Influence of Nucleating Agent on Properties of Isotactic Polypropylene

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

Keywords: Isotactic polypropylene, Nucleating agent, Crystallization properties, Mechanical properties.

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, isotactic polypropylene 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 provides an efficient way to overcome the disadvantages of isotactic polypropylene. That is to add the nucleating agent to semicrystalline polymers, so that the nucleating agent will control crystallization process of isotactic polypropylene[1]. Nucleating agents provide a large number of nuclei, which can significantly modify the crystallization behaviour of isotactic polypropylene, 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 crystalline form of isotactic polypropylene. 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*-hydroxy)benzylidene sorbitol (DHDBS) on crystallization, thermal and mechanical properties of polypropylene.

EXPERIMENTAL

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

Specimen preparation: The solution of 20 g/L was prepared by a solution/precipitation method, dissolving polypropylene mixed with various concentrations of DHDBS (0.1, 0.2, 0.3, 0.4, 0.5 and wt. %) in *p*-xylene at 130 °C for 30 min, 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 24 h. Finally, the specimen was used to measure crystallization and thermal properties.

Isotactic polypropylene was mixed with various concentrations of DHDBS (0.1, 0.2, 0.3, 0.4, and 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 rpm. Temperatures of nine control zones of the extruder were maintained at 170, 175, 180, 190, 190, 190, 185 and 180 °C from hoppinger to die. After pelletized and dried, the extruded specimens were compression molded in an injection molding machine at temperatures of four zones of 180, 185, 190 and 180 °C and at the pressure of 60 MPa. Then mechanical properties of the compressed specimens were measured.

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 plate 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 h.

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

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 50 mA was used to obtain the XRD spectra. The scanning 2θ range was from 5° to 45° with a scanning rate of 5°/min.

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 min to erase the thermal history of processing. Melting temperatures were measured and DSC thermograms were recorded.

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 min 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.

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 enginery 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 were 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.

RESULTS AND DISCUSSION

Crystallization morphology: The concentration effects of the nucleating agent on crystallization morphology of isotactic polypropylene are presented in Fig. 1. The spherulite structure of pure isotactic polypropylene is typically radial shapes growing along the radial direction. The spherulites dimensions first diminish. With the increasing of nucleating agent DHDBS, 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 hydroxy group 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
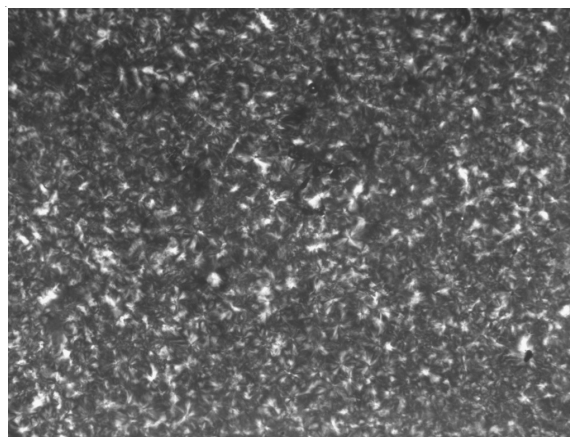

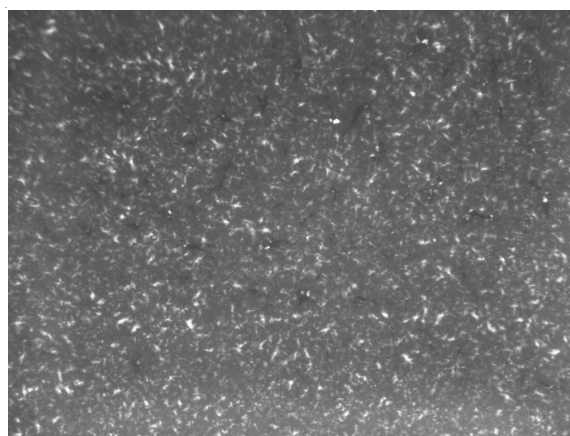
Fig. 1. (a) PLM of pure isotactic polypropylene

