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Nucleation effect of montmorillonite with β-nucleating surface on polymorphous of melt-crystallized isotactic polypropylene nanocomposites

Xin Dai, Zishou Zhang, Chunguang Wang, Qian Ding, Juan Jiang, Kancheng Mai *

Materials Science Institute, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Key Laboratory of Polymeric Composites and Functional Materials of Ministry of Education, Key Laboratory of High Performance Polymer-based Composites of Guangdong Province, Guangzhou 510275, PR China

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ABSTRACT

Neat montmorillonite (MMT) causes strong heterogeneous nucleation of α-phase crystallites in isotactic polypropylene (iPP). By surface modification of MMT with pimelic acid (PA) MMT with tailored β-nucleation capacity (β-MMT) has been prepared and nanocomposites with β-iPP have been made. The polymorphism of the iPP in the nanocomposites, the effect of β-MMT on the morphology and its crystallization and melting behavior of iPP has been investigated by POM, DSC and XRD. β-MMT raises the crystallization temperature to a higher value than neat MMT. The β-nucleation ability of β-MMT depends both on the MMT/PA ratio and on the β-MMT content in the composite. The fraction of β-crystals with respect to the total amount of crystals increases with increasing β-MMT content and decreasing MMT/PA ratio. It can be adjusted between 0% and 98%. The accomplished surface modification of the MMT provides a simple and efficient way to prepare β-iPP nanocomposites.

1. Introduction

Polymer nanocomposites with montmorillonite (MMT) have attracted great interest, because they often exhibit remarkable improvement in materials properties such as high modulus, increased strength and heat resistance, decreased gas permeability and flammability [1–4]. Isotactic polypropylene (iPP) nanocomposites with MMT have been widely studied [5–8]. Since the physical and mechanical properties of iPP are dependent of the crystallization behavior and morphology, lots of researches on the heterogeneous nucleation of MMT and crystallization behavior of iPP/MMT nanocomposites were reported [9–15].

A great number of researches indicated that the heterogeneous nucleation of MMT accelerates the crystallization rate of iPP and the crystallization rate increases with the increase in MMT content [10–12,14]. MMT can act as nucleating agent to decrease the crystalline size of iPP and increases the crystallization activation energy of iPP/MMT nanocomposite. Medellín-Rodríguez et al. [13] observed that low MMT content could induce the formation of β-crystal, but its formation was inhibited with high MMT contents.

Up to now, the researches on the crystallization behavior of iPP/MMT nanocomposites indicated that MMT generally exert α-nucleating ability to result in the formation of α-crystal in iPP/MMT nanocomposites. It is well known that α-iPP and β-iPP exhibit different physical and mechanical properties. The β-iPP not only maintains a good overall performance of the α-iPP, but also performs a higher notch impact strength and high heat distortion temperature [16–23]. Therefore, the preparation, physical and mechanical properties of β-nucleated iPP attract many research interests [24–29]. Filled composites with β-iPP as matrix would be a potential method to obtain β-iPP composites with higher impact toughness and heat distortion temperature than α-iPP composites.

Generally, the β-iPP composites are prepared by simultaneously adding β-nucleating agent and rigid inorganic particles into the iPP matrix [30–35]. A great number of investigations indicated that it is difficult to obtain the β-iPP composites with high relative β-crystal fraction, especially at high inorganic particle content. Inorganic particles with heterogeneous α-nucleating ability have an influence on the β-crystal fraction in the β-iPP crystallization process. On the other hand, the β-nucleating agent as aggregate particles dispersed in the matrix can hardly provide high surface area to increase the nucleating ability. In order to prepare the β-iPP composites with high content of inorganic particle, nano-$CaCO_3$, wollastonite and zeolite with β-nucleating surface and their β-iPP composites were prepared in our lab [35–38]. In this paper, MMT with tailored β-nucleation capacity (β-MMT) was first prepared through the reaction between MMT and pimelic

* Corresponding author. Tel./fax: +86 20 84115109.
E-mail address: cesmkc@mail.sysu.edu.cn (K. Mai).

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acid in our lab. The crystallization behavior and morphology, melting characteristic and β-crystal fraction of iPP nanocomposites filled by MMT and β-MMT were compared by DSC, XRD and POM. The influence of β-MMT content and MMT/PA mass ratio of the prepared β-MMT on the crystallization behavior, melting characteristics and relative β-crystal fraction of iPP/MMT nanocomposites were discussed in this paper.

2. Experiment

2.1. Materials

The DK4 Ca-montmorillonite (MMT) modified by cetyl quaternary ammonium was purchased from Zhejiang Fenghong Clay Chemicals Co., Ltd. The isotactic polypropylene (iPP) used in this study was HP500N (MFR = 12 g/10 min), provided by Cnooc and Shell Petrochemicals Company Ltd., China. Chemical grade pimelic acid (PA) was purchased from Shanghai Hongsheng Industry Limited Company, China. Analytical grade acetone was supplied by Guangzhou Chemical Reagent Factory, China. Calcium pimelate (CaPA) was made in our laboratory [39].

