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Additive effects of *N*,*N*,*N*′,*N*′-tetraalkyl terephthalamide on crystalline morphology and mechanical properties of polypropylene*

SHENTU Bao-qing†, LI Ji-peng, WENG Zhi-xue

(*Polymer Reaction Engineering Division, State Key Laboratory of Chemical Engineering, Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, China*)

†E-mail: shentu@zju.edu.cn

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Abstract: The effect of *N*,*N*,*N*′,*N*′-tetraalkyl terephthalamide (TATA) on the crystallization of polypropylene (PP) was studied by means of differential scanning calorimetry, wide angle X-ray diffraction and polarized optical microscopy. It was found that the addition of TATA effectively induced the formation of β-crystalline form of PP. With the increase of TATA content both the total crystallinity degree (x) and crystallinity degree for β-crystalline form (x_β) of PP increased significantly, while the crystallinity degree for α-crystalline form (x_α) decreased. Polarized optical micrographs indicated that the addition of TATA led to a substantial decrease in the size of spherulites of PP and the boundaries of spherulites were hardly distinguished. TATA could significantly improve the impact strength, flexural strength and modulus of PP, while the tensile strength of PP did not change greatly with TATA content.

Key words: Polypropylene (PP), *N*,*N*,*N*′,*N*′-tetraalkyl terephthalamide, Crystallization, Morphology, Mechanical property
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INTRODUCTION

Polyprolylene (PP) is a large tonnage polymer and has been extensively used in various areas, such as automotive parts, furniture and containers due to its low cost and weight, anti-corrosion property, good processibility, good mechanical properties and other attractive properties. Its production and consumption rate are increasing more rapidly in comparison with other polymers (Nitta *et al*., 2005).

PP is a typical semicrystalline polymer, whose crystalline phase might consist of α-, β-, γ- and δ-crystalline form. Under actual processing conditions PP usually crystallizes to α-crystalline form, which, however, shows poor impact strength at lower and room temperatures so as to restrict its application as an engineering plastics (Zhang *et al*., 2004).

In comparison with α-crystalline PP, β-crystalline PP shows good impact strength at lower room temperature and high distortion temperature. Therefore, β-crystalline PP has been paid attention to due to its unique properties (Raab *et al*., 2004). However, β-crystalline form is pseudostationary in thermodynamics, and it is difficult to form in dynamics for PP (Zhang and Shi, 1992).

Leugering and Einflu (1967) first reported γ-quinacridone's use as a nucleating agent for the formation of β-crystalline PP. Mubarak *et al*.(2000) also found that quinacridone red pigment was an effective nucleating agent for β-crystalline form of PP, and that the elongation at break and impact strength of PP increased with increasing content of β-crystalline form. The drawback of quinacridone was its intense red color and its polymorphic nature, which made PP red color. Grein *et al*.(2002) reported that β-nucleation had great effect on the mechanical properties of PP.

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Therefore, the addition of β-nucleating agents is one of the effective means to form β-crystalline form of PP, and consequently improves the mechanical properties. Kawai *et al*.(2002) found that *N*,*N*,*N*′,*N*′-dicyclohexyl-2,6-naphalenedicarboxamide could be used as β-nucleating agents inducing PP to exist in β-crystalline form. Recently we observed that *N*,*N*,*N*′,*N*′-tetraalkyl terephthalamide (TATA) was also an effective β-nucleating agent. However, there are few reports on the additive effects of TATA on the crystalline morphology and mechanical properties of PP. In the present work, the effect of TATA on the melting behavior of PP was studied by means of DSC; crystalline morphology was investigated using wide angle X-ray diffraction and polarized optical microscopy, and the mechanical properties of PP containing TATA were also studied.

EXPERIMENT DETAILS

Materials

Commercially available PP (grade F401, tacticity≥97%, melt index=2 g/10 min, supplied by Yangzi Petrochemical Corporation) was used in this study. *N*,*N*,*N*′,*N*′-tetraalkyl terephthalamide (TATA, supplied by Shanxi Institute of Chemical Engineering) was a white powder with size <250 μm and its structure was shown in Fig.1 in which both R_1 and R_2 are alkyls.

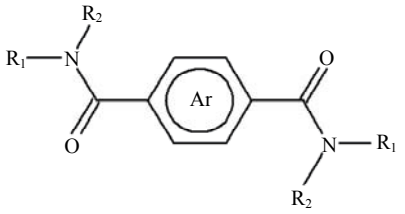


Fig.1 Structure of *N*,*N*,*N*′,*N*′-tetraalkyl terephthalamide

Sample preparation

TATA was dissolved easily in volatile solvent and the solution was mixed with PP in a high-speed mixing machine. After the solvent had evaporated completely, the mixture was extruded in a twin-screw TE35 extruder (Keya Plastic Mechanical Factory of Jiangsu, China) at temperature of 195~210 °C and a screw speed of 40 r/min. The extruded products were frozen in-line in a water bath and granulated to less than 3 mm. The resulting pellets were injection moulded into test specimens using an Arburg Allrounder 221-55-250 injection moulding machine. The barrel had a flat temperature profile of 220 °C, the mould temperature was kept at 40 °C and injection pressure of 55 bar, holding pressure was kept at 45 bar. Three types of specimens were made: flexural test bars with dimension of 80 mm×10 mm×4 mm, impact test bars with dimension of 80 mm×8 mm×4 mm, and tensile test bars with a dumbbell shape. Each Izod impact specimen was notched using a TMI cutter to produce notches with radius of 0.254 mm and depth of 2.54 mm according to ASTM D256. PP alone was also treated similarly as a blank sample.

Apparatus and experimental procedures

Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC-7 to examine the melting behavior. Ten mg samples sealed in aluminum pans were heated from room temperature to 200 °C at a scanning rate of 10 °C/min under nitrogen atmosphere. The temperature scale of the DSC was calibrated using an indium (melting point, 156.63 °C).

Wide angle X-ray diffraction (WAXD) measurements were performed at room temperature using a Shimazu XD-3A X-ray diffractometer. The experiments were carried out using CuK_α radiation at 30 kV and 15 mA and a scanning rate 2 °/min.

The crystalline morphology of PP was investigated using a Nikon-E600 polarized optical microscope (POM).

The Izod impact test was run using a Tinius 892 impact test machine with pendulum speed at impact of 3.46 m/s. Tensile and flexural strength tests were carried out on a LWK-5 tester at a crosshead speed of 10 and 2 mm/min, respectively. The mechanical properties reported hereinafter were the average of five successful tests.

RESULTS AND DISCUSSION

Effect of TATA on the melting behavior of PP

The effect of TATA content on the melting behavior of PP was studied at a heating rate of 10 °C/min, with the result shown in Fig.2. It was found that after the introduction of TATA into PP, there

were peaks at 153 °C and 166 °C corresponding to the melting peaks of α- and β-crystalline form, respectively (Labour *et al*., 2001). When TATA content was more than 0.3 wt%, PP crystallized mainly in β-crystalline form and only a small peak indicating the presence of α-crystalline form appeared in the melting curve, while there was only one melting peak at 166 °C indicating the presence of α-crystalline form of pure PP. It could also be seen that the heat of fusion for β-crystalline form increased with increasing TATA content, while that for α-crystalline form decreased, indicating that TATA induced the formation of β-crystalline form and was an effective β-nucleating agent for PP (Kawai *et al*., 2002).