Fig. 1. (b) PLM of isotactic polypropylene with 0.1 wt. % nucleating agent DHDBS

Fig. 1.   (c) PLM of isotactic polypropylene with 0.2 wt. % nucleating agent DHDBS

Fig. 1.   (d) PLM of isotactic polypropylene with 0.3 wt. % nucleating agent DHDBS
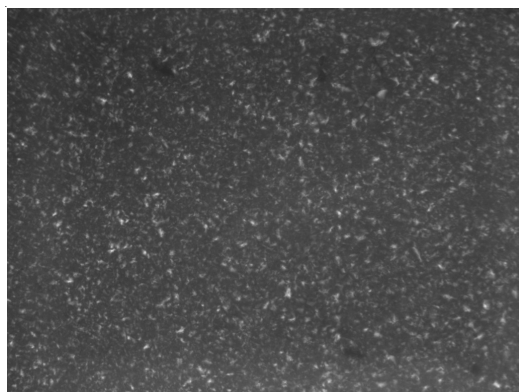

Fig. 1.   (e) PLM of isotactic polypropylene with 0.4 wt. % nucleating agent DHDBS
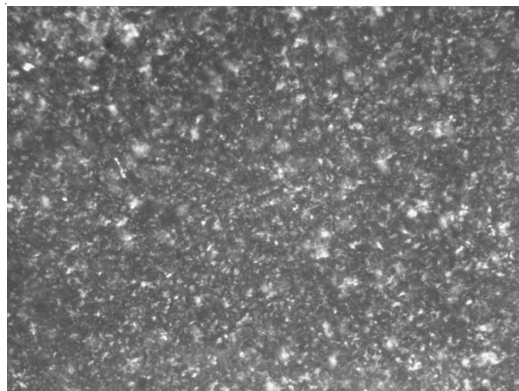

Fig. 1.   (f) PLM of isotactic polypropylene with 0.5 wt. % nucleating agent DHDBS

isotactic polypropylene. 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 0.3 wt. % of DHDBS, the spherulites dimensions has been found to minimize.

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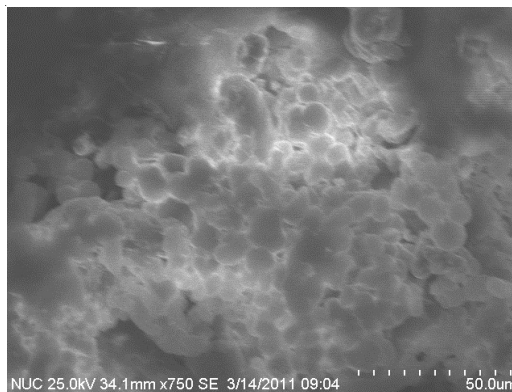

Fig. 2. (a) SEM of pure isotactic polypropylene
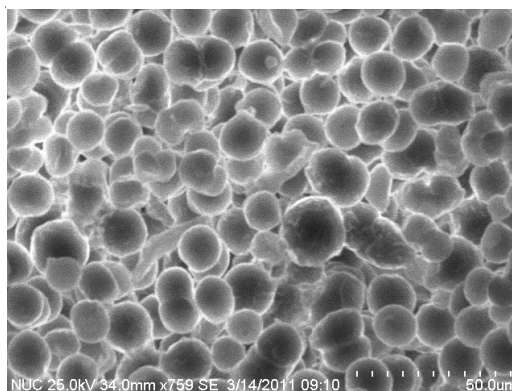

Fig. 2.   (b) SEM of isotactic polypropylene with 0.3 wt. % nucleating agent DHDBS

X-ray diffraction measurements are shown in Fig. 3. It reveals that pure isotactic polypropylene and isotactic polypropylene with 0.3 wt. % DHDBS crystallize in the monoclinic α-form at the diffraction angles $2\theta = 14.2°$, $17.1°$, $18.6°$, $21.2°$, $21.9°$, which respectively correspond to the (110), (040), (130), (131) and (111) planes of isotactic polypropylene. 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 shown that the degrees of crystallization of isotactic polypropylene increase by 17.48 % with

