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Improve the gas barrier property of PET film with montmorillonite by in situ interlayer polymerization

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Abstract

We obtain the organical clay (OMMT) by processing the Na–MMT using a kind of interlayer agent which contains –COOH in its structure. The interlayer distance of OMMT is 2.47 nm which is larger than the Na–MMT (1.90 nm). We synthesize the PET/OMMT nanocomposite by in situ interlayer polymerization and then make the composite into film by bi-axis orientation. We find that the barrier property of PET/OMMT film is greatly better than pure PET film.

Keywords: Montmorillonite; Poly(ethylene terephthalate); In situ polymerization; Barrier; Film

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1. Introduction

Poly(ethylene terephthalate) (PET) was first prepared in 1946 [1] and has become one of the most widely used polymers materials. Because of its low cost and high performance such as high transparency, high stability in dimension and good mechanism property, it can be used in lots of fields including film, bottle and fibre.

Bi-axis-oriented PET (BOPET) film is an important product of PET. The throughput of BOPET in China will be 560,000 t/year in 2005 and this number is about five times as in 2002. But BOPET film's deficiency in gas barrier makes it unusable in some package fields that need high barrier property, for example some oxygen-sensitive foods such as beer and tomato-based food.

The montmorillonite has a natural nano-scaled layer structure; the gas can hardly permeate through it. Adding it into PET can increase the gas barrier property of the film. Several methods have been used to obtain polymer/organoclay composite materials, for example, solution intercalation, melt intercalation and in situ interlayer intercalation [2–6]. Among them, in situ interlayer polymerization relies on swelling of the organoclay by the monomer, followed by in situ polymerization initiated thermally or by the addition of a suitable compound. The chain growth in the clay galleries accelerates clay exfoliation and nanocomposite formation. This technique of in situ interlayer polymerization is also particularly attractive due to its versatility and compatibility with reactive monomers and is beginning to be used for commercial applications [7–9].

In this paper, the montmorillonite was organically modified and then was added into the PET resin by in situ polymerization. The content of the montmorillonite varied from 1% to 4%. We measured the layer spacing distance of the Na–MMT and OMMT by XRD and observed the morphology of the OMMT in the PET resin by TEM. At last, we measured the gas barrier property of the film.

2. Experimental

2.1. Materials

All materials we used in this paper are of industrial grade.

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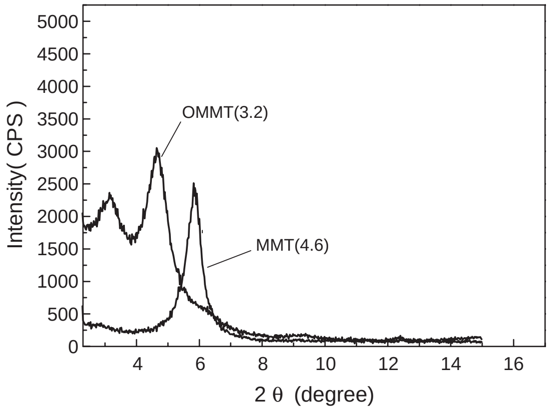

Fig. 1. XRD patterns of MMT and OMMT.

2.2. Preparation of the organoclay

The Na–MMT we used in this paper was not organically modified. The process of organically modifying Na–MMT is shown as follows:

1) 500 ml absolute ethyl alcohol and distilled water (1 : 1, volume ratio) were added into a flask, then put into a water-bath;
2) 50 g Na–MMT was put into the flask and stirred intensely for 1.5 h to disperse it evenly;
3) the water-bath was heated up to 75 °C;
4) 0.1 mol quaternary ammonium salt which contains Cl^- and –COOH in its structure was added into the flask, stirring the mixture for 4 h;
5) the mixture in the flask was taken out and then was filtered. The solid part was washed by distilled water several times until no white participates were observed when 0.1 mol/L $AgNO_3$ solution is dropped into the filtrate, which meant that no more Cl^- in the solid part; and
6) the solid part was dried in the vacuum oven at 80 °C for 48 h, comminuted and sieved. The preparation of organoclay (OMMT) was finished.

