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Polymer-layered silicate nanocomposites. 1. A study of poly(ethylene oxide)/Na$^+$-montmorillonite nanocomposites as polyelectrolytes and polyethylene-block-poly(ethylene glycol) copolymer/Na$^+$-montmorillonite nanocomposites as fillers for reinforcement of polyethylene

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Abstract

Poly(ethylene oxide) PEO/Na$^+$-montmorillonite and polyethylene–poly(ethylene glycol) (PE–PEG) diblock copolymer/Na$^+$-montmorillonite nanocomposites have been prepared by melt intercalation method. The effect of thermal treatment on the amount of PEO and PE–PEG diblock copolymer intercalated into layers of Na$^+$-montmorillonite and on ionic conductivity of PEO/Na$^+$-MMT nanocomposites have been evaluated. It was found that PEO can be intercalated into the layers of Na$^+$-MMT by simple mechanical blending and part of PE in PE–PEG diblock copolymers was also intercalated into the layers of Na$^+$-MMT. The intercalated amount increases with thermal treatment time, which improves the ionic conductivity of the PEO/Na$^+$-MMT nanocomposites. PE–PEG diblock copolymer/Na$^+$-MMT hybrids can be considered as a new kind of fillers for the reinforcement of polyethylene. By only adding a small amount (1–15% by weight) of these fillers, tensile strength of polyethylene was improved significantly. This research provides valuable information for the development of new kinds of fillers for polymer reinforcement, and polyelectrolytes.

Keywords: Na$^+$-montmorillonite; Melt intercalation; Nanocomposites

1. Introduction

In recent years, the study of organic–inorganic nanocomposites has become a very important field since these materials exhibit unexpected synergistical properties derived from two components [1–12]. One of the most promising composites systems would be hybrids based on organic polymers and inorganic clay minerals consisting of layered silicates.

Various polymer/clay nanocomposites (or hybrids) were reported, such as nylon 6/clay hybrid [12,13], epoxy polymer/clay nanocomposite [14,15], acrylic polymer/clay [16] hybrid, and polystyrene/clay [17,18] nanocomposite. The polymer-layered silicate nanocomposites have several advantages [19]. (1) They are lighter in weight compared to conventionally filled polymers because high degree of stiffness and strength are realized with far less high density inorganic materials. (2) Their mechanical properties are potentially superior to fiber-reinforced polymers because reinforcement from the inorganic layers will occur in two rather than in one dimension without special efforts to laminate the composites. (3) They exhibit outstanding diffuse barrier properties without requiring a multi-polymer-layered design, allowing for recycling. An intercalated nanocomposite is normally inter-layered by only a few molecular layers of polymer and the properties of the composite typically resemble those of the ceramic host. The most commonly used layered silicates are the smectite group of clay minerals such as montmorillonite (MMT). The layered structure of MMT consists of two silica tetrahedral sheets and an aluminum octahedral sheet. Stacking of the layers of ca. 1 nm thickness and about 100 nm width and length by weak dipolar force leads to interlayer galleries. The galleries are normally occupied by cations

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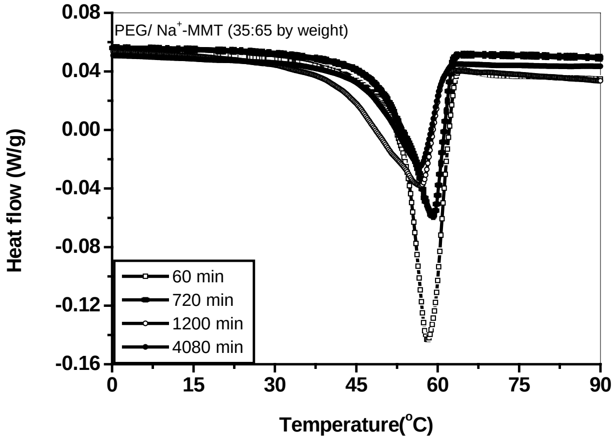

Fig. 1. Heat flow vs. temperature signals for PEO/Na$^+$-MMT (35:65 by weight) nanocomposites with different annealing times.

such as Na$^+$, Ca^{2+} and Mg^{2+} and easily to form organophilic clay by the introduction of alkylammonium ions or other organic cation exchange reaction in water.

In the paper, the idea whether poly(ethylene oxide) based layered silicate nanocomposites can be considered as polyelectrolytes, and whether polymer/layered silicate nanocomposites can be considered as new kind of the fillers for reinforcement of polymers, was developed. Poly(ethylene oxide) (PEO)/Na$^+$-montmorillonite and polyethylene–poly(ethylene glycol) (PE–PEG) diblock copolymer/Na$^+$-montmorillonite nanocomposites were prepared by melt intercalation method. The effect of thermal treatment on the amount of PEO and PE–PEG diblock copolymer intercalated into layers of Na$^+$-montmorillonite and on ionic conductivity of PEO/Na$^+$-MMT nanocomposites were evaluated. PE–PEG diblock copolymer/Na$^+$-MMT composites as a new kind of fillers for reinforcement of polyethylene was developed.

2. Experimental

2.1. Materials

Sodium montmorillonite (Na$^+$-MMT) with a cation exchange capacity of 90 mequiv./100 g was provided kindly by Zhangjiakou Clay Mineral Corporation. Prior to use it was washed by saturated NaCl solution and dried in a vacuum oven at 85°C for more than one week. PEO (M_n: 20,000, Aldrich), two kinds of PE–PEG diblock copolymers ($M_n(1)$ is 1400 and content of ethylene oxide is 50% by weight, and $M_n(2)$ is 875 and content of ethylene oxide is 20% by weight, Aldrich) were used as received.

2.2. Melt intercalation of PEO and PE–PEG diblock copolymers into the layers of Na$^+$-MMT

Melt intercalation method was used for preparation of PEO/Na$^+$-MMT and PE–PEG diblock copolymer/Na$^+$-MMT nanocomposites. Mechanical blending of Na$^+$-MMT with PEO and with PE–PEG was carried out using a Haake Rheochord. A total charge of 60 g was used. The rotor speed was 60 rpm and the temperature was 100°C for PEO/Na$^+$-MMT blend and 135°C for PE–PEG diblock copolymer/Na$^+$-MMT blend, respectively. For the blending of Na$^+$-MMT with PEO and with PE–PEG, the PEO or PE–PEG diblock copolymer was added first, and masticated for 30 s. The Na$^+$-MMT was then added and blended for a further 12 min before removal of the blend from the mixing chamber while still hot.

Further thermal treatment for PEO/Na$^+$-MMT and PE–PEG diblock copolymer/Na$^+$-MMT nanocomposites was carried out at 80°C in vacuum oven.

Polyethylene blended with PE–PEG/MMT Nanocomposites was prepared by using two-roll blender at 140°C.

2.3. Instrumentation

Thermal analysis. A TA Instruments M-TDSC 2920 calorimeter was used. An oscillation amplitude of ±0.2°C, an oscillation period of 60 s and a heating rate of 2°C/min were used. The calorimeter was calibrated with a standard indium sample.

Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA 2950 under a nitrogen atmosphere. A heating rate of 10°C/min was used.

Ionic conductivity. Complex impedances were measured in air atmosphere and at room temperature by a LF Impedance Analyzer controlled by a computer. The graphite was used as the electrode material. The ionic conductivity was calculated from the complex impedance.

Mechanical property. Tensile strength was measured using an Instron Materials Tester (UK) at room temperature.

3. Results and discussion

3.1. Effect of thermal treatment on the amount of PEO intercalated into the layers of Na$^+$-MMT

Heat flow vs. temperature signals for PEO/Na$^+$-MMT (35:65 by weight) nanocomposites with different annealing times annealed at 80°C are shown in Fig. 1. It can be seen that the endotherm-peak area of PEO melt decreased with increasing annealing time. The endotherm-peak area of PEO melt against time is shown in Table 1. This indicates that the crystallinity of PEO decreased. With increasing annealing time, the amount of PEO intercalated into the layers of Na$^+$-MMT increases. After 68 h, the endotherm-peak area becomes very small, showing that most PEO were intercalated into the layers of Na$^+$-MMT. The melt temperature shifts to lower temperature. This shows that crystalline structure of PEO was affected.

Figs. 2–4 show heat flow vs. temperature signals for PEO/Na$^+$-MMT nanocomposites with different composition ratios. It was confirmed again that the endotherm-peak area

Table 1
Endotherm-peak area of PEO melt against time

Annealing time (min)	ΔH (peak area) (J g^{-1})	Melting temperature (°C)
60	29	58
720	19	59
1200	16	56
4080	13	56

Table 2
Endotherm-peak area of PE melt against time

Annealing time (min)	ΔH (peak area) (J g^{-1})	Melting temperature (°C)
As prepared	68	103
1980	59	103
4080	54	103

of PEO melt decreased with the increase of annealing time and the melt temperature also shifts to lower temperature.

In lower content of PEO (Fig. 4), the endotherm-peak area of PEO melt almost disappeared after annealing for 68 h, which confirmed again that most of PEO was intercalated into the layers of Na$^+$-MMT.

From the above study, it can be concluded that thermal treatment has a big influence on the amount of polymers intercalated into the layers of Na$^+$-MMT. With increasing time of thermal treatment, the amount of PEO intercalated into the layers of Na$^+$-MMT increased.

However, a question arises: whether the blending of polymer and layered clay is uniform. Fig. 5 shows weight loss vs. temperature for three PEO/Na$^+$-MMT (15:85 by weight) samples. The three samples were chosen randomly. The amount of PEO in the three samples is nearly the same, which indicates that the samples made by melt intercalation are uniform. This fact shows that an uniformed blend of polymer and layered clay can be obtained.

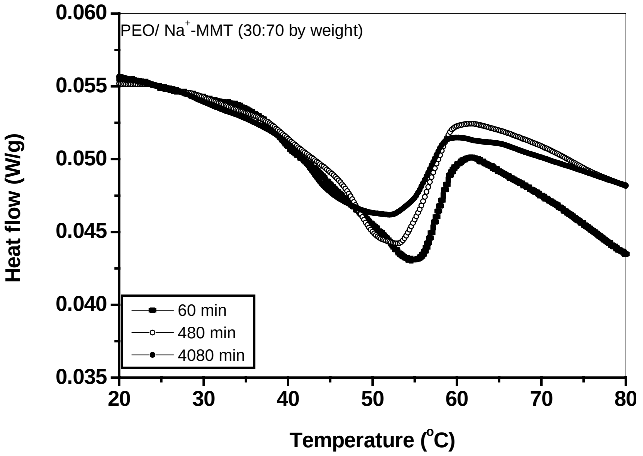

Fig. 2. Heat flow vs. temperature signals for PEO/Na$^+$-MMT (30:70 by weight) nanocomposites with different annealing times.

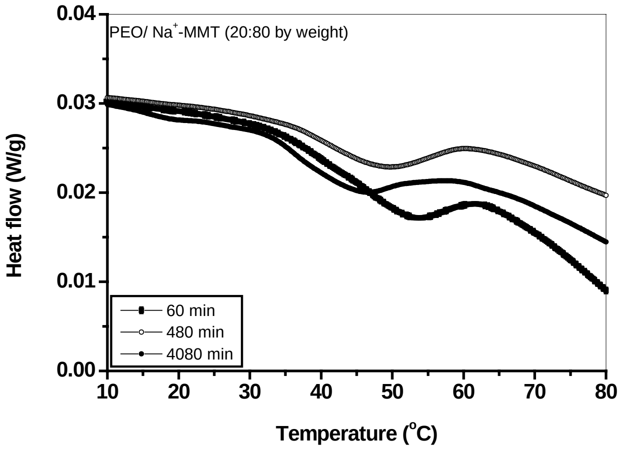

Fig. 3. Heat flow vs. temperature signals for PEO/Na$^+$-MMT (20:80 by weight) nanocomposites with different annealing times.

