

Structure and thermal/mechanical properties of poly(ethylene oxide)–clay mineral blends

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(Received 25 September 1996; revised 13 December 1996)

Montmorillonite was organically modified with distearyldimethyl-ammonium chloride. This organically modified clay mineral and poly(ethylene oxide), (PEO), were solvent-cast blended with chloroform, and the structure and properties of the resulting blends were investigated. The effects of the clay mineral content on the isothermal crystallization of PEO are discussed. From small and wide angle X-ray scattering measurements of the blends, it was found that the clay mineral forms a remarkable geometrical structure in the blend and induces a preferred orientation of PEO crystallites. The effects of the clay mineral content on dynamic behaviour were also studied. © 1997 Elsevier Science Ltd.

(Keywords: poly(ethylene oxide); montmorillonite; intercalation)

INTRODUCTION

Inorganic particles are widely used as reinforcement materials for polymers. Among these inorganic materials, special attention has been paid to clay minerals in the field of nanocomposites because of its small particle size and intercalation properties¹. Since clay minerals have an organophobic nature, they should be organically modified to be well blended with hydrophobic polymers. Polymers have been intercalated into the layered silicates of the clay mineral by mainly using two approaches: insertion of a suitable monomer and subsequent polymerization, and direct insertion of polymer chains from solution or the melt. Nylon 6–clay hybrids (NCH) have been developed by using the first method². It was reported that the silicate layers in NCH were individually well dispersed in the nylon 6 matrix, and that the hybrid showed good physical properties, e.g. high modulus, high distortion temperature³, and good water barrier properties⁴. In the previous work^{5,6}, poly(*l*-lactide) (PLLA)–clay mineral and poly(ϵ -caprolactone) (PCL)–clay mineral blends were produced by using polymer intercalation from solution into layered smectite-type clay mineral known as montmorillonite (MON). We investigated the structure and thermal/mechanical properties of the blends, and found that the clay mineral has a notable structure in these blends. Our interest in the present study is to investigate whether such geometry is observed in solvent-cast poly(ethylene oxide) (PEO)–clay mineral blends.

PEO is a non-charged polymer that can act as a solid solvent for metal salts. Therefore, particular attention has been given to the polymer because it can be used as electrolyte material for solid-state batteries, sensors, etc. In order to improve the electrochemical performance of the polymer electrolytes, the addition of inorganic fillers, especially montmorillonite, has been studied^{7,8}.

The purpose of this study was to synthesize a PEO–clay mineral composite using polymer intercalation from solution. Furthermore, we studied the structure and the thermal/mechanical properties of the PEO–clay mineral blend. Although this study is not directly related to the electrolytes, some information on the interaction between the organically modified clay mineral and PEO would be obtained.

EXPERIMENTAL

Materials

Montmorillonite 'Kunipia F', (MON), was supplied by Kunimine, Tokyo. This clay mineral has exchangeable sodium ions, and a cation exchange capacity of *ca* 120 meq per 100 g. PEO, with average $M_v = 300\,000$ was purchased from Aldrich, Tokyo.

Preparation of organophilic clay mineral

MON (1 g) and 50 ml of distilled water at 80°C were placed in a 100-ml beaker, and 1 g of distearyldimethyl-ammonium chloride was added to the solution. The mixture was stirred vigorously for 1 h, and then it was filtered and washed three times with 100 ml of hot water to remove NaCl. After being washed with ethanol (50 ml) to remove any excess of ammonium salt, the product was freeze-dried, and kept in a vacuum oven at room temperature for 24 h. The resulting organically modified montmorillonite (OMON) dispersed well in chloroform, although neat MON did not do so. Therefore, this organic modification was found to be effective.

Preparation of PEO–clay mineral blends

Specified amounts of well-dried OMON and powder PEO were placed in a petri dish, hot chloroform was

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added and then the solution was kept at 50°C. After chloroform was vaporized, homogeneous films, *ca* 0.1 mm in thickness, were obtained. The weight percentage of OMON in the blend will be represented by *Y* in PEO Y ; e.g. PEO10 indicates a PEO-clay mineral blend containing 10 wt% OMON. OMON will be also referred to as the clay mineral.

Characterization of the blends

Wide angle X-ray scattering (WAXS) photographs were taken of the PEO-clay blends with a flat camera having a pinhole slit, and with a JEOL (DX-GE-E) apparatus. Small angle X-ray scattering (SAXS) photographs were also taken with a JEOL (JDX-8750) operated at 420 kV and 200 mA.

