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Influence of Nucleating Agent on Properties of Isotactic Polypropylene

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Abstract

As a nucleating agent, 1, 3-2, 4-di (p-hydroxyl) benzylidene sorbitol (DHDBS) at mass percents (0.1 wt%, 0.2 wt%, 0.3 wt%, 0.4 wt% and 0.5 wt%) was added into isotactic polypropylene (IPP) matrix by solution/precipitation method and compression-molded method. The crystallization morphology, spherulite dimensions, and crystallinity, was studied by polarizing microscope (PLM), scanning electron microscope (SEM) and X-ray diffraction (XRD). The result showed that DHDBS can induce α crystal and increase the degree of crystallization of IPP. The melting peak of IPP analyzed by differential scanning calorimetry (DSC) was raised. It explains that crystalline perfect degree of PP were increased. Thermo-gravimetric (TG) analysis showed that adding DHDBS can improve the stability of IPP. Mechanical properties of IPP, which were measured by use of impact test enginery and micro-computer control universal test machine, were improved. And the optimal amount of nucleating agent was 0.3wt %.

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Keywords: isotactic polypropylene; nucleating agent; crystallization properties; mechanical properties

1. Introduction

Isotactic polypropylene (IPP) is one of the most important commercial thermoplastics because of its relatively low cost, versatility, recyclability and good mechanical performance in engineering applications. However, IPP also has its own disadvantages such as low impact strength, especially at a low temperature, toughness and notch-sensitive, which limit its application range. This paper finds out an efficient way to overcome the disadvantages of IPP. That is to add the nucleating agent to semicrystalline polymers, so that the nucleating agent will control crystallization process of IPP [1]. Nucleating agents provide a large number of nuclei, which can significantly modify the crystallization behaviour of IPP, for example, accelerate formation of crystalline, decrease spherulites dimensions and increase crystallinity, thus improve the thermal and mechanical properties [2-4].

As efficient nucleating agents, sorbitol derivatives have abilities to make the α crystal form of IPP. This point is well known and has been thoroughly investigated [5-8]. In contrast with many other

nucleating agents, the sorbitol derivatives are designed to dissolve and recrystallize in the melted polymer, causing the formation of a well-dispersed, large surface area, tridimensional nanofibrillar network [9].

The main objective of this study is to investigate the influence of nucleating agent 1, 3-2, 4-di (p-hydroxyl) benzylidene sorbitol (DHDBS) on crystallization, thermal and mechanical properties of PP.

2. Experiments

2.1. Materials

The isotactic polypropylene was purchased from Lanzhou petrochemical company in china. The nucleating agent 1, 3-2, 4-di (p-hydroxyl) benzylidene sorbitol (DHDBS) was synthesized in our laboratory, and was characterized by melting point detector and Fourier transform infrared spectrometer. P-xylylene (supplied by Shanghai crystal pure reagent Co. Ltd.) was used in this study. Ethyl alcohol was purchased from Damao chemical reagent company in Tianjin.

2.2. Specimen preparation

The solution of 20g/L was prepared by a solution/precipitation method, dissolving PP mixed with various concentrations of DHDBS (0.1 wt%, 0.2 wt%, 0.3 wt%, 0.4 wt%, 0.5 wt%) in p-xylylene at 130°C for 30min, then quickly pouring them into beaker and cooling them down to room temperature. The solution was added into ethyl alcohol, filtered and dried at 80°C for 24h. Finally, the specimen was used to measure crystallization, thermal properties.

IPP was mixed with various concentrations of DHDBS (0.1 wt%, 0.2 wt%, 0.3 wt%, 0.4 wt%, 0.5 wt%) firstly, then extruded with SHJ-36 co-rotating twin-screw extruder under a nitrogen blanket. The screw rotation speed was 85.8 r/min. Temperatures of nine control zones of the extruder were maintained at 170°C, 175°C, 180°C, 190°C, 190°C, 185°C and 180°C from hoppers to die. After pelletized and dried, the extruded specimens were compression molded in an injection molding machine at temperatures of four zones of 180°C, 185°C, 190°C and 180°C and at the pressure of 60MPa. Then the compressed specimens were used to measure mechanical properties.