3.2. *Effect of annealing time on the amount of PE–PEG diblock copolymers intercalated into the layers of Na$^+$-MMT*

The endotherm-peak area of PE melt in the PE–PEG (80:20 by weight) diblock copolymer/Na$^+$-MMT (35:65 by weight) has wide range and larger shoulder before annealing in Fig. 6. It may be caused by the melting of PEG. It can be found that the endotherm peak became sharp with annealing time. Crystallinity of PE in the PE–PEG slightly decreased. The endotherm-peak area of PE melt against time is shown in Table 2. The same results can also be found for the PE–PEG (50:50 by weight)/Na$^+$-MMT (35:65 by weight) (Fig. 7). This indicates that some of PE also diffused into the layers of Na$^+$-MMT. However, the melt temperature of PE does not vary before or after annealing, showing that crystalline structure of PE was not affected.

Above results indicates that most part of PE is left outside the layers of Na$^+$-MMT while PEG diffused into the layers

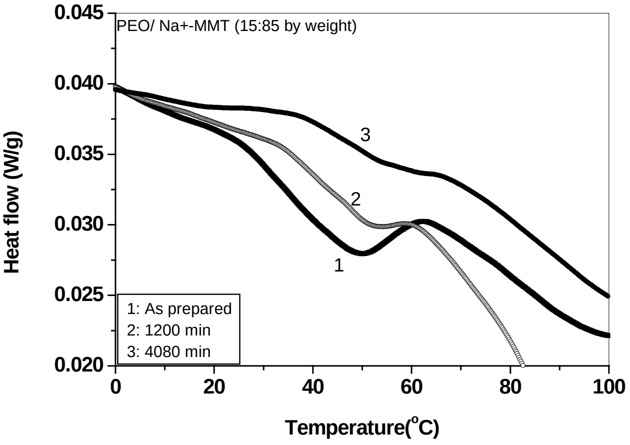

Fig. 4. Heat flow vs. temperature signals for PEO/Na$^+$-MMT (15:85 by weight) nanocomposites with different annealing times.

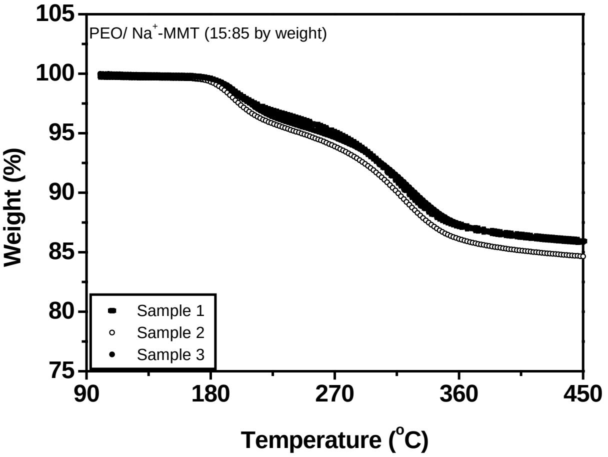

Fig. 5. Weight loss vs. temperature signals for PEO/Na$^+$-MMT (15:85 by weight) nanocomposites.

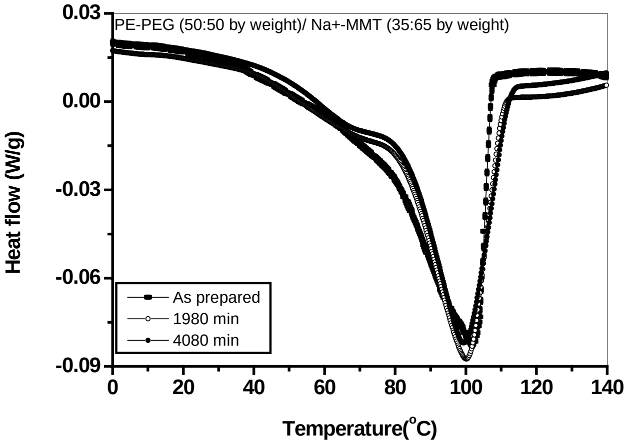

Fig. 7. Heat flow vs. temperature signals for PE–PEG (50:50 by weight)/ Na$^+$-MMT (35:65 by weight) nanocomposites with different annealing times.

of Na$^+$-MMT. This type of PE–PEG/Na$^+$-MMT nanocomposites should be considered as fillers, which may have good compatibility with polyethylene. This will be studied later.