Thermal behaviour of the blends was measured on a Perkin Elmer DSC-7 at a heating rate of 10°C min⁻¹. Melting point, T_m , and heat of fusion, ΔH_m , were evaluated from a maximum position of the endothermic peak, and its area on the differential scanning calorimetry (d.s.c.) curves, respectively. Isothermal crystallization of the blends and pure PEO was carried out under a nitrogen atmosphere with a Perkin Elmer DSC-7 apparatus. Neat PEO and the clay blends (5.0 ± 0.3 mg) encapsulated in aluminium pans were heated to 105°C at a rate of 20°C min⁻¹, held at this temperature for 5 min to destroy all the crystallites, and cooled down to appropriate crystallization temperatures ($T_i = 52$ and 53°C), at 200°C min⁻¹ cooling rate.

Dynamic mechanical analyses (d.m.a.) of the blends, well-dried with P₂O₅, were performed with a Rheometrics Scientific RSA II Viscoelastic Analyser. Temperature scans (from -130 to 55°C) at 1 Hz frequency were carried out with a heating rate of 2°C min⁻¹.

RESULTS AND DISCUSSION

Thermal behaviour

The effect of the clay mineral content on T_m and ΔH_m is shown in Figure 1. A straight solid line was drawn through the values of ΔH_m at PEO0 and PEO100, where the value for ΔH_m at PEO100 was equal to zero. It can be seen that T_m decreases slightly with increasing the clay mineral content (ϕ_{mon}). This result implies that small PEO crystallites are formed in the presence of the clay

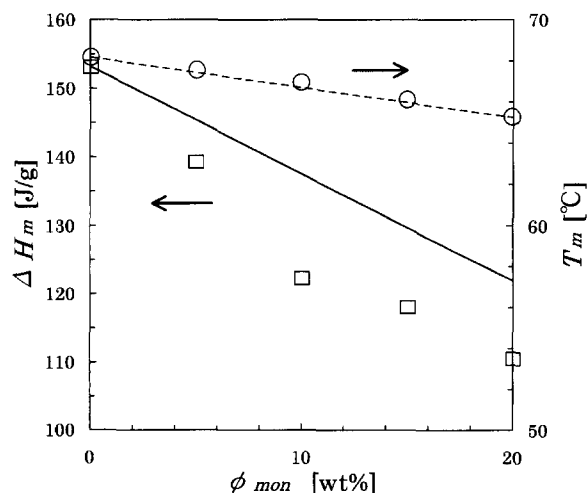


Figure 1 Effect of the clay content on the melting temperature, T_m , and the heat of fusion, ΔH_m , of the blends

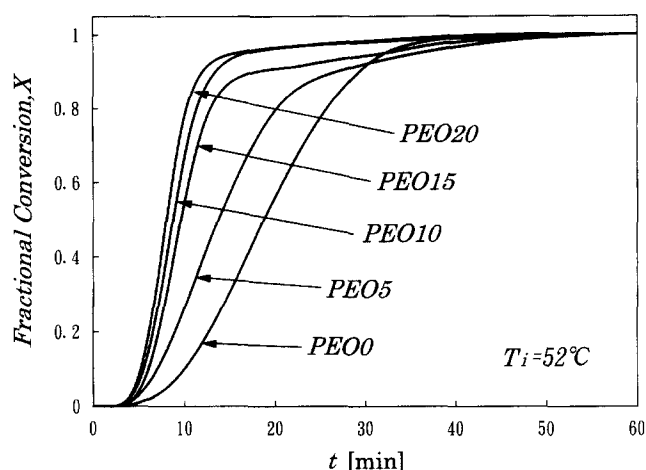


Figure 2 Effect of the clay content on the isothermal crystallization of the blends; the crystallization temperature $T_i = 52^\circ\text{C}$

mineral. It can be also seen that the experimental ΔH_m values are plotted almost under the straight line. This result means that the total crystallinity of PEO is influenced by the presence of the clay mineral. In other words, this result may imply that intercalation of PEO molecules into the silicate layers takes place to some extent. From isothermal crystallization experiments, the fractional crystallinity conversion, X , was calculated as the ratio of the area under the exotherm at time t to the total area. There was no large difference between the X vs t curves measured at $T_i = 52^\circ\text{C}$ and those measured at $T_i = 53^\circ\text{C}$. That is, a similar trend could be seen in the effect of ϕ_{mon} on the crystallization kinetics between two temperatures. Figure 2 shows a typical example of the relationship between X and t . Since the crystallization rate increases with increasing ϕ_{mon} , the clay mineral seems to act as a good nucleating agent.

Structure of PEO-clay mineral blends

An X-ray beam was incident on the blend films in through and edge directions and WAXS and SAXS photographs were taken; the through (thru) and edge directions were perpendicular and parallel to the film surface, respectively. Since the thru-view photographs did not show characteristic patterns, we will not show the view photographs in the following discussion. That is, only the edge-view patterns will be discussed mainly. Figures 3 and 4 show the WAXS and SAXS photographs for the blends, respectively. In these photographs, the equator and the meridian are parallel to the film thickness direction and the film surface, respectively. In the WAXS patterns for the blends, strong and anisotropic intensity distribution can be seen around the beam stopper. Furthermore, a pair of intensity peaks, which corresponds to the (001) reflection of MON⁹ can be seen on the equator near the beam stopper; naturally, the neat PEO does not exhibit the (001) reflection. By using Bragg's equation, we calculated the spacing of the reflection for the blends. The value was found to be *ca* 1.8 nm, regardless of ϕ_{mon} . However, the thru-view pattern of the blends did not show the (001) reflection. Since the intensity maxima caused by the periodical silicate layers (1.8 nm) can be clearly seen only on the equator for the edge-view pattern of the blends, the surface planes of silicate layers seem to be almost parallel

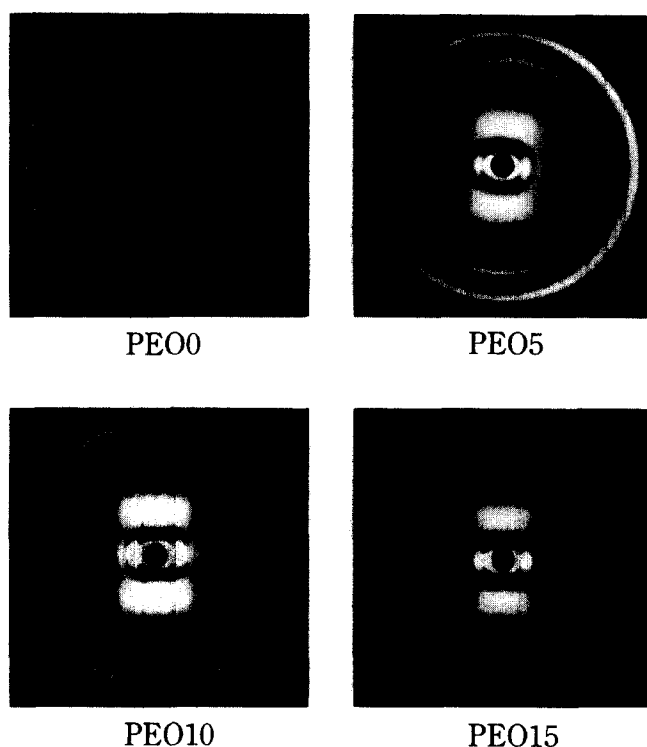


Figure 3 Edge-view WAXS photographs of the blends

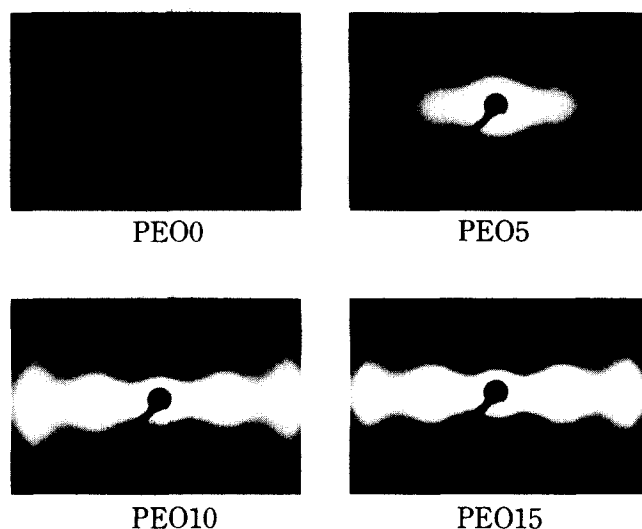


Figure 4 Edge-view SAXS photographs of the blends

to the film surface. As will be explained later, the clay mineral exists in the form of a tactoid that consists of some stacked silicate layers. In the WAXS photographs of the blends, we can also see a pair of arc-like reflection spots on the meridian and four reflection spots off the meridian. These spots are derived from crystalline PEO and become clear with increasing ϕ_{mon} . A similar WAXS pattern was obtained from the sedimented mat of solution crystallized PEO single crystals when the X-ray beam was parallel to the mat plane¹⁰. On the other hand, regardless of ϕ_{mon} , the thru-view patterns showed two Debye-Scherrer rings, suggesting that the molecular axes of the PEO crystallites were randomly oriented on the film plane. In addition, the neat PEO0 does not exhibit such preferred orientation. By taking account of

the WAXS pattern of the PEO mat and the results obtained here, we deduce that the chain direction of the PEO crystallites is perpendicular to the tactoid surface. The cast temperature used (50°C) was so high that the preferred orientation of PEO crystallites would be induced under the influence of the clay mineral; in fact, the blend cast at 10°C did not show such preferred orientation. Appearance of preferred orientation means that there is an interaction between the PEO crystallites and the clay mineral. Furthermore, since there exists an interaction between the crystalline PEO and the clay mineral, the PEO crystallites are probably formed on the surface of the tactoid.