TABLE-1
DEGREES OF CRYSTALLIZATION OF SAMPLES

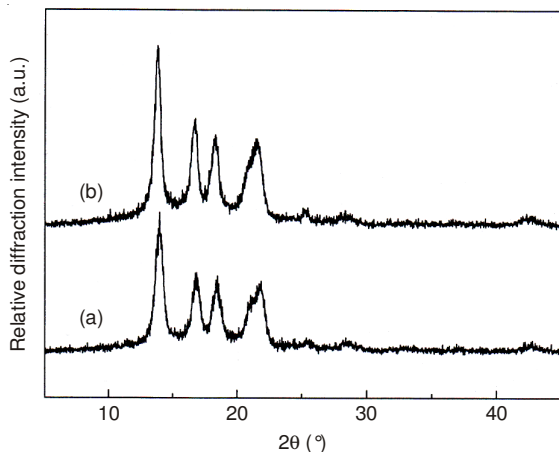| Sample	Degrees of crystallization (%)
Pure isotactic polypropylene	45.03
Isotactic polypropylene with 0.3 wt. % DHDBS	62.51

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

addition of 0.3 wt. % DHDBS. It also has indicated that DHDBS effectively induces the formation of α-crystals in isotactic polypropylene[11].

Thermal properties: In Fig. 4, DSC melting behaviors of isotactic polypropylene and isotactic polypropylene with the 0.3 wt. % nucleating agent DHDBS are shown. From the curves, it can be observed that melting peak of isotactic polypropylene with 0.3 wt. % 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 isotactic polypropylene. The thermal stability of samples was measured by TG. The result was shown in Fig. 5. It can be seen that decomposition temperature of isotactic polypropylene increases by 36 °C. Segmental activity becomes higher, which benefits the formation of more perfect crystallization in such a temperature. Thus addition of 0.3 wt. % DHDBS can improve crystallinity and crystallization perfect degree of isotactic polypropylene. Consequently, the thermal stability of isotactic polypropylene
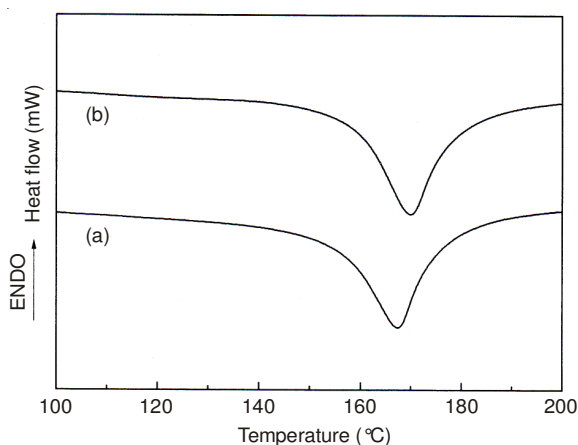

Fig. 4.   DSC of pure isotactic polypropylene (a) and isotactic polypropylene with 0.3 wt. % DHDBS (b)
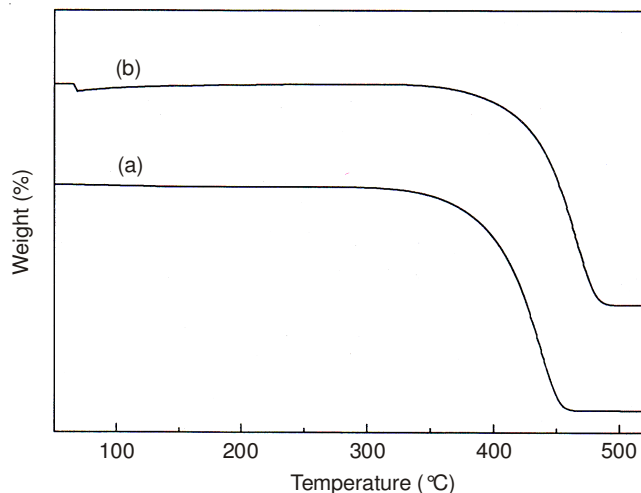