2.3. Polarization microscope (PLM)

Crystallization morphology was surveyed by BK-POL polarization microscope. For the isothermal crystallization tests, the films were first heated on a hot stage from room temperature to 200°C at a heating rate of 10°C/min and were pressed with cover glass and then were moved rapidly into vacuum constant temperature drying oven at 120°C for 2 hours.

2.4. Scanning electron microscope (SEM)

Surfaces of the samples were characterized by HITACHI SU1500 scanning electron microscope. Samples were dried for 24h and fixed on a sample platform.

2.5. X-ray diffraction (XRD)

The XRD tests of the samples were carried out on a Rigaku D/max—RB instrument. A conventional CuK α X-ray tube at a voltage of 40 kV and a filament current of 50mA was used to obtain the XRD spectra. The scanning 2 θ range was from 5° to 45° with a scanning rate of 5°/min.

2.6. Differential scanning calorimeter (DSC)

DSC scanning of the samples was performed on a NETZSCH STA 449 C differential scanning calorimeter in a nitrogen atmosphere. The sample weight was about 5.536 mg. The temperature range of the test was set as 30~230°C. To determine the melting behavior of these samples, the scanning speed was set as 10°C/min from 30 to 230°C. After the first heating run the sample was kept at 230°C for 5 minutes to erase the thermal history of processing. Melting temperatures were measured and DSC thermograms were recorded.

2.7. Thermogravimetric analysis (TG)

Thermogravimetric analysis (TG) of the samples was performed on a NETZSCH STA 449 C thermogravimetric analyzer in a nitrogen atmosphere. The sample weight was about 5.536 mg. The temperature range of the test was set as 30~550°C. The scanning speed was set as 10°C/min from 30 to 230°C. During each run the sample was kept at the highest temperature for 5 minutes before cooling in order to ensure complete melting of the polymer and prevent self nucleation. The decomposition temperatures of these samples were measured and TG curves were recorded.

2.8. Mechanical properties

Three different dimensions of specimens, 80×10×4 mm, dumbbell-shaped 4.1×2 mm and 6.36×2.87 mm, were prepared by an injection molding machine, and were used for the impact strength, tensile properties and bending properties tests respectively.

Following the GB/T 1843-1980 standards, the impact strength was tested by the notched Izod impact method, using XJU-22 impact test machinery at room temperature, at the impact speed of 3.46 m/s, toss energy corrected in all cases and drop height fixed at 61.0 cm. Both tensile properties (following the GB/T 1040-1992 standard) and bending properties (following GB/T 9341-2000 standard) were measured by CMT6104 micro-computer control universal test machine. The samples for tensile tests were stretched at room temperature, at the initial gauge length of 25 mm, at a constant elongation speed of 50 mm/min. The tensile stress was determined by dividing the tensile load by the initial cross-section. The tensile strain was calculated by the ratio of the increment of the length between clamps to the initial gauge length. The mean values reported are derived from at least seven parallel tests. The samples for bending tests were bended at crosshead speed of 20 mm/min and span of specimens was 48 mm.

3. Results and discussion

3.1. Crystallization morphology

The concentration effects of the nucleating agent on crystallization morphology of IPP are presented in Fig.1. The spherulite structure of pure IPP is typically radial shapes growing along the radial direction. The spherulites dimensions first diminish. With the nucleating agent DHDBS increasing, spherulites dimensions increases and reaches a maximum at a critical value (0.3 wt% DHDBS), even only large numbers of spots are seen, but then with DHDBS concentration further increasing, the dimensions increases. The reason is that hydroxyl of DHDBS permits the formation of a well-dispersed, large surface area, tridimensional nanofibrillar network by the hydrogen bonding interaction. So the nucleating agent displays a heterogeneous nucleation effect, supplies a large number of nuclei, and enhances crystallization rate of IPP. However, it does not enhance the crystallization of the polymer at high additive concentrations, as it reunites with these compositions [10]. Polarization microscopy studies have confirmed that as a nucleating agent, DHDBS acts at low concentrations. At the content of 0.3wt% of DHDBS, the spherulites dimensions have been found to minimize.

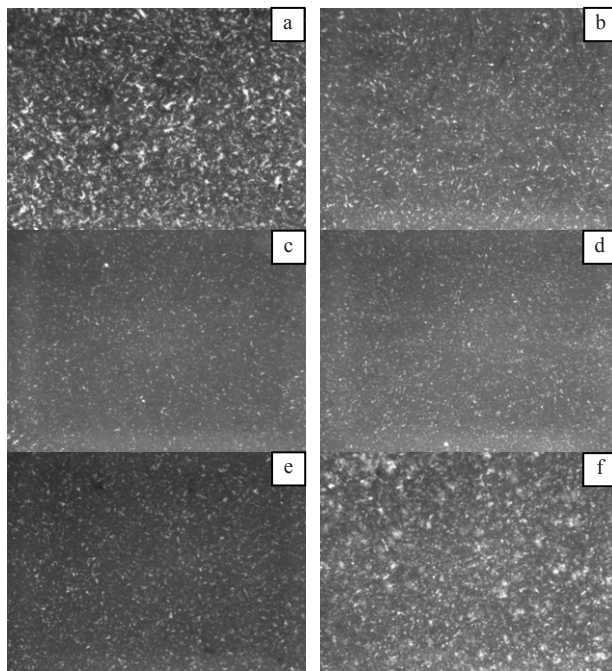


Fig.1 Polarizing microscope of pure IPP(a), IPP with 0.1wt% DHDBS (b), IPP with 0.2wt% DHDBS (c), IPP with 0.3wt% DHDBS (d), IPP with 0.4wt% DHDBS (e), IPP with 0.5wt% DHDBS (f)

Fig.2 shows the appearances of IPP and nucleated IPP (0.3wt% DHDBS), respectively. It is obvious to see that spherulites of IPP with DHDBS have uniform dimensions and neat arrangement. Spherulites dimensions are about $12\mu\text{m}$. However, the largest and smallest spherulites can be observed for pure IPP. Spherulites stop growing when they collide with each other. Homogeneous nucleation, which is mainly crystallization behavior of pure IPP, supplies small amounts of nuclei. So pure IPP gets lower probability of collision, and its spherulites dimensions are larger than modified IPP.

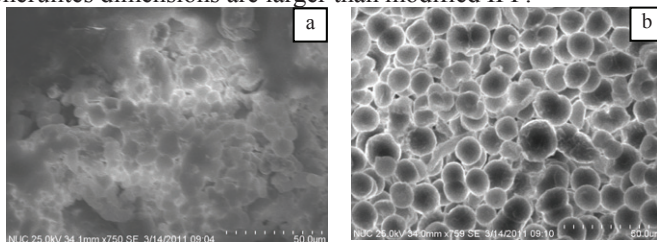


Fig.2 SEM of pure IPP(a) and IPP with 0.3wt% DHDBS (b)

X-ray diffraction measurements are showed in Fig.3. It reveals that pure IPP and IPP with 0.3 wt% DHDBS crystallize in the monoclinic α -form at the diffraction angles $2\theta=14.2^\circ$, 17.1° , 18.6° , 21.2° , 21.9° , which respectively correspond to the (110), (040), (130), (131) and (111) planes of IPP. Degrees of crystallization were obtained by use of MDI Jade 5.0 software and computational multi-peak procedure and they are shown in table 1. The result has showed that the degrees of crystallization of IPP increase by 17.48% with addition of 0.3wt% DHDBS. It also has indicated that DHDBS effectively induces the formation of α -crystals in IPP [11].