Now, let us discuss the edge-view SAXS photograph of the blends except for PEO0. The SAXS patterns exhibit two pairs of intensity maxima on the equator. The peaks become clear with increasing ϕ_{mon} . The peaks were numbered in series from the peak near the beam stopper; the first and second peaks indicate a low and a high angle reflection, respectively. The intensity distribution in the azimuthal direction for the second peak is broader than that for the first peak, and their spacings calculated by using Bragg's relation are almost integral multiples of each other. Consequently, these two peaks would arise from the same periodic structural source. The long spacing calculated from these maxima was found to be *ca* 7.0 nm, regardless of ϕ_{mon} . As proved in the previous papers^{5,6}, these peaks were derived from the existence of the clay mineral because the peaks remained on the equator when the PCL-clay mineral and PLLA-clay mineral blends were highly drawn parallel to the meridian. Therefore, the appearance of these reflections implies that the tactoids form a super-lattice with a long period in the thickness direction of the film; the surfaces of the tactoids are almost parallel to the film surface. Of course, such periodicity was not seen in the thru-view patterns. The crystalline PEO lamellae are probably inserted between the parallel tactoids because there is an interaction between PEO crystallites and the clay mineral, as described previously. By taking account of the long period of the tactoids (7.0 nm) and the spacing of the clay mineral layers (1.8 nm), we calculated the maximum number of silicate monolayers forming the tactoids which was found to be approximately four. The tactoid should consist of some periodic silicate layers to exhibit the (001) reflection of the clay mineral. Therefore, the maximum number of silicate layers in the tactoids is so small that the PEO lamellae between the tactoids seem to have a small size in the direction of the film thickness. Apparently, the size of the tactoids in the thickness direction is smaller than 7.0 nm. There is an alternative explanation for the SAXS photographs of PEO-OMON blends. That is, the long period of 7.0 nm is a basal spacing of intercalated compound of OMON and PEO, and the spacing of 1.8 nm is derived from the clay mineral tactoids that do not form the compounds. In this work, we cannot find definite evidence for a reasonable choice between these proposals. Anyway, it is found that the structure of the clay mineral seen in an aliphatic polyether (PEO) is almost similar to that seen in aliphatic polyesters such as PCL and PLLA.

Dynamic mechanical properties of PEO-clay mineral blends

The temperature dependence of the storage E' , loss E'' tensile modulus, and $\tan \delta (= E''/E')$ of the blends was

