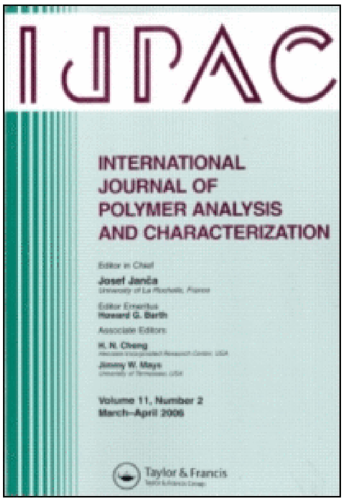

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Li, Xun , Zhang, Yue-fei and Xie, Dan(2009) 'Effects of Bicyclic [2,2,1] Heptane Di-carboxylate on Properties, Crystallization, and Melting Behaviors of Isotactic Polypropylene', International Journal of Polymer Analysis and Characterization, 14: 7, 569 — 574

To link to this Article: DOI: 10.1080/10236660903086888

URL: http://dx.doi.org/10.1080/10236660903086888

International Journal of Polymer Anal. Charact., 14: 569–574, 2009

ISSN 1023-666X print
DOI: 10.1080/10236660903086888

Effects of Bicyclic [2,2,1] Heptane Di-carboxylate on Properties, Crystallization, and Melting Behaviors of Isotactic Polypropylene

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Abstract: Effects of a novel nucleating agent bicyclic [2,2,1] heptane di-carboxylate (HPN-68) on the properties, crystallization, and melting behavior of isotactic polypropylene (iPP) were studied. The results showed that HPN-68 is a typical nucleating agent for α-iPP and it has high nucleation efficiency. Addition of a small amount of HPN-68 to iPP can obviously increase crystallization peak temperature and mechanical properties of iPP. When the concentration of HPN-68 is 0.2 wt.%, the crystallization peak temperature can be increased by about 15°C, and the tensile strength and flexural modulus of iPP can be increased by 12.74% and 18.24%, respectively.

Keywords: Bicyclic [2,2,1] heptane di-carboxylate; Crystallization; Isotactic polypropylene; Melting behavior; Nucleating agent

INTRODUCTION

Isotactic polypropylene (iPP) is one of the most commonly used thermoplastics. The market share of iPP increases steadily because of its

Submitted 3 April 2009; revised and accepted 3 June 2009.

The authors are grateful for financial support from the Ministry of Science and Technology of the People's Republic of China (Grant No. 2008AA05Z405, No. 2007BAD41B05, and No. 2006DFA62370) and the Hunan Provincial Bureau of Science and Technology (Grant No. 06GK3066 and No. 05C229).

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relatively low cost, versatility, recyclability, and good mechanical performance in engineering applications and the possibility of modifying the polymer to expand its range of properties.[1,2] Therefore, from the commercial point of view, it is very important to enhance the physical properties of iPP such as mechanical properties, optical properties, and thermal stability. It is well known that an addition of nucleating agents during the course of processing plays an important role for this purpose. Furthermore, by using nucleating agents, the cycle time can be considerably reduced, especially in injection molding, which can have a decisive influence on processing costs. At present, the commonly used nucleating agents include aromatic heterocyclic phosphate salts and sorbitol derivatives. There are many studies concerning nucleated iPP.[2–10] Zhang et al.[8] studied the nucleation efficiency of organic phosphates in polypropylene and the crystallization kinetics of nucleated iPP. Marco et al.[11,12] studied the nucleation activity of the third-generation sorbitol-based nucleating agents for iPP and isothermal crystallization of iPP nucleated with sorbitol derivatives. Shepard et al.[13] studied the nucleation efficiency of 1,3: 2,4-di-p-methylbenzylidene sorbitol in iPP.

Bicyclic [2,2,1] heptane di-carboxylate (commercial product name: HPN-68) is a novel nucleating agent recently developed by Milliken Chemical.[14] Compared to the conventional nucleating agents such as MDBS and ADK NA-11, the nucleating agent HPN-68 can increase the crystallization rate of iPP more, so that the particles have less deflection in molding and shorter molding cycle periods. However, there are few articles reporting nucleation effects of HPN-68 in iPP. In this article, the properties and crystallization and melting behavior of iPP nucleated with HPN-68 are reported, with the objective to provide some foundations for application of the nucleating agent in iPP.

EXPERIMENTAL SECTION

iPP powders with a melt flow rate (MFR) of 2.5 g/10 min, supplied by SINOPEC Jiujiang Company (China), were used in this work. Nucleating agent bicyclic [2,2,1] heptane di-carboxylate (commercial product name: HPN-68) was provided by Milliken Chemical.

The iPP powders and 0.2 wt.% of HPN-68 were mixed in a high-speed mixer for 5 min. Then the mixture was extruded by a twin-screw extruder and pelletized. The pellets were molded into standard test specimens by a CJ-80E injection-molding machine.

Crystallization and melting behaviors of iPP nucleated with HPN-68 were studied by using a Perkin Elmer Pyris 1 differential scanning calorimeter (DSC) (Perkin Elmer, USA). All operations were carried out under nitrogen atmosphere. In order to erase the thermal history, samples of about 3 mg were heated from 50° to 200°C at a heating rate of 20°C/min and maintained at 200°C for 5 min. Then the samples were cooled to 50°C at a cooling rate of 20°C/min. On completion of crystallization, the sample was heated again from 50° to 200°C at the heating rate of 20°C/min to compare the melting behaviors of the samples.

The mechanical and optical properties of virgin iPP and iPP nucleated with HPN-68 were measured according to ASTM test methods, namely, ASTM D-638 for the tensile properties and ASTM D-790 for the flexural properties, using a universal testing machine. The Izod impact strength was tested on the basis of ASTM D-256 and the haze value was tested on the basis of ASTM D-1003.