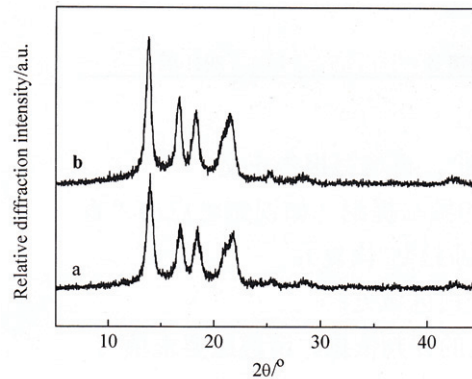


Fig.3 XRD of pure IPP (a) and IPP with 0.3wt% DHDBS (b)

3.2. Thermal properties

In Fig.4, DSC melting behaviors of IPP and IPP with the 0.3wt% nucleating agent DHDBS are shown. From the curves, it can be observed that melting peak of IPP with 0.3wt% nucleating agent DHDBS increases by about 3°C, the melting peak is sharper, and the range of melting temperatures is narrower than that of pure IPP. The thermal stability of samples was measured by TG. The result was showed in Fig.5. It can be seen that decomposition temperature of IPP increases by 36°C. Segmental activity becomes higher, which benefits the formation of more perfect crystallization in such a temperature. Thus addition of 0.3wt% DHDBS can improve crystallinity and crystallization perfect degree of IPP. Consequently, it has improved the thermal stability of IPP. DSC and TG analysis have revealed that the thermal stability of IPP is significantly affected by addition of 0.3wt% DHDBS.

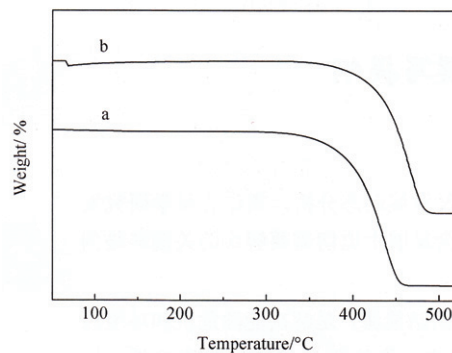
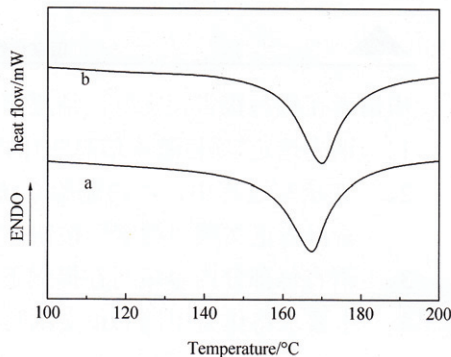


Fig.4 DSC of pure IPP (a) and IPP with 0.3wt% DHDBS (b) Fig.5 TG of pure IPP (a) and IPP with 0.3wt% DHDBS (b)

3.3. Mechanical properties

The mechanical properties of compression molded IPP samples comprising DHDBS were investigated for blends comprising from 0 to 0.4wt% of the additive. When DHDBS was added into IPP matrix, an increase in the notched Izod impact strength, elongation at break, tensile strength, flexural modulus and flexural strength of IPP was detected. At this time, concentrations of the nucleating agent DHDBS were equal to or higher than 0.1wt%. Furthermore, a slight decrease was found for samples containing more than 0.3wt% DHDBS. It has revealed that the addition of 0.3wt% DHDBS greatly improves toughness of the

IPP. When 0.3wt% DHDBS was added into IPP, the notched Izod impact strength, elongation at break, tensile strength, and flexural strength of IPP were increased by 19.37%, 44.94%, 69.59%, 47.87% and 85.34%, respectively.

These results of the mechanical properties are in general accord with the crystallization properties presented above. Generally, mechanical properties of crystalline PP depend on the degree of crystallinity, the dimensions and distribution uniformity of spherulites. The fineness of the crystal grain must be beneficial to impact strength. Furthermore, the nucleating agent impels the degree of orientation of the polymer and improves the crystallization rate, retards the relaxation of the cooling process of the polymeric melt. This will produce a more tied-molecule structure among the intra- and inter-spherulite to improve the molecular entanglement between the crystal grains. Therefore, the boundary strength between spherulites increases, thus it will be beneficial to the improvement of the impact strength of the materials. Adding the nucleating agent makes the number of nuclei increasing, crystallization rate accelerating, spherulite dimensions decreasing, particle dimensions distribution of crystallization uniformed, which eliminate the phenomenon of stress concentration under loading. It has demonstrated that crystallization properties of the IPP are directly related to mechanical properties of IPP [12].