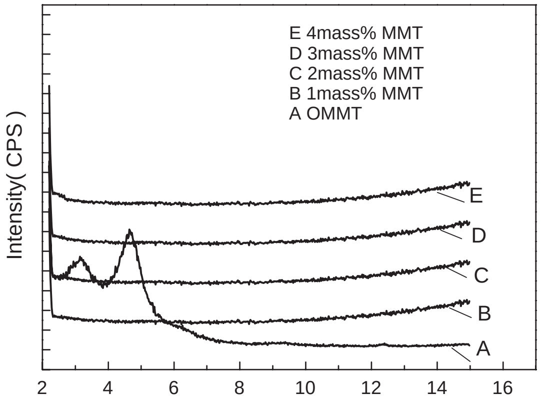

Fig. 2. The XRD patterns of PET/OMMT nanocomposite.

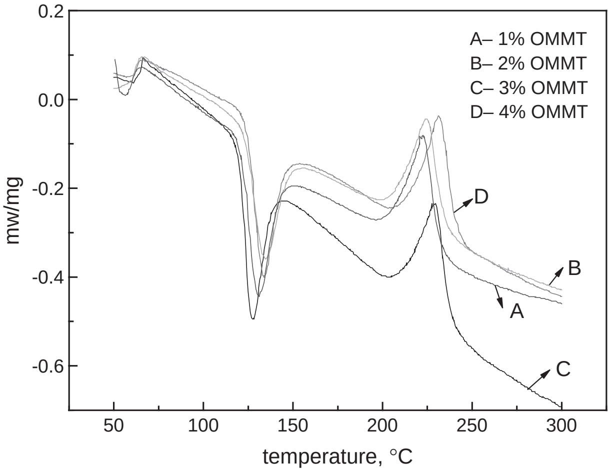

Fig. 3. The DSC result of PET/OMMT composite.

The change of interlayer spacing between the Na–MMT and the OMMT was observed by X-ray diffraction (XRD).

2.3. Preparation of PET/OMMT nanocomposite by in situ polymerization

In this paper, we used ester interchange of dimethyl terephthalate (DMT) and ethylene glycol (EG) to prepare the PET/OMMT nanocomposite. The synthetic procedures are shown as follows.

Twenty-seven grams of OMMT were dispersed in 50 g EG and stirred for 24 h at room temperature.

Two kilograms of DMT, 1.4 kg EG (DMT : EG = 1 : 2.2, mole ratio) and 0.8 g zinc acetate (0.04% weight of DMT) were put into the reactor; the mixture was heated up to 140 °C, starting the stirrer at 60 r/min, and the temperature was raised to 180~220 °C. The ester interchange reaction was stopped when the mass of methanol reach 90% of the theoretical yield (330 g methanol per 1 kg DMT). Then the bis-hydroxyethyl terephthalate (BHET) was synthesized. Added into the reactor were 0.6 g triphenyl phosphite (TPP, 0.03% weight of DMT), 0.8 g Sb(EG) (0.04% weight of DMT) and 13.5 g OMMT (dispersed by EG).

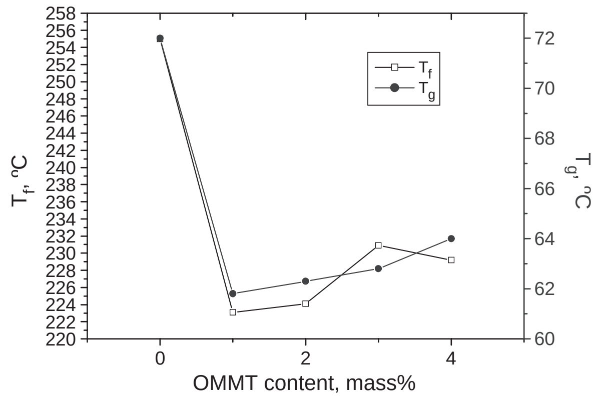

Fig. 4. The relationship between OMMT content and T_g of composite.