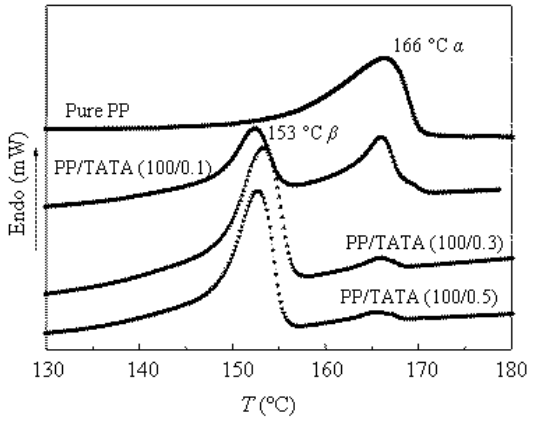


Fig.2 Effect of TATA content on the melting behavior of PP

The degree of crystallinity (x) could be determined from the calorimetric data with the knowledge of the melting enthalpy of the completely crystallized α- and β-crystalline form (ΔH_o). Although the literature values of the melting enthalpy varied, a comparison between $\Delta H_o(\alpha)$ and $\Delta H_o(\beta)$ determined via identical methods always revealed a higher value for α-crystalline form of PP. The values for degree of crystallinity (x_α and x_β) were calculated using $\Delta H_o(\alpha)$=209 J/g and $\Delta H_o(\beta)$=151.2 J/g (Avella *et al*., 1993). The effect of TATA content on x ($x=x_\alpha+x_\beta$), x_α and x_β of PP is shown in Table 1.

With the increase of TATA content both x and x_β increased significantly, which indicated that TATA not only induced the formation of β-crystalline form of PP, but also caused the non-crystallizing PP chain to crystallize due to the heterogeneous nucleation. Meanwhile x_α decreased abruptly with the increase of TATA content, and PP crystallized mainly in β-crystalline form at a TATA content of 0.3 wt%. With further increase of TATA content, there was only slight increase for both x and x_β.

Table 1 Effect of TATA content on x, x_α and x_β of PP

TATA content (wt%)	x (%)	x_α (%)	x_β (%)
0	46.3	46.3	0
0.1	56.8	22.6	34.2
0.3	62.8	3.4	59.4
0.5	64.1	3.1	61.0

Effect of TATA on the crystalline morphology of PP

WAXD studies were also carried out to obtain information on the crystalline property of PP. The diffraction angle (2θ) curves are shown in Fig.3. Diffraction peaks at 2θ=14.1°, 18.4°, and 21.7° ascribed to the (110), (040), and (130) plane, respectively, suggesting that pure PP crystallized in α-crystalline form (monoclinic) because there were no peaks at 2θ=16.1° associated with β-crystalline form (hexagonal) and 2θ=20.1° associated with γ-crystalline form (triclinic) (He *et al*., 1998). Whereas there were diffraction peaks at 2θ=16.1° and 21.2° ascribed to the (300) and (301) plane for PP containing TATA, which further indicated that TATA effectively induced the formation of β-crystalline form of PP.

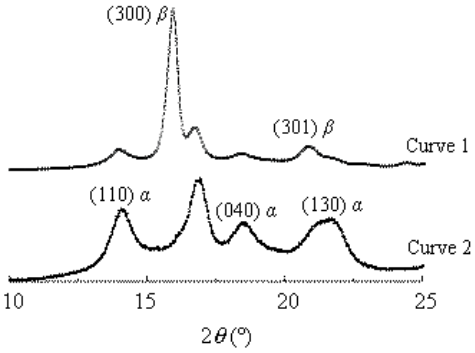
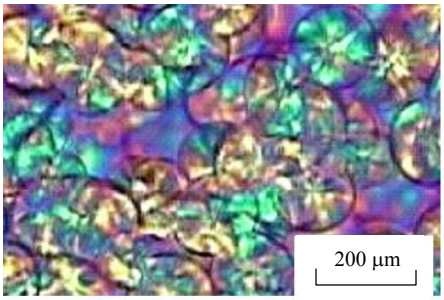


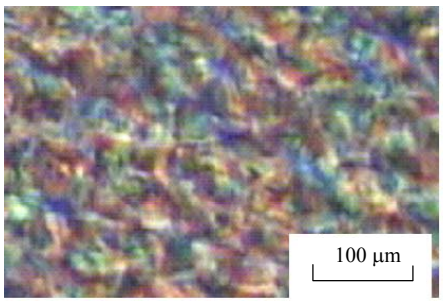
Fig.3 X-ray diffraction patterns of pure PP (Curve 1) and PP containing 0.3 wt% TATA (Curve 2)

Fig.4 compares the polarized optical micrographs of the spherulite morphology of pure PP and PP containing 0.3 wt% TATA. These micrographs indicated that the addition of TATA led to a substantial

decrease in the size of PP spherulites. Moreover, the spherulites in β-crystalline form of PP exhibited a distinct morphology, and sheaf-like aggregates of lamellar crystals were generally observed. Furthermore, the boundaries of spherulites were hardly distinguishable. On the other hand, the spherulites of the α-crystalline form of pure PP consisted of an aggregate of lamellae that radiated from the center outward with the spherulites having distinct boundaries. This morphological feature accorded with Tjong's results (Tjong *et al*., 1996).



(a)



(b)

Fig.4 Optical micrographs of spherulites for PP (a) and PP containing 0.3 wt% TATA (b)

Effect of TATA on the mechanical properties of PP

The effects of TATA on impact strength and tensile strength of PP were plotted against TATA content in Fig.5. It was found that with increasing TATA content, the impact strength of PP increased significantly first, and then decreased slightly with further increase of TATA content. Maximum impact strength occurred at a TATA content of 0.3 wt%, where impact strength increased about 230% in comparison with pure PP.

The increase of PP impact strength after the introduction of TATA into PP probably contributed to the formation of β-crystalline form and the decrease in the size of spherulites. Tjong *et al*.(1996) also reported that in comparison with α-crystalline form, β-crystalline PP showed good impact strength at room temperature. It was also shown that the tensile strength of PP was not significantly affected by adding TATA.

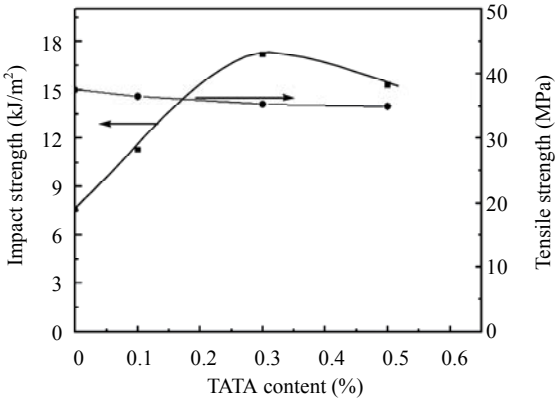


Fig.5 Impact strength and tensile strength of PP as a function of TATA content

The effects of TATA on the flexural strength and modulus of PP were also studied and the result is shown in Fig.6. It was found that the PP flexural strength and modulus first increased significantly with the increase of TATA content, and finally almost remained unchanged with the increase of TATA content, and that in this situation, the flexural strength increased about 28% in comparison with that of PP.

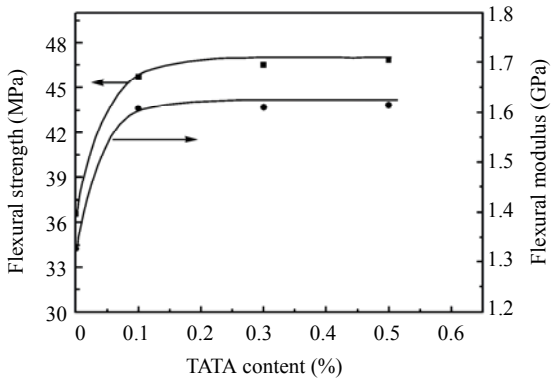


Fig.6 Flexural strength and modulus of PP as a function of TATA content

The increase of the flexural strength and modulus of PP was probably due to the increase of the total degree of crystallinity of PP after the introduction of

TATA into PP (Gahleitner *et al*., 1996). When TATA content was more than 0.3 wt%, the total degree of crystallinity of PP did not change significantly with TATA content, which resulted in the unchanged flexural strength and modulus of PP.

CONCLUSION

TATA significantly changed the crystalline form and melting behavior of PP, and not only induced the formation of β-crystalline form, but also resulted in the increase of the total degree of crystallinity of PP due to the heterogeneous nucleation. In comparison with PP, the addition of TATA led to a substantial decrease in the size of spherulites. TATA could significantly improve the impact strength, flexural strength and modulus of PP, while the tensile strength did not change greatly.

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