RESULTS AND DISCUSSION

Effects of Nucleating Agent HPN-68 on Crystallization and Melting Behaviors of iPP

In order to evaluate the crystallization rate of polymers, four parameters are often used[15]: (1) crystallization peak temperature of polymer; (2) crystallization halftime $t_{1/2}$ of polymer or crystallization rate constant K in the Avrami equation under isothermal crystallization; (3) nuclei density of crystallization or spherulite size after crystallization is finished; and (4) surface free energy of crystallization nucleation. The simplest method is adoption of crystallization peak temperature to evaluate the overall crystallization rate of polymers. In general, the higher the crystallization peak temperature, the faster the crystallization rate. Melting and crystallization curves of virgin iPP and iPP nucleated with HPN-68 at a heating or cooling rate of 20°C/min are shown in Figure 1.

It can be seen from the melting curves of iPP and iPP/HPN-68 in Figure 1 that the melting peak temperature of iPP nucleated with HPN-68 is higher than that of virgin iPP. This is because the addition of nucleating agent HPN-68 can improve the crystallization temperature of iPP. The melting thermogram shows that there is only a single melting peak in the DSC curves of iPP nucleated with HPN-68, and the temperature of the melting peak is about 163°C, which is the typical melting temperature of α-iPP. This means HPN-68 acts as a nucleating agent for α-spherulites of iPP. It can be also seen from crystallization curves of iPP and iPP/HPN-68 in Figure 1 that the addition of HPN-68 can increase the crystallization peak temperature of iPP. When the concentration of HPN-68 is 0.2 wt.%, the crystallization peak temperature of iPP can be increased from about 115°C for virgin iPP to about 130°C. The stronger the nucleating efficiency, the higher the melting temperature.

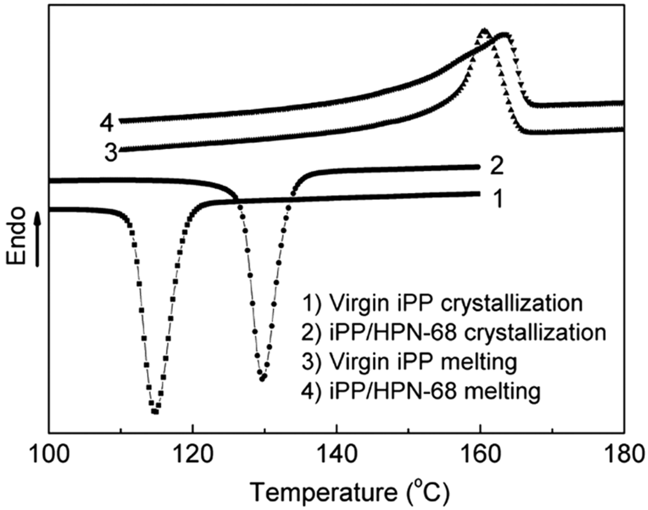

Figure 1. DSC crystallization and melting curves of virgin iPP and iPP nucleated with HPN-68 at the cooling or heating rate of 20°C/min.

As the nucleating agents increase the crystallization temperature so that iPP crystallizes at a higher temperature, the perfection of nucleated iPP increases with the increment of crystallization temperature, which makes the melting temperature of iPP rise. In addition, incorporation of HPN-68 into iPP can make the crystallization peak of iPP become sharper and the scope of crystallization temperature become narrower, which shows that the addition of HPN-68 can increase the crystallization rate of iPP significantly.

Effects of Nucleating Agent HPN-68 on Mechanical Properties and Optical Properties of iPP

Effects of nucleating agent HPN-68 on the mechanical and optical properties of iPP were examined when the addition concentration of HPN-68 was 0.2 wt.% (Table I).

It can be seen from Table I that the addition of nucleating agent HPN-68 can increase tensile properties and flexural properties of iPP markedly. When concentration of HPN-68 is 0.2 wt.%, compared to those of virgin iPP, tensile strength and flexural modulus of iPP can be increased by 12.74% and 18.24% respectively, which shows that HPN-68 has obvious nucleation effects in iPP. As the addition of HPN-68 increases crystallinity of iPP and reduces mean size of spherulites, tensile and flexural properties of iPP are improved. According to the conclusion

Table I. Effects of nucleating agent HPN-68 on mechanical and optical properties of iPP

Properties	Tensile strength, MPa	Tensile modulus, MPa	Flexural strength, MPa	Flexural modulus, MPa	Impact strength, J/m	Haze value, %
Virgin iPP	30.85	1280	46.01	1530	31.75	80.12
iPP/HPN-68	34.78	1410	55.88	1809	32.06	62.36

obtained from the above studies on crystallization and melting behaviors of iPP nucleated with HPN-68, HPN-68 is a typical nucleating agent for α-iPP, so it has few effects on impact strength. However, compared to typical organic phosphorous salts and sorbitol derivative nucleating agents, HPN-68 exhibits smaller improvements on the haze value of iPP,[16] which might be attributed to the fact that HPN-68 is a carboxylate-type nucleating agent; however, this should be studied in future research.

CONCLUSIONS

In this article, the effects of a novel nucleating agent bicyclic [2,2,1] heptane di-carboxylate (HPN-68) on properties and crystallization and melting behavior of iPP were studied. HPN-68 is a typical nucleating agent for α-iPP and it has high nucleation efficiency in iPP. It can markedly increase crystallization peak temperature and overall crystallization rate of iPP by low concentration. In addition, incorporation of HPN-68 into iPP can also greatly improve tensile and flexural properties of iPP.

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