Structural, Thermal, and Electrical Characterization of Layered Nanocomposites Derived from Na–Montmorillonite and Polyethers

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Nanocomposites are prepared from Na–montmorillonite and poly(ethylene oxide) or poly[oxymethylene oligo(oxyethylene)] and characterized by X-ray diffraction, impedance spectroscopy, DTA, and TGA. Two ordered phases with intersheet spacings of 13.6 and 17.7 Å, accommodating either single or double polymer layers within the montmorillonite galleries, are formed with polymer/Na–montmorillonite stoichiometries of 0.15 and 0.30 g/g, respectively. Materials prepared with intermediate stoichiometries yield diffraction profiles characteristic of solid solutions of these two phases. The details of composition and structure provide strong evidence that the polymer conformation is not helical as in crystalline PEO but more closely resembles an adsorbed layer. Sodium salts such as $NaClO_4$ can also be incorporated into the polyether/clay phases. The double-layer phase exhibits a maximum stable ionic conductivity between 10^{-5} and 10^{-6} S cm^{-1} at 520 K.

Introduction

The incorporation of poly(ethylene glycols) or poly(ethylene oxide) by smectite clays has been known for over two decades.[1] More recently, novel materials derived from polyethers and other low-dimensional solids, MS_2,[2–4] V_2O_5,[5] or MPS_3[6] have also been described. In each case, a significant increase in the interlayer spacing is observed, indicating that oligomers or polymers are incorporated within the galleries and that a new phase is produced. The descriptive appellation "nanocomposite" underlines the unusual architecture of single-phase materials which incoporate structural elements as diverse as polymer chains and two-dimensional lattices. We here present results obtained from structural, thermal and electrical studies of nanocomposites prepared with crystalline or amorphous polyethers and Na-montmorillonite.

Experimental Section

Montmorillonite (SWy-1), Source Clays Repository) was dissolved in distilled water and filtered to remove noncolloidal impurities such as quartz and feldspar. Ion exchange to obtain the pure Na-clay was performed by (1) suspension in a 1 M NaCl solution, (2) stirring for a week at 40 °C, (3) repeated washing with distilled water and methanol, and (4) centrifugation. The product obtained was air-dried and heated to 100 °C *in vacuo* for 2 days.

Poly[oxymethylene oligo(oxyethylene)] (PEM), $[OCH_2(OCH_2CH_2)_m]_n$ (m = 8–10), was prepared as described previously[7] and PEO (Aldrich, mw = 100 000) was used as received. Nanocomposites were obtained by the stoichiometric addition of polymer and montmorillonite to CH_3CN or water. In some samples, $NaClO_4$ (EM, reagent grade) was included as a reagent. The colloidal suspension was stirred for 1 day at ambient temperature and then thoroughly dried *in vacuo* at elevated temperature.

Impedance measurements were collected from 350 to 710 K on cylindrical pellets using a Solartron 1260 impedance analyzer. The $^1/_2$-in.-diameter pellets were formed with a hydraulic press using 300 MPa of pressure. A hermetically-sealed cell containing an inert atmosphere was employed to exclude air from the sample during measurements. Data were obtained by applying a 100-mV sinusoidal potential in a frequency range of 10 MHz to 0.3 Hz. The impedance response typically showed a single arc in the Nyquist plot, and the sample bulk conductivity was determined from the low-frequency touchdown and the known cell geometry.

X-ray data between 2 and 60° 2θ were collected at 0.2°/min on a Siemens D5000 diffractometer using Cu Kα radiation. DTA and TGA data were simultaneously obtained from 20 and 450 °C using a Netzsch, Inc. STA 419C scanning calorimeter. Samples (approximately 10 mg) were loaded into alumina crucibles in a dry atmosphere and the sample chamber was purged with dry N_2 prior to heating at 10 °C/min.

Results and Discussion

X-ray diffraction data of the products obtained show that the montmorillonite galleries are expanded from the 9.6-Å basal plane spacing of anhydrous Na-montmorillonite, indicating that the polymer and clay form a nanocomposite. The diffraction pattern displayed in Figure 1 is representative of those observed for the double-layer phase (vide infra) and indicates a regular lattice spacing of 17.7 Å, an expansion of the clay galleries by 8.1 Å.

The relation between stoichiometry and intersheet spacing is illustrated in Figure 2. The lattice spacings are obtained from the (001) peak only as higher-order reflections are not observed at all stoichiometries. At polymer/montmorillonite ratios of 0.15 and 0.30 g/g, single-phase products exhibit relatively sharp diffraction peaks and several higher-order (00*l*) reflections. Peak widths indicate ordered domains of 150 Å (approximately 10 layers) along the stacking direction for these products. Least-squares fits to these data yield lattice spacings of 13.73(4) Å and

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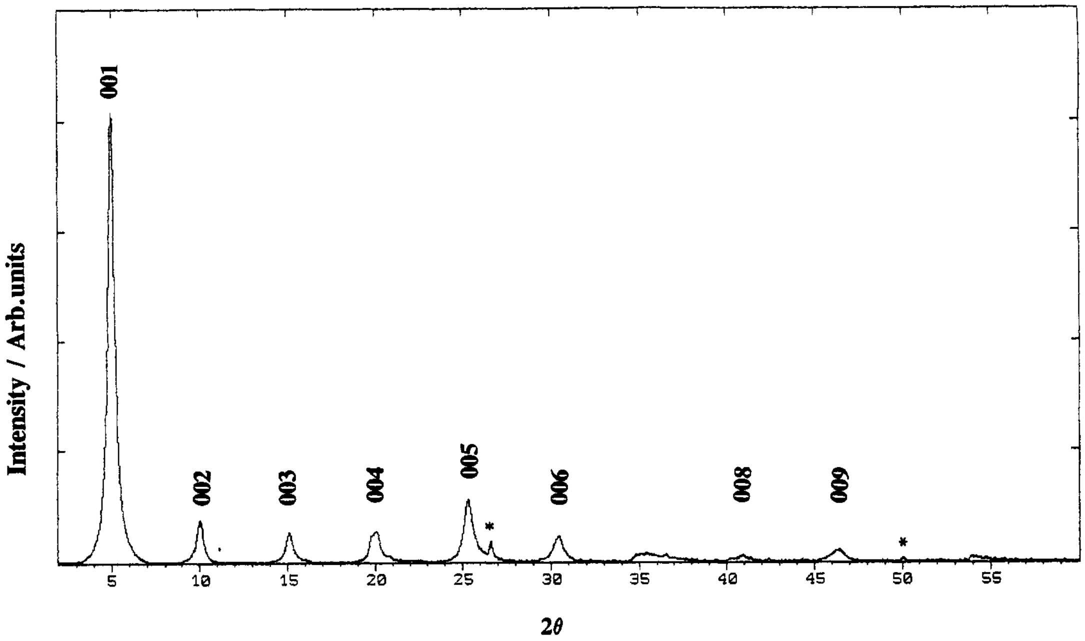


Figure 1. X-ray powder diffraction data obtained on PEO/Na–montmorillonite nanocomposite (0.30 g/g).

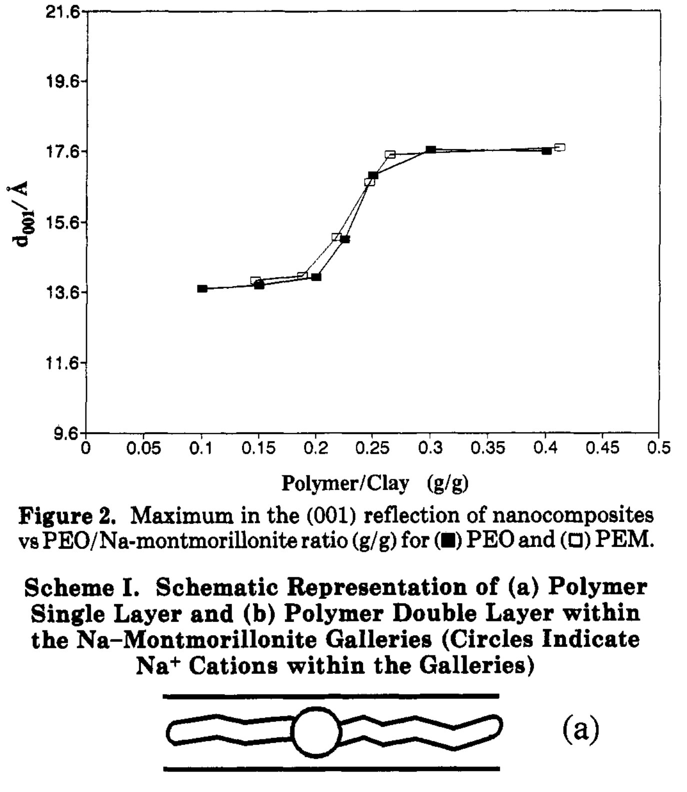
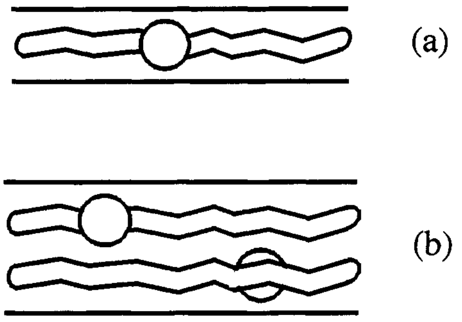


Figure 2. Maximum in the (001) reflection of nanocomposites vs PEO/Na-montmorillonite ratio (g/g) for (■) PEO and (□) PEM.

Scheme I. Schematic Representation of (a) Polymer Single Layer and (b) Polymer Double Layer within the Na–Montmorillonite Galleries (Circles Indicate Na$^+$ Cations within the Galleries)



17.65(4) Å. At stoichiometries richer in polymer than 0.30 g/g an admixture of the 17.7-Å phase and unreacted, crystalline PEO is obtained. The incorporation of polymer by the method employed is therefore limited to 0.30 g/g. No significant differences are observed between reactions of montmorillonite with PEO and PEM, although a crystalline polymer phase is not observed at stoichiometries above 0.30 g of PEM/g of montmorillonite (PEM and its salt complexes are amorphous at ambient temperature[8]).

The polymer conformation in these nanocomposites raises significant fundamental issues and will also govern important properties such as ion transport and mechanical strength. Two models which may be considered are a helical conformation similar to that observed in crystalline PEO or an adsorbed polymer layer on the clay surfaces. Recent reports cite IR and NMR spectroscopic evidence to support the helical polymer conformation for these materials.[9–11] X-ray data do not provide usable information on the polymer conformation within the galleries.

The formation of a 13.6-Å phase involves a gallery expansion of 4.0 Å, which sterically limits the polymer conformation to approximate a single adsorbed layer between the clay surfaces. The 17.7-Å phase displays twice the gallery expansion and also twice the polymer content of 13.6-Å phase and therefore is entirely consistent with the incorporation of two such polymer layers. This architecture can be derived from the coalescence of colloidal clay sheets with single adsorbed polymer layers on both surfaces. Although a helical polymer conformation cannot be excluded by steric interactions within an 8-Å gallery, this would require very different polymer morphologies for the two ordered phases obtained. The similarity of complexes prepared from PEO and PEM is also significant in that the helical conformation is disrupted in the PEM copolymer by the presence of irregularly situated methylene linkages in the polymer backbone.

The 4- and 8-Å gallery expansions are also consistent with those obtained when oligomeric (PEG) or even small-molecule ethers such as ethylene glycol are incorporated into montmorillonite. The similarity in lattice expansion

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[9] Ruiz-Hitzky, E.; Aranda, P. *Adv. Mater.* **1990**, *2*, 545.

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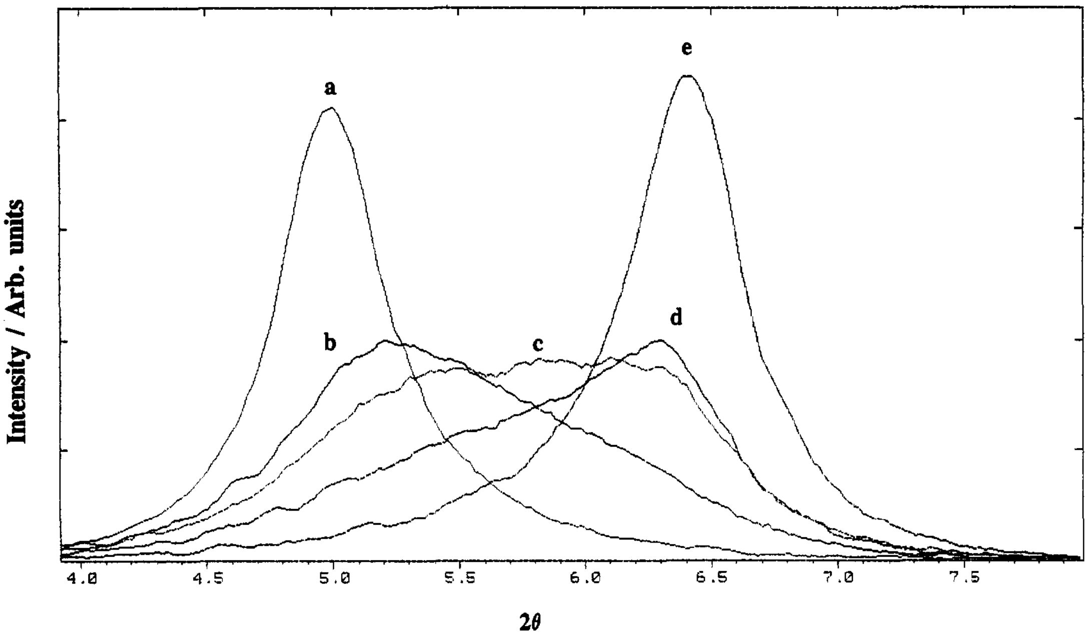

Figure 3. Profiles of (001) peaks for PEO/Na-montmorillonite nanocomposites; (a) 0.30 g of polymer/g of Na-montmorillonite, (b) 0.25 g/g, (c) 0.225 g/g, (d) 0.20 g/g, and (e) 0.15 g/g.

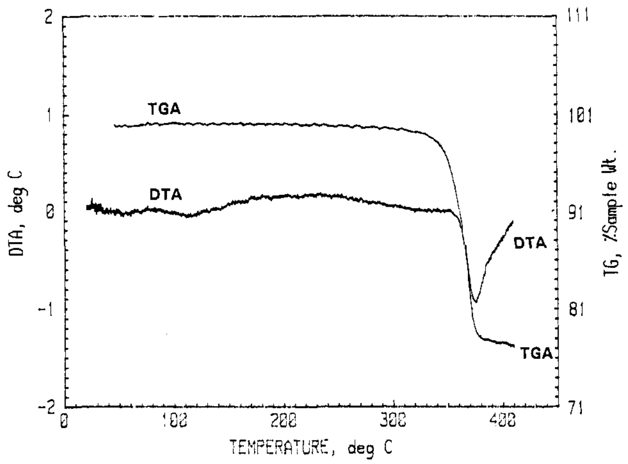

Figure 4. DTA and TGA profiles for PEO/Na-montmorillonite (0.30 g/g).

is best explained by each of these species adopting an adsorbed-layer conformation within the expanded galleries.