3.3. The conductivity of PEO/Na$^+$-MMT nanocomposites

Fig. 8 shows the effect of the content of PEO on the ionic conductivity of the PEO/Na$^+$-MMT nanocomposites. It can be seen that the ionic conductivity of the PEO/Na$^+$-MMT nanocomposites increased with increasing PEO first and reached a maximum value near 25 wt% of PEO, then the ionic conductivity decrease with increasing PEO. This is because the crystallization of PEO results in the decrease of ionic conductivity.

Here we want to know whether the ionic conductivity of the PEO/Na$^+$-MMT nanocomposites can be improved by thermal treatment. Fig. 9 shows the effect of thermal treatment time on the ionic conductivity. The ionic conductivity of PEO/Na$^+$-MMT nanocomposites, indeed, increased with increasing annealing time. The ionic conductivity of PEO/Na$^+$-MMT nanocomposites reached $10^{-4.6}$ S/cm from $10^{-5.0}$ S/cm after annealing for 68 h. It is well known that the ionic conductivity of PEO electrolytes decreases rapidly below PEO melting temperature. This decrease is due to the crystallization of PEO that results in the decrease of the ionic mobility. When PEO is intercalated into the layers of Na$^+$-MMT, the PEO is confined. From Fig. 1, it can be seen that with increasing annealing time, much more PEO was intercalated into the layers of Na$^+$-MMT. Crystallization of PEO is restricted and the weight fraction of amorphous phase increases, and then the ionic conductivity of the electrolytes is improved.

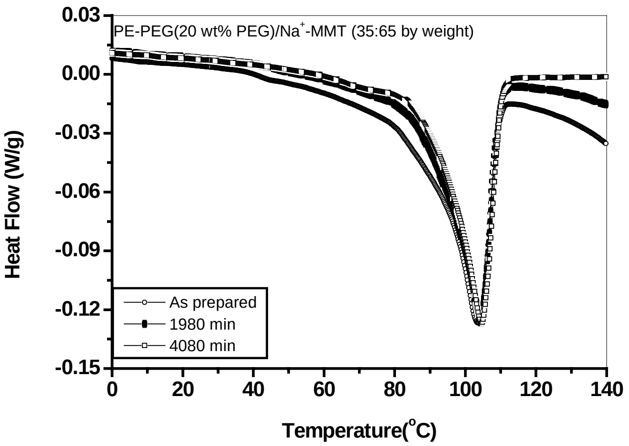

Fig. 6. Heat flow vs. temperature signals for PE–PEG diblock copolymer (20 wt% ethylene glycol)/Na$^+$-MMT (35:65 by weight) nanocomposites with different annealing times.

3.4. The tensile strength of polyethylene blended with PE–PEG diblock copolymer/Na$^+$-MMT

The PE–PEG diblock copolymer/Na$^+$-MMT nanocomposites as fillers were blended with PE. Fig. 10 gives a comparison of PE blended with PE–PEG diblock copolymer/Na$^+$-MMT nanocomposites and PE blended with Na$^+$-MMT.

