this sample was shown to have a relatively small amount of residual interlayer DMSO (see below). In support of this, IR bands indicating the presence of DMSO in Kao−PEG 3400 at 3022 cm^{-1} (Figure 2) and 1428 cm^{-1} (Figure 3) have relatively insignificant intensities compared to the intensities of the bands associated uniquely with the presence of intercalated PEG 3400.

Moreover, the analysis of the Kao−PEG 3400 product when Kao−NMF was used as the starting material (**2**) showed that in addition to C−H deformation bands at 1248, 1358, and 1460 cm^{-1}, a band at 1315 cm^{-1} was observed, although at slightly weaker relative intensity than the 1318 cm^{-1} band observed for Kao−PEG 3400 in Figure 3c. Kao−NMF was verified to have no absorption bands which might, like Kao−DMSO, interfere with the assignment of this band.

The presence of a band at 1326 cm^{-1} for molten PEO has been attributed to a combination of CH_2 wagging and twisting modes.[53] This band is not present for solid PEO presumably because, in the solid state, the $-OCH_2CH_2O-$ groups are mainly in the gauche conformation and the presence of a band in this region has been proposed to be due to $-OCH_2CH_2O-$ groups in the trans conformation.[52] In fact, the lack of a band near 1322 cm^{-1} for PEO/M^{n+} montmorillonite has been used as evidence supporting the hypothesis that the $O-CH_2-CH_2-O$ groups of the interlayer PEO chains are all in the gauche conformation.[4] For Kao−EG 9.4 Å, the presence of a band at 1325 cm^{-1} was also used to support the hypothesis that the ethylene glycol moiety was in the trans conformation.[20b] The above discussion suggests that for Kao−PEG 3400, at least a portion of the oxyethylene units are in a trans conformation.

Finally, the bands at 1268 and 1248 cm^{-1} are attributed to the CH_2 twisting vibrations of the oxyethylene units.[50] Similar bands were found, for example, at 1265 cm^{-1} for an 18C6/Ba^{2+} montmorillonite complex[51] and at 1274 and 1248 cm^{-1} for PEO/Na^{+} montmorillonite.[4]

The region 1200−800 cm^{-1} provides information regarding any perturbations to the kaolinite lattice vibrations (1150−1000 cm^{-1}) and any changes in the Al−O−H bending modes of kaolinite (900−980 cm^{-1}).

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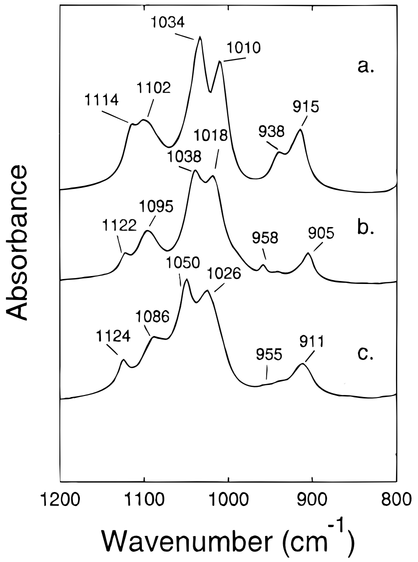

Figure 4. FTIR spectra (1200−800 cm^{-1}) of kaolinite (a), Kao−DMSO (b), and Kao−PEG 3400 (**6**) (c).

Figure 4a−c shows the differences in the IR patterns (1200−800 cm^{-1}) for kaolinite, Kao−DMSO and Kao−PEG 3400, respectively. The pattern of Kao−PEG 3400 shows strong perturbation of the kaolinite lattice vibrations. The two most intense vibrations of kaolinite at 1034 and 1010 cm^{-1} are both shifted to higher frequencies by 16 cm^{-1} for the Kao−PEG 3400. These bands have been previously assigned to the in-plane Si−O−Si stretching vibrations of kaolinite,[54] and are often shifted slightly upon intercalation of guest species such as DMSO, as can be seen for the Kao−DMSO starting material, where these bands are blue-shifted slightly to 1038 and 1018 cm^{-1} (Figure 4b). The fact that these bands are shifted to yet greater frequencies when PEG is intercalated indicates a greater perturbation of the silicate surface on the part of the oxyethylene species. The perpendicular Si−O vibrations found in kaolinite at 1102 and 1114 cm^{-1} [54] (Figure 4a) are also more perturbed for Kao−PEG 3400 than for Kao−DMSO.

The kaolinite band at 938 cm^{-1} has been assigned to the in-plane bending vibrations of surface hydroxyl groups, whereas the band at 915 cm^{-1} has been assigned to the inner hydroxyl.[35,54] Upon intercalation of DMSO, the band at 938 cm^{-1} decreases greatly in intensity and another band of 20 cm^{-1} higher frequency appears at 958 cm^{-1} (Figure 4b).[33,44] The band at 915 cm^{-1} is shifted 10 cm^{-1} to a lower frequency at 905 cm^{-1}, presumably due to a repulsive interaction between one of the methyl groups of DMSO which is proposed to be keyed into the (SiO−)$_6$ macroring of the silicate surface[44,55−57] and the internal hydroxyl of kaolinite. For Kao−PEG, the inner hydroxyl band of kaolinite is not as perturbed as it was for Kao−DMSO, and this is plausibly due to the inability of the oxyethylene species to key in as well to the (SiO−)$_6$ macrorings of the silicate surface.

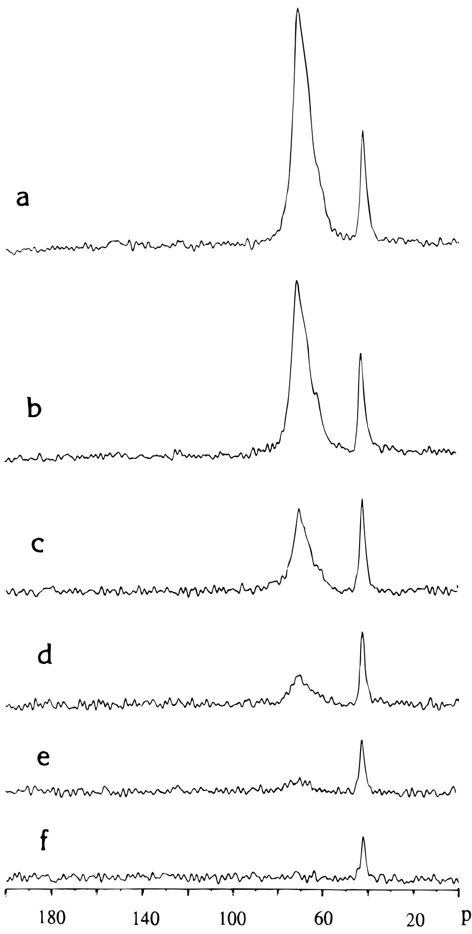

Figure 5. Solid-state ^{13}C CP/MAS NMR spectra for Kao−PEG 3400 (**6**): (a) no dipolar dephasing (a); (b−f) with dipolar dephasing: $\tau = 10$ μs (b); 20 μs (c); 30 μs (d); 40 μs (e); 50 μs (f).

Solid-State NMR Results. A series of ^{13}C CP/MAS (cross polarization) and DD/CP-MAS (58−60 dipolar dephasing) experiments were performed on Kao−PEG 3400 in order to obtain information regarding the interlayer structure and dynamics of the intercalated hosts (Figure 5).

The ^{13}C chemical shift values of Kao−PEG 3400 ($\approx$70 ppm) compared with both Kao−EG 9.4 Å and Kao−EG 10.8 Å ($\approx$65 ppm) confirm that depolymerization of the PEG 3400 did not occur in the interlamellar space of kaolinite to yield an intercalated ethylene glycol monomer in either its 9.4 or 10.8 Å form. The polymer remains intact in the interlayers.

The ^{13}C CP/MAS spectra show the presence of amounts of residual interlayer DMSO, as evidenced by resonances at 41−42 ppm. The oxyethylene unit (OEU)/DMSO ratio based on the ^{13}C CP/MAS peak integrations was crudely estimated to be 5.9 and 2.8 for Kao−PEG 3400 and Kao−PEG 1000, respectively. It is noteworthy that in all cases where DMSO is co-intercalated with oxyethylene species, only one ^{13}C methyl resonance could be found for DMSO, whereas for the pure Kao−DMSO intercalate, two resonances were observed.[55−57]

The ^{13}C CP MAS NMR spectrum of pure poly(ethylene glycol) has been previously reported.[4] Two signals at 70.6 and 71.9 ppm were detected: the first was due to a relatively narrow peak, and the second to a broader resonance (about 440 Hz). For poly(ethylene oxide) intercalated into Na$^+$ hectorite (PEO/Na$^+$−hectorite), Aranda and Ruiz-Hitzky observed a single broad peak

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at around 70 ppm ($\nu_{1/2} \approx 440$ Hz at 100.63 MHz) which they attributed to a helicoidal PEO conformation where all the methylene groups adopt a gauche conformation.[4] In solution, PEO was reported to have a ^{13}C chemical shift of 71.5–72.4 ppm.[61] It was found that the chemical shift was dependent on both concentration and average trans–gauche conformation.

In this study, PEG 3400 gave a resonance at about 72 ppm with a half-height line width of 750 Hz. The broadness of this line is likely due to polymer molecular motions interfering with the efficiency of the proton decoupling.[62] By contrast, PEG 1000 gave a much narrower resonance at 72.9 ppm with a half-height line width of 40 Hz. PEG 3400 and PEG 1000 were both found to be relatively mobile in the solid state since after 40 μs of dipolar dephasing (see below), a significant signal could still be detected, with I_{DD}/I_0 equal to 0.26 for PEG 3400 and 0.18 for PEG 1000.

For Kao–PEG 3400, the resonance at about 70 ppm (Figure 5a) is not significantly shifted from that of the bulk polymer. However, the line width of this resonance was significantly diminished upon polymer incorporation, from about 750 to 450 Hz. This decrease in line width can plausibly be attributed to the fact that, upon intercalation, the molecular motion of the polymer no longer interferes as much with the proton decoupling. The decreased line width is not thought to be due to any increase in polymer crystallinity.

For the dipolar dephasing technique, the ratio of I_{DD}/I_0, where I_{DD} and I_0 are the peak intensities of the ^{13}C resonance obtained respectively with and without dipolar dephasing conditions, is a semiquantitative measure of the dynamic state of the molecular group.[58-60] If a molecular group is rigidly bound, the ratio I_{DD}/I_0 will be decreased. The overall signal decay for carbons strongly coupled to protons, such as methylene carbons has been shown to be best described by the following equation:[59]

$$I_{\mathrm{DD}} = I_0 e^{-\tau^2/(2T_2{}^2)} \qquad (1)$$

where τ is the dipolar dephasing delay time and T_2 is the transverse relaxation time constant.

In a series of experiments, the dipolar dephasing time (τ) was varied from 0 to 50 μs for the Kao–PEG 3400 sample, and the variation in intensity was monitored (Figure 5). This qualitatively showed that the polymer chains in the interlamellar spaces of kaolinite are more constrained and less mobile than in its bulk form. After 40 μs dephasing time, only a residual signal for Kao–PEG 3400 could be detected ($I_{\mathrm{DD}}/I_0 < 0.10$). The plot of $\ln(I_{\mathrm{DD}}/I_0)$ vs τ^2, as predicted by eq 1, is linear (statistical linear regression factor of 0.993) with a T_2 value of 14.7 μs.

In the liquid and solid states, the two methyl groups in DMSO give resonances at respectively 40.3[56] and 40.0 ppm.[55] For ordered Kao–DMSO, the two methyl groups are inequivalent, yielding two resonances in the range 42–44 ppm,[55-57,63] which was confirmed in this work, with the observation of two ^{13}C resonances at 43.7 and 42.7 ppm. The line widths of these resonances were about 80 Hz. ^{13}C DD/MAS NMR using a 40 μs dipolar dephasing time showed that both resonances had an I_{DD}/I_0 ratio of about 0.60.

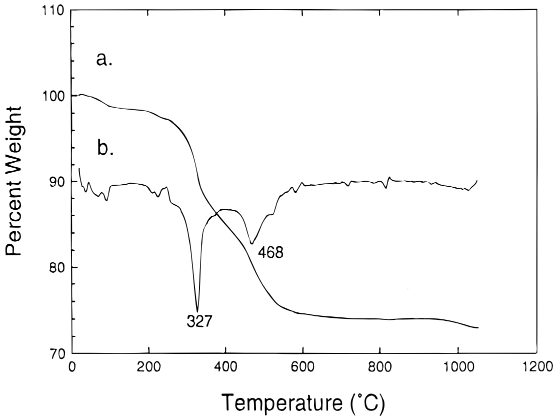

Figure 6. TGA (a) and corresponding DGA (b) curve (20–1050 °C) for Kao–PEG 3400 (**7**) (air atmosphere).

For Kao–PEG 3400, where DMSO was present in the interlayers as unreacted starting material, only one ^{13}C resonance could be observed at about 42 ppm with a line width in the range 110–150 Hz. The I_{DD}/I_0 ratio ($\tau = 40$ μs) for the DMSO resonance in these cases was 0.48. The presence of only one DMSO methyl resonance for residual DMSO as well as the different DD/MAS results when compared to the pure Kao–DMSO intercalate imply that the DMSO molecules are in different local environments. This would be expected if DMSO was randomly entangled in the oxyethylene–kaolinite 2-D matrix, and not found in discrete Kao–DMSO and Kao–oxyethylene layers. This is also probably the reason why the intercalated DMSO is so difficult to completely remove. For example, even after heating at 150 °C for 16 h, some traces of intercalated DMSO could still be found in Kao–PEG 3400 and Kao–PEG 1000.

Thermal Analysis. The thermal decomposition of Kao–PEG 3400 in air atmosphere can be observed in Figure 6. The decomposition followed a multistep process where some of the decomposition steps overlapped, with a total weight loss for the TGA run up to 1050 °C of 28%. Initially, there was a 1.2% weight loss from 25 to 100 °C due to the loss of surface-adsorbed volatiles followed by a further 0.6% weight loss from 100 to 200 °C. Aranda and Ruiz-Hitzky observed that the characteristic endothermic DTA peak associated with the melting of PEO at 72 °C was missing in the DTA of PEO/M^{n+}–montmorillonite.[5] This was also found to be the case for Kao–PEG 3400 where the endothermic DSC melting peak of PEG 3400 at 65 °C was not observed for Kao–PEG 3400. This confirms that the polymer chains in the bulk and intercalated states are in different aggregation states.

From 200 to 340 °C, one observes a 9.5% weight loss attributable to the combustion of organic material (Figure 6). This was supported by the DSC run (not shown) which indicated a very strong exothermic event

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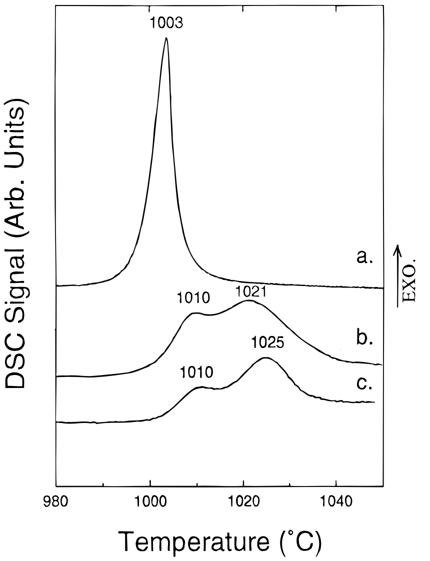

Figure 7. DSC traces (980−1050 °C) for kaolinite (a), Kao−PEG 3400 (**7**) in air (b), and N_2 (c).

with a peak of 327 °C. For comparison, it was found that for the thermal decomposition of pure PEG 3400 in air atmosphere, a very strong exotherm was observed centered at 342 °C corresponding to a 95.7% combustion weight loss. In contrast, no thermal event for kaolinite was detected in this region, and for Kao−PEG 3400 in nitrogen atmosphere, one observed an endothermic event with a peak at 324 °C probably due to the pyrolytic decomposition of the organic component. For the N_2 atmosphere decomposition of Kao−PEG 3400 one observes an additional endothermic peak at 405 °C. Similarly, for the air decomposition of Kao−PEG 3400, the presence of an exothermic shoulder at 367 °C suggests a multistep combustion process.