4. Conclusions

In this study, properties of IPP with nucleating agent 1, 3-2, 4-di (p-hydroxyl) benzylidene sorbitol (DHDBS) are investigated. The result has showed that DHDBS is an effective nucleating agent. It can greatly improve crystallization properties, such as uniform spherulites dimensions, neat arrangement and high crystallinity. 0.3wt% DHDBS improves crystallinity and crystallization perfect degree of IPP, so increase melting peak and decomposition temperature and improve the thermal stability of IPP. Mechanical properties of IPP are related to crystallization properties. Due to addition of DHDBS, the notched Izod impact strength, elongation at break, tensile strength, and flexural strength of IPP are increased by 19.37%, 44.94%, 69.59%, 47.87% and 85.34% respectively. And the optimal amount of nucleating agent was 0.3wt %.

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References

- [1] B. Z. Luo, J. Zhang, X. L. Wang, Y. Zhou, and J. Z. Wen, "Effects of nucleating agents and extractants on the structure of polypropylene microporous membranes via thermally induced phase separation," *Desalination*, vol. 192, pp. 142-150, May, 2006.
- [2] N. Fanegas, M. A. Gómez, C. Marco, I. Jiménez, and G. Ellis, "Influence of a nucleating agent on the crystallization behaviour of isotactic polypropylene and elastomer blends," *Polymer*, vol. 48, pp. 5324-5331, August, 2007.
- [3] J. Výchopňová, R. Čermák, M. Obadal, M. Raab, V. Verney, and S. Commereuc, "The role of specific nucleation in polypropylene photodegradation," *Polymer Degradation and Stability*, vol. 92, pp. 1763-1768, October 2007.
- [4] P. Y. Zhang, X. X. Liu, Y. Q. Li, "Influence of β -nucleating agent on the mechanics and crystallization characteristics of polypropylene," *Materials Science and Engineering: A*, vol. 434, pp. 310-313, October 2006.
- [5] Y. P. Huang, G. M. Chen, Z. Yao, H. W. Li, and Y. Wu, "Non-isothermal crystallization behavior of polypropylene with nucleating agents and nano-calcium carbonate," *European Polymer Journal*, vol. 41, pp. 2753-2760 November 2005.
- [6] A. Menyhard, M. Gahleitner, J. Varga, K. Bernreiter, P. Jääskeläinen, H. Øysæd, and B. Pukánszky, "The influence of nucleus density on optical properties in nucleated isotactic polypropylene," *European Polymer Journal*, vol. 45, pp. 3138-3148, November 2009.

- [7] Q. Shi, C. L. Cai, Z. Ke, L. G. Yin, Y. L. Liu, L. C. Zhu, and J. H. Yin, "Effect of the nucleating agent 1,3:2,4-di(3,4-dimethylbenzylidene) sorbitol on the γ phase content of propylene/ethylene copolymer," *European Polymer Journal*, vol. 44, pp. 2385-2391, July 2008.
- [8] M. Raab, Š. Jaroslav, and K. Jan, "The effect of specific nucleation on tensile mechanical behaviour of isotactic polypropylene," *European Polymer Journal*, vol. 40, pp. 1317-1323, July 2004.
- [9] K. Bernland, T. Tervoort, and P. Smith, "Phase behavior and optical- and mechanical properties of the binary system isotactic polypropylene and the nucleating/clarifying agent 1,2,3-trideoxy-4,6:5,7-bis-O-[(4-propylphenyl) methylene]-nonitol," *Polymer*, vol. 50, pp. 2460-2464, May 2009.
- [10] T. Xu, H. Lei, and C. S. Xie, "The effect of nucleating agent on the crystalline morphology of polypropylene (PP)," *Materials & Design*, vol. 24, pp.227-230, May 2003.
- [11] J. W. Housmans, M. Gahleitner, G. W. M. Peters, and H. E. H. Meijer, "Structure–property relations in molded, nucleated isotactic polypropylene," *Polymer*, vol. 50, pp. 2304-2319, May 2009.
- [12] K. H. Nitta, and K. Odaka, "Influence of structural organization on tensile properties in mesomorphic isotactic polypropylene," *Polymer*, vol. 50, PP. 4080-4088, July 2009.