For these reasons the two phases observed are best described by the incorporation of single and double polymer layers within the montmorillonite gallery (see Scheme I). The density of pellets pressed from the double-layer phase (1.88 g/cm^3) indicates that the polymer layers are far less efficiently packed (1.88 g/cm^3 × 0.3/1.3 × 17.7/9.6 = 0.8 g/cm^3) than in the native PEO (1.2 g/cm^3).

Nanocomposites prepared with stoichiometries between 0.15 and 0.30 g/g do not produce a sharp (001) peak but show highly asymmetric peak profiles (Figure 3). When physical mixtures of the single-layer (0.15 g/g) and double-layer (0.30 g/g) phase are ground together at ambient temperature, two sharp peaks corresponding to the discreet phases are obtained, but a diffraction profile similar to those shown in Figure 3 appears upon annealing this mixture at 100 °C for 2 days. These patterns therefore appear to correspond to homogenous nanocomposites of intermediate composition (0.15–0.30 g/g) which are a solid solution of the single- and double-layer phases, that is, they contain a homogeneous distribution of these expanded galleries rather than a uniform basal plane spacing. Preliminary results from computer modeling indicate that the X-ray profiles of this interphase region are closely simulated by nanocomposite structures with ordered domains of approximately 100 Å containing both single and double polymer layers. This model controls the abundance of single and double layers to reflect the overall stoichiometry but allows the two types of layers to be randomly distributed. Details of these results will be published elsewhere.[12]

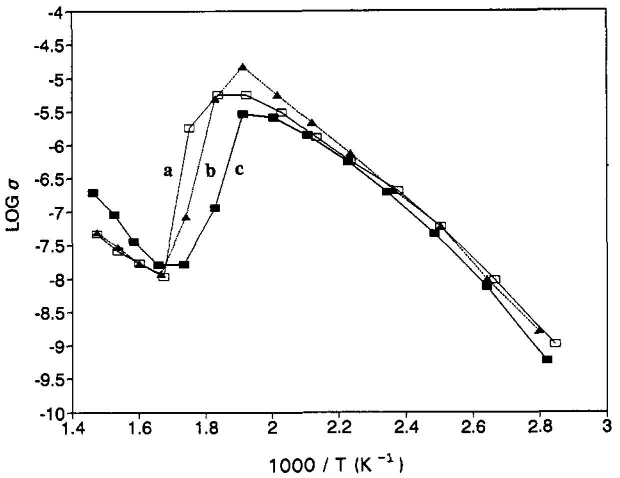

Figure 5. Arrhenius plots for (a) PEM/Na-montmorillonite nanocomposite (0.30 g/g), (b) crystalline PEO/Na-montmorillonite nanocomposite (0.30 g/g), (c) PEO/Na-montmorillonite nanocomposite with $NaClO_4$ (0.30 g of polymer/0.10 g of salt/1.0 g of Na-montmorillonite).

TGA and DTA data (Figure 4) indicate a single, irreversible, endothermic event at 360 °C corresponding to polymer decomposition. Although decomposition products were not identified, samples maintained briefly above this temperature are discolored to brown or black, which is consistent with the expected carbonization of the organic component. The total weight loss recorded by

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[12] Wu, J.; Lerner, M., to be submitted for publication.

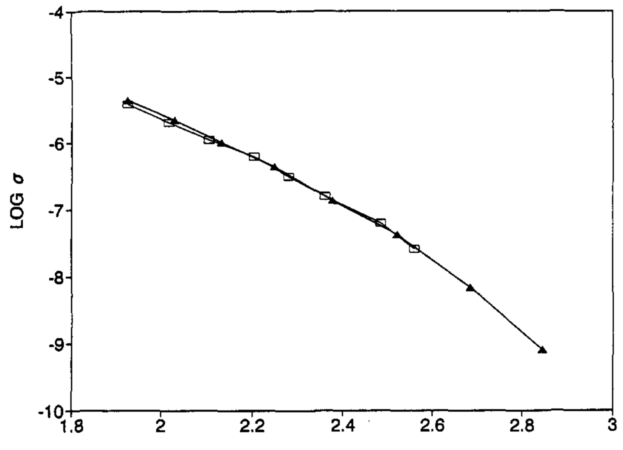

Figure 6. Arrhenius plot for PEO/Na-montmorillonite nanocomposite (0.30 g/g). Data were recorded for sample heating from 350 to 520 K (△) and subsequent cooling (□). Time between readings is approximately 1 h.