Overlapping with the weight loss associated with the organic decomposition reactions of Kao−PEG 3400, is the weight loss associated with the dehydroxylation reaction of kaolinite itself between 440 and 650 °C (Figure 6). This was the case for both air and nitrogen TGA runs for all of the oxyethylene-based organokaolinites analyzed. For Kao−PEG 3400 in air, the dehydroxylation reaction of kaolinite was estimated to involve an 8.6% weight loss, compared to a weight loss of 13.1% found for the kaolinite starting material (theoretical weight loss = 14.0%). The dehydroxylation reaction for kaolinite exhibits an endothermic peak at 538 °C, whereas it appears at 480 and 474 °C for Kao−PEG 3400 in air and nitrogen atmospheres, respectively. The presence of PEG in the interlayers of kaolinite significantly reduces the peak dehydroxylation temperature. However, the dehydroxylation reaction is not complete until about 600 °C. This is also reflected in the slow tailing off of the DSC signals between 500 and 600 °C.

Finally, there occur two separate exothermic events for Kao−PEG 3400 between 950 and 1050 °C (Figure 7). These occur at 1010 and 1021 °C in air atmosphere with a small 1.0% weight loss associated with these events. In nitrogen atmosphere, the two exotherms were also present at 1010 and 1025 °C. In contrast, kaolinite exhibits one sharp exothermic peak at 1003 °C, which has been attributed to a structural reorganization forming either mullite nuclei and spinel (γ-Al_2O_3) or both.[64,65]

It is evident that the intercalation of oxyethylene species into the interlamellar spaces of kaolinite has dramatically altered the decomposition sequence of kaolinite, in a manner which is very much different from classical intercalates such as Kao−DMSO and Kao−NMF. This is seen in the reduced temperatures of kaolinite dehydroxylation as well as the appearance of an additional exothermic peak between 950 and 1050 °C.

It is believed that the complete combustion of the oxyethylene species cannot occur once the structure has collapsed after the initial decomposition reactions before 400 °C. Structural collapse followed by the dehydroxylation of the kaolinite itself then causes the residual interlayer carbonaceous material to be trapped within a metakaolinite matrix, forming a carbon−aluminosilicate nanocomposite material.

Some of this carbonaceous material may be released once the material undergoes structural reorganization between 1000 and 1030 °C. In air atmosphere, this is then combusted relatively fast and a weight loss is observed associated with a structural reorganization which normally should have no associated weight loss.

Structural Model for Kao−PEG. Kao−PEG 3400 (**6**) and Kao−PEG 1000 (**1**) were analyzed for % C and % H. This was performed at high temperature (>1000 °C) to ensure the complete combustion of the nanocomposite. The chemical formula for samples **1** and **6** were calculated on the basis of the calcination weight losses at 1100 °C for the samples. The OEU/DMSO ratio for **1** and **6** were estimated to be approximately 2.8 and 5.9, respectively, from the CP/MAS NMR data, and the calcination weight losses were 29.1 and 29.4%, respectively. Using these data, the formula for sample **1** was estimated to be $Al_2Si_2O_5(OH)_4(-OCH_2CH_2-)_{0.77}(DMSO)_{0.27}$ and, similarly, sample **6** was estimated to be $Al_2Si_2O_5(OH)_4(-OCH_2CH_2-)_{0.99}(DMSO)_{0.17}$. The calculated formula for both samples is consistent with one unit of oxyethylene or DMSO per $Al_2Si_2O_5(OH)_4$ unit. This stoichiometry is similar to that which one obtains for Kao−DMSO where TGA measurements indicate that for every $Al_2Si_2O_5(OH)_4$ unit there is close to 1.0 intercalated DMSO molecule.[27,55] Given the large uncertainty associated with the quantitative CP/MAS NMR data under the conditions of this study, the ratio OEU/DMSO should be taken only as a crude approximation.