Fig. 5.   TG of pure isotactic polypropylene (a) and isotactic polypropylene with 0.3 wt. % DHDBS (b)
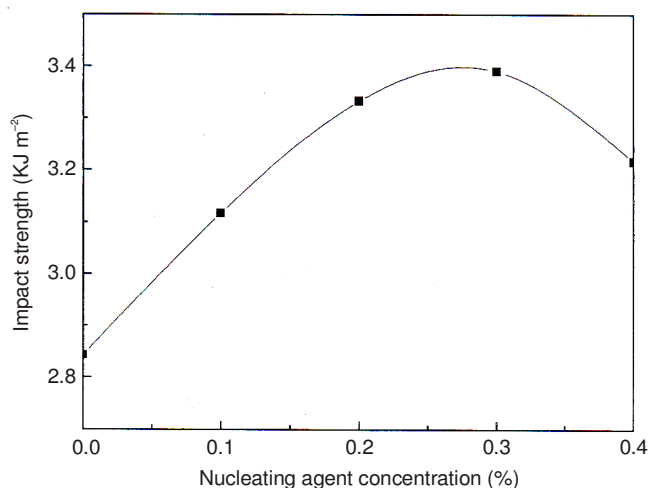

Fig. 6.(a) Effect of nucleating agent concentration on impact strength of isotactic polypropylene
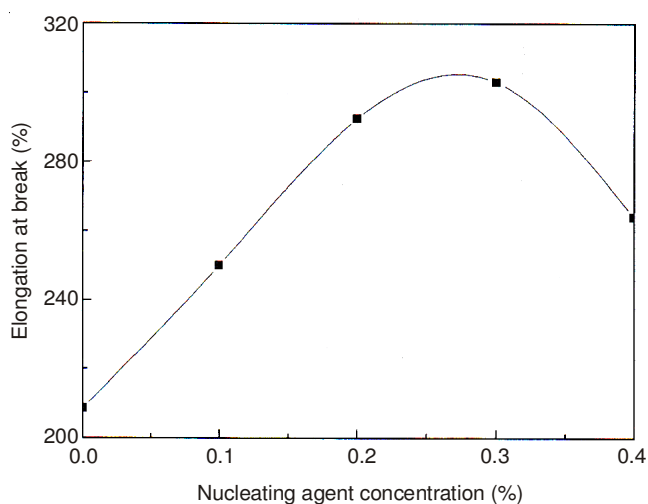

Fig. 6. (b) Effect of nucleating agent concentration on elongation at break of isotactic polypropylene

was improved. DSC and TG analysis have revealed that the thermal stability of isotactic polypropylene is significantly affected by addition of 0.3 wt. % DHDBS.
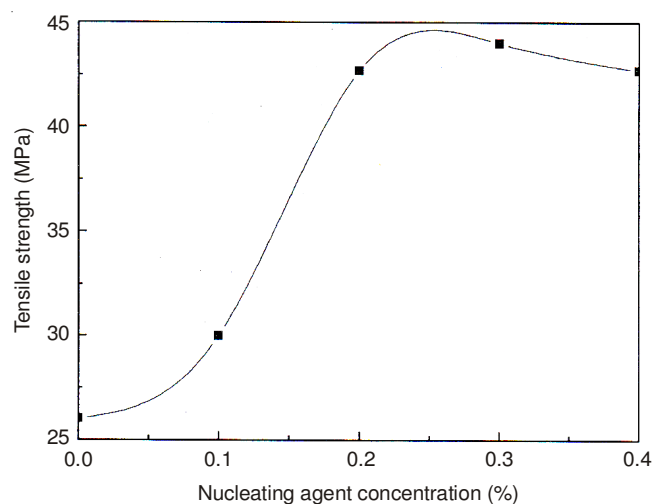
Fig. 6. (c) Effect of nucleating agent concentration on tensile strength of isotactic polypropylene
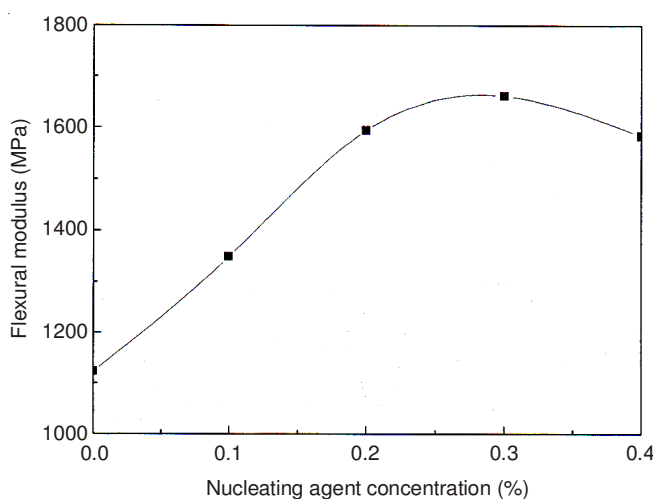

Fig. 6. (d) Effect of nucleating agent concentration on flexural modulus of isotactic polypropylene
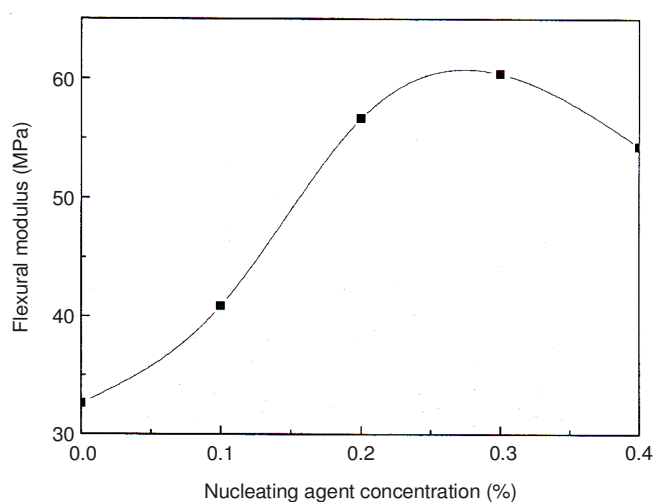

Fig. 6. (e) Effect of nucleating agent concentration on flexural strength of isotactic polypropylene

Mechanical properties: The mechanical properties of compression molded isotactic polypropylene samples containing 0 to 0.4 wt. % of DHDBS were investigated. The results

are presented in Fig. 6. When DHDBS was added into isotactic polypropylene matrix, an increase in the notched Izod impact strength, elongation at break, tensile strength, flexural modulus and flexural strength of isotactic polypropylene was detected. At this time, concentrations of the nucleating agent DHDBS were equal to or higher than 0.1 wt. %. Furthermore, a slight decrease was found for samples containing more than 0.3 wt. % DHDBS. It has revealed that the addition of 0.3 wt. % DHDBS greatly improves toughness of the isotactic polypropylene. When 0.3 wt. % DHDBS was added into isotactic polypropylene, the notched Izod impact strength, elongation at break, tensile strength and flexural strength of isotactic polypropylene 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 polypropylene 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 isotactic polypropylene are directly related to mechanical properties of isotactic polypropylene[12].

Conclusion

In this study, properties of isotactic polypropylene 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. 0.3 wt. % DHDBS improves crystallinity and crystallization perfect degree of isotactic polypropylene, so increase melting peak and decomposition temperature and improve the thermal stability of isotactic polypropylene. Mechanical properties of isotactic polypropylene are related to crystallization properties. Due to addition of DHDBS, the notched Izod impact strength, elongation at break, tensile strength and flexural strength of isotactic polypropylene are increased by 19.37, 44.94, 69.59, 47.87 and 85.34 %, respectively. And the optimal amount of nucleating agent was 0.3 wt. %.

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