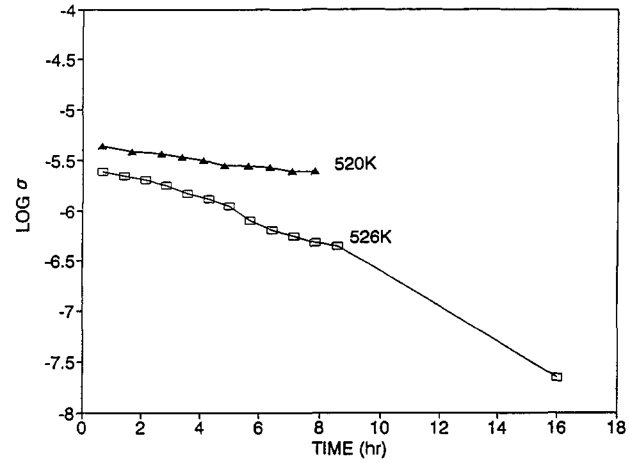

Figure 7. Time dependence of ionic conductivity for PEO/Na–montmorillonite nanocomposite (0.30 g/g) at 520 and 526 K.

400 °C is 23% and corresponds to the initial stoichiometry of polymer in the nanocomposite. The melting transition of crystalline PEO, which provides a strong endotherm at 67 °C, is absent in these profiles. The lack of either glass or melting transitions indicates the absence of a discrete polymer phase, and again demonstrates that these two dimensional polymer layers are not structurally similar to the native polymers.

Arrhenius plots for selected nanocomposites (Figure 5) indicate a increase of several orders of magnitude in the conductivity relative to the native anhydrous Na–montmorillonite. A peak in the Arrhenius plot for several samples is observed at 250 °C. An increase in conductivity observed above 320 °C is likely an artefact arising from sample decomposition. The highest values obtained, near 10^{-5} S cm^{-1}, are less than those reported previously for PEO–salt complexes (which exhibit maximum conductivities of 10^{-3}–10^{-4} S cm^{-1} [13]), and occur at higher temperatures. It should be noted that the conductivity may be anisotropic in these low-dimensional materials, and observed values may reflect dimensional averaging. The ionic conductivity is assumed to arise from an enhanced mobility for Na^+ within the polymer-containing galleries. One possible mechanism for enhanced Na^+ mobility is a decrease in interactions with the negatively-charged clay surface resulting from solvation by the polymer layers.

The maxima in the conductivity plots consistently occur below the decomposition temperatures observed in thermal experiments. Conductivity plots do not display hysteresis below 247 °C, and the conductivity is fairly constant for several hours at this temperature (Figures 6 and 7). The same sample, however, displays a significant loss in conductivity when held at temperature (526 K) just above the peak maximum in the Arrhenius plot. This conductivity decrease occurs well below the decomposition temperature obtained by DTA and TGA. These observations point to a change in polymer conformation at 520 K.

The addition of $NaClO_4$ to the polymer/Na–montmorillonite nanocomposites in concentrations as high as 0.33 g of salt/g polymer (0.125 $NaClO_4$ for each monomer repeat unit) results in similar diffraction profiles without evidence of new crystalline phases, thus the salt appears to be incorporated into the nanocomposites. As can be seen in Figure 5, the addition of $NaClO_4$ results in a conductivity decrease at lower temperatures. The structural and electrical effects of salt type and concentration are being investigated.

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