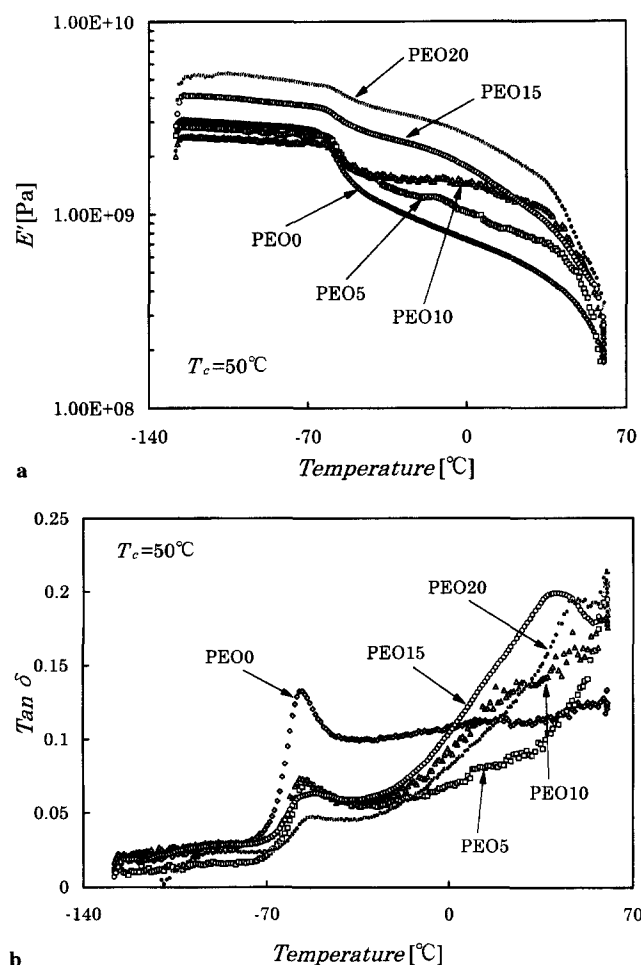


Figure 5 D.m.a. curves of the blends cast at 50°C. (a) E' curves; (b) $\tan \delta$ curves

investigated; $\tan \delta$ is a measure of the ratio of energy lost to energy stored per cycle of deformation. Figure 5 shows the experimental results obtained from the samples cast at $T_c = 50^\circ\text{C}$. Regardless of the clay mineral content, E' decreases with increasing temperature, and the glass transition can be seen at *ca* -65°C ; this temperature will be referred to as T'_g . Roughly speaking, E' at a given temperature above T'_g increases with increasing the clay mineral content (ϕ_{mon}). Furthermore, the change in E' at T'_g becomes small with increasing ϕ_{mon} . These results imply that the clay mineral restricts the segmental motions of the PEO amorphous chains. The $\tan \delta$ curves of the blends show a large maximum at *ca* -60°C , regardless of the clay mineral content. This temperature will be referred to as T_g . Although the value of T_g is not largely influenced by ϕ_{mon} , the value of $\tan \delta$ at T_g apparently decreases and the peak becomes broad with increasing ϕ_{mon} . This suggests that the clay mineral introduces many kinds of relaxation modes of PEO chains. Its value is noted to be markedly decreased by the addition of the small amount of the clay mineral. This would mean that the small tactoids were dispersed well in the blends.

Above T_g , the values for $\tan \delta$ of the sample containing the clay mineral increase with increasing temperature. This suggests that a large amount of energy is dispersed

in the blends during the tests. The dispersion would be originated from the interfacial friction between the clay mineral and PEO molecules. Because T_g is not very influenced by ϕ_{mon} , interaction between the clay mineral and PEO molecules does not seem to be very strong. From this result and discussion in the previous section of the thermal behaviour of the blends, intercalation of some polymer chains into narrow silicate layers does not seem to take place completely in the PEO-OMON blends. If such intercalation occurred completely, T_g for the matrix polymer would increase, and become absent because the polymer chains were confined to the two-dimensional galleries of the layered clay mineral¹¹.

CONCLUSION

The structure and mechanical properties of PEO-clay mineral blends have been investigated. The following conclusions are deduced from the results and discussion.

1. The organically modified clay mineral accelerates the crystallization of PEO.
2. Preferred orientation of PEO is induced by the presence of the clay mineral. The chain direction of PEO crystallites is perpendicular to the surface of the clay mineral tactoids and the silicate layers are parallel to the surface of blend films.
3. The clay mineral in the blends shows two reflections, on the equator of SAXS patterns. From this result, we propose alternative structures for the clay mineral in the blends; (i) clay minerals would exist in the form of a tactoid in the PEO-clay mineral blend, and the tactoids are stacked in the thickness direction of the film with insertion of PEO lamellae between the parallel tactoids, (ii) clay minerals exist in the form of two structural types: the intercalated compound of OMON and PEO, and the tactoids of OMON that do not form the compounds.
4. The glass transition temperature is not influenced by the clay mineral content. However, the value of $\tan \delta$ at this temperature decreases with increasing clay mineral content.

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