2.2. Preparation of MMT with β-nucleating surface

MMT generally shows α-nucleating ability in iPP/MMT nanocomposites. In order to obtain MMT with tailored β-nucleation capacity (β-MMT), pimelic acid (PA) was used to react with calcium ion on the surface of MMT. MMT and PA were dried in a vacuum oven at 80 °C for 30 min, then well mixed directly at room temperature. Finally, the powder was placed in an oven to fully react at 120 °C for 30 min. The β-MMT prepared by MMT/PA mass ratios of 1000/1, 4000/1, 8000/1, 16,000/1 and 32,000/1, was denoted as M_1, M_4, M_8, M_{16} and M_{32}. Untreated MMT was denoted as M_0.

2.3. Preparation of β-iPP/MMT nanocomposites

MMT and β-MMT were dried in a vacuum oven at 80 °C for 30 min before mixing with iPP. The iPP/MMT and β-iPP/MMT nanocomposites were prepared by an HL-200 internal mixer (Jilin University Science and Education Instrument Factory, China) under 50 rpm for 8 min at the temperature of 190 °C.

2.4. Characterization

The crystallization behavior and melting characteristics of iPP and filled iPP nanocomposites were carried out on a TA DSC Q10 differential scanning calorimeter (DSC) under N_2. The sample about 5 mg was rapidly heated up to 220 °C from room temperature and kept at 220 °C for 5 min to remove the thermal history, residual stress and so on. After that, the sample was cooled to 100 °C at rate of 10 °C/min and then reheated to 220 °C at rate of 10 °C/min. The crystallization and melting parameters were recorded from the cooling and reheating scans.

The crystal form and relative content of β-crystal were measured by wide-angle X-ray diffraction (XRD). The measurement was conducted with a Rigaku Geigerflex Model D/Max-IIIA rotating anode X-ray diffractometer. The radiation source was graphite monochromatized Cu Kα and the X-ray source was set at a voltage of 40 kV and a current of 20 mA. The scanning range was 5–40° with a step scanning rate of 4°/min. The samples were pretreated by DSC with the same crystallization conditions as DSC analysis. The relative content of β-crystal was calculated according to Turner–Jones formula which was described in the literature [40]:

$$K_\beta = \frac{H_{300}}{H_{110} + H_{040} + H_{130} + H_{300}} \quad (1)$$

where H_{110}, H_{040} and H_{130} were the intensity of the (110) (040) and (130) reflections of α-crystal, appearing at 2θ around 14.1°, 16.9°, and 18.5°, respectively, and H_{300} was the intensity of the (300) reflections of β-crystal at 2θ around 16.0°. If no β-crystal existed in iPP, $K_\beta = 0$; if iPP totally formed β-crystal, $K_\beta = 1$.

The spherulitic morphology of specimens was observed with a Leitz Orthoplan Pol polarized optical microscope (POM) equipped with a LINKAM THMS600 hot stage.

3. Results and discussion

3.1. Nucleation effect of iPP nanocomposites filled by β-MMT prepared with same MMT/PA mass ratios

Figs. 1 and 2 are the DSC and XRD curves of iPP nanocomposites filled by different contents of β-MMT (M_1) prepared with MMT/PA of 1000/1, respectively and the corresponding DSC data and relative β-crystal fractions (K_β) is listed in Table 1. It can be

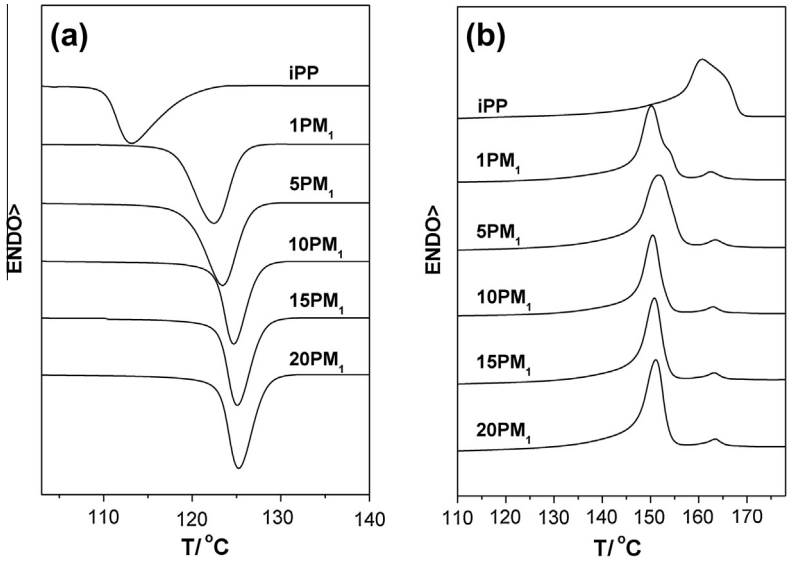

Fig. 1. DSC crystallization (a) and melting (b) curves of β-iPP/MMT nanocomposites.