On the basis of recently published unit-cell dimensions,[39] the surface area of one interlamellar face of one $Al_4Si_4O_{10}(OH)_8$ unit is calculated to be 23.0 Å^2. The approximate area, based on CPK models, that one side of a flattened oxyethylene unit occupies is about 14 Å^2, so that to a first approximation there remains some void space in the interlamellar regions of kaolinite.

One can expect that the main driving force for the intercalation reaction results from an orientation of the oxygens of the polymer chains such that they hydrogen bond with the hydroxylated aluminate surface of kaolinite. To obtain maximum hydrogen-bonding interaction, the polymer should adopt a conformation such that its oxygens match up with the surface hydroxyl groups

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of the kaolinite. This means that the distances between oxygens in the polymer chain be roughly comparable to the distances between hydroxyl groups in kaolinite. The interhydroxyl distance is about 2.8 Å as determined recently by a Rietveld refinement of the kaolinite structure.[66] It is then expected that a polymer conformation where ethyleneoxy groups repeat every 2.8 Å with the oxygens all facing toward the hydroxyl surface would be particularly favorable. This type of polymer conformation has been described previously in a polyethylene oxide−$HgCl_2$ complex.[67,68] It has been given the designation PEO−$HgCl_2$ type II complex and has been found to be nearly in the form $TG_2T'G_2'$; that is

$$-CH_2-(\underset{167^\circ}{-}O\underset{81^\circ}{-}CH_2\underset{73^\circ}{-}CH_2\underset{-167^\circ}{-}O\underset{-81^\circ}{-}CH_2\underset{-73^\circ}{-}CH_2-)_n-$$

The angle values indicated are those determined in the study of the PEO/$HgCl_2$ complex. These are given here only as an indication of a possible conformation of this Kao−PEO intercalate. With this conformation, the repeat unit per ethyleneoxy group is 2.94 Å, and all the oxygens are lined up on one side of the chain. The tension resulting from the imperfect fit could be relaxed by a certain degree of trans conformations. These conformations are shown by IR (see above) to be present.

Conclusion

It has been shown that it is possible to intercalate PEG into kaolinite by displacing DMSO from Kao−DMSO. These include PEG 1000 and PEG 3400 with the presence of some residual DMSO molecules. XRD showed that the intercalated oxyethylene units were arranged in flattened monolayer arrangements, such that the interlayer expansion was 4.0 Å. Infrared analysis of Kao−PEG 3400, supported the assignment of a trans conformation to at least a portion of the (O−CH_2CH_2−O) groups of the PEG polymer while ^{13}C DD/MAS NMR indicated that the polymer was intercalated intact and was more constrained in the interlamellar spaces of kaolinite than it was in its bulk form.

TGA/DSC analysis revealed that the complete decomposition of the organic component of the oxyethylene-based organokaolinites did not occur until greater than 1000 °C. A small weight loss was observed for the air atmosphere TGA/DSC runs associated with the two exothermic transitions between 990 and 1040 °C. This weight loss was thought to be the result of the release of carbonaceous material trapped within a metakaolinite matrix during the structural reorganization of metakaolinite which takes place above 1000 °C.

This work represents the first example of the direct intercalation of a polymer into the interlamellar surface of kaolinite, and this material may prove to have interesting intercalation properties, since both kaolinite and PEO are known to intercalate various alkali salts. A Kao-PEG salt complex would represent a second-generation nanocomposite material, whereby within the rigid inorganic kaolinite lattices, the intercalated PEG polymer could in turn aid in the complexation of the salt. This material would then be a suitable candidate to act as an anisotropic solid electrolytic material. Materials derived from the intercalation of crown ether into the structure of kaolinite may also fulfill this role.[69]

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