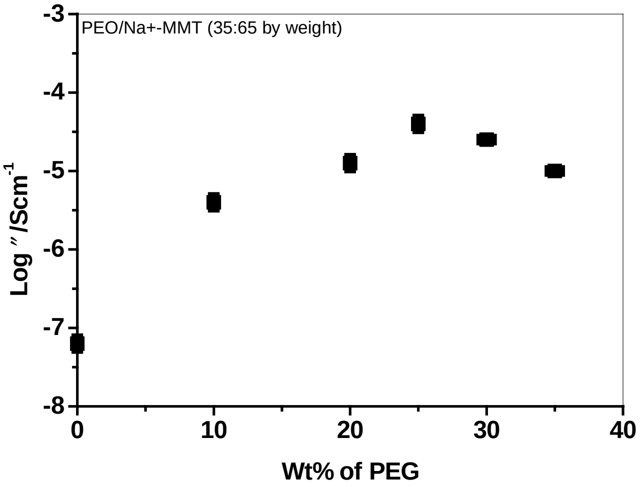

Fig. 8. The effect of the content of PEO on ionic conductivity of PEO/Na$^+$-MMT nanocomposites (thermal treatment at 80°C for 10 min).

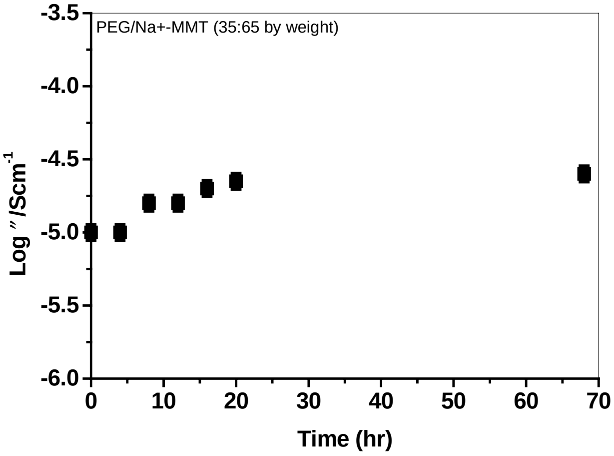

Fig. 9. The effect of annealing time on ionic conductivity of PEO/Na^+-MMT (35:65 by weight) nanocomposites.

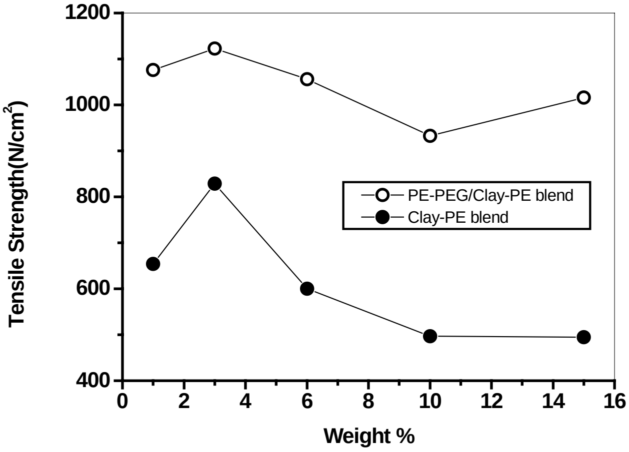

Fig. 10. The tensile strength of polyethylene/PE–PEG/clay and polyethylene/clay blend.

Results indicated that the tensile strength of PE blended with PE–PEG/Na^+-MMT nanocomposites is higher than that of PE blended with Na^+-MMT. This implies that such PE–PEG/Na^+-MMT nanocomposites as fillers have good compatibility with PE. From this study, it can be believed that new kinds of fillers for reinforcement of polymers can be obtained by preparation of polymer/Na^+-MMT hybrids.

4. Conclusions

Thermal treatment has important influence on the amount of PEO intercalated into the layers of Na^+-MMT and on the ionic conductivity of PEO/Na^+-MMT composites. The amount of PEO intercalated into the layers of Na^+-MMT increased with increasing annealing time. Some of PE in the PE–PEG can also be intercalated into the layers of Na^+-MMT while PEG was intercalated into the layers of Na^+-MMT. This type of nanocomposites showed good compatibility with polyethylene. The tensile strength of polyethylene blended with PE–PEG/Na^+-MMT blend was higher that that of polyethylene blended with Na^+-MMT. Such nanocomposites can be considered as new kinds of fillers for the reinforcement of polyethylene.

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