Influence of heterogeneous nucleation on thermodynamic properties of isotactic polypropylene

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In this paper we have investigated the effect of 1,2,3-trideoxy-4,6:5,7-bis-O-[(4-propylphenyl)methylene]-nonitol sorbitol used in varying amounts (0.01 – 1 wt %) on isotactic polypropylene (iPP) matrix. We have used dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) to study glass transition temperatures and crystallinity as a function of the nucleating agent concentration. Isotactic polypropylene samples showed a strong dependency on amount of α nucleating agent used. An increasing content of sorbitol based nucleating agent led to an increase of crystallization temperature upon cooling from the melt at constant rate and a decrease of the glass transition temperatures.

Keywords: isotactic polypropylene, PP, heterogeneous, nucleation, modification, sorbitol, DMTA, DSC.

INTRODUCTION

Relatively low prices and good mechanical properties have made isotactic polypropylene one of the most often used thermoplastic polymeric material[1, 2]. Due to its high level of crystallinity and good processability, many applications are possible and definitely not limited just to injection molding processes[2–5]. However, there is still a wish to improve the mechanical properties of iPP that leads to a further improvement of products quality without increasing the costs and simplifying the production. One the most common modification method is a heterogeneous nucleation which causes changes in a polymer structure but requires the addition of nucleating agents (NAs)[2, 4–9]. They are additives which provide additional nuclei that accelerate crystallization process and promote nucleation for crystal growth[2]. As a result, a larger amount of smaller spherulites is generated. High efficiency of nucleating agents allows to add even very small amounts of NAs into polymer matrix (15 to 30 · 10^4 ppm) to gain specified properties[1–3]. The economical aspect of nucleation is a lower crystallization time that results in a higher processing efficiency and more beneficial production. Moreover, the use of NAs in specific conditions leads to a modification of a crystal structure, i.e. the possibility of various crystallographic forms creation, such as α, β or γ in isotactic polypropylene[1–12].

Among many α nucleating agents widely used in industry like sodium benzoate or quinacridone ER01 and E5B, the most effective ones are the derivates of sorbitol. From the chemical point of view they are condensation products of two substrates: aromatic aldehyde and sorbitol[2]. The biggest benefit resulting from sorbitol derivatives activity, apart from changing the crystallographic structure and properties, is gaining a transparent polymer matrix which indicates that the sorbitols also act as clarifying agents[2, 7, 12].

We performed the dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) to describe the influence of nucleating agent on crystallization and glass transition temperatures of modified polymer matrix. The DMTA method was used to determine the glass transition temperatures, while the DSC method was applied to obtain the required information about the crystallization processes[6, 13–16].

The aim of our studies was to define the influence of the sorbitol based nucleating agent addition on the thermomechanical properties of modified isotactic polypropylene.

EXPERIMENTAL

Materials

The commercial isotactic polypropylene (iPP) Moplen HP456J, with a MFR = 3.4 g/10 min (230°C, 2.16 kg) from the Basell Orlen Polyolefins (Poland) was used in our experiments. The selected polymeric matrix is characterized by a low modification level and is defined as suitable for thermoforming applications.

The nucleating agent was 1,2,3-trideoxy-4,6:5,7-bis-O--[(4-propylphenyl)methylene]-nonitol sorbitol, Millad, abbreviated NX8000, by the Milliken Chemical Company (USA) used as a clarifying agent. The chemical formula of the nucleating agent is presented in Figure 1.

The preliminary thermogravimetric investigations (TGA) proved that the NX8000 5 wt % mass loss occurred at 292.8°C. This allowed for a statement that the nucleating agent was thermally stable at commonly used iPP processing temperatures (190–230°C).
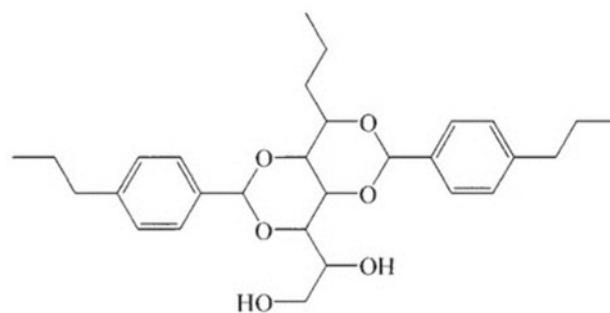
Figure 1. The chemical formula of 1,2,3-trideoxy-4,6:5,7-bis--O-[(4-propylphenyl)methylene]-nonitol sorbitol

Sample preparation

Before mixing in a molten state, iPP pellets were milled into powder in a Tria high-speed grinder. Then iPP and NX8000 powders were premixed using the high speed rotary mixer Retsch GM200 (t = 3 min, n = 6000 rpm) with different amounts of nucleating agent (0; 0.01; 0.05; 0.1; 0.25; 0.5; 1 wt %). Next, all blends were mixed in a molten state using the ZAMAK twin screw extruder operated at 190ºC and 80 rpm, and pelletized after cooling in a water bath. The screws were configured to process polyolefins with a low amount of additives. The specimens were prepared with the Battenfeld Plus 35T injection molding machine. After the injection molding process, all specimens were conditioned for 3 days prior to further tests.

Differential Scanning Calorimetry (dsc)

The DSC was performed using the Netzsch DSC 204 F1 Phoenix® with aluminum crucibles and approximately 5 mg samples, under a nitrogen flow. All of the samples were heated up to 230°C and held in a molten state for 5 min, followed by cooling down to 20°C. The heating and cooling rates were equal to 10°C/min. This procedure was conducted twice to evaluate the DSC curves obtained from the second melting procedure and gain broad information about iPP matrix modification.

Dynamic Mechanic Thermal Analysis (DMTA)

The DMTA tests were run on the Anton Paar MCR 501 rheometer equipped with a torsion DMA measuring tool. Investigations were carried out with a constant frequency of 1 Hz and a strain of 0.01%. All samples were cooled down to –30ºC and heated up to 140ºC with a temperature ramp of $\Phi = 2$°C/min.

RESULTS AND DISCUSSION

Crystallization and melting behavior by DSC

The DSC calorimetric investigations were intended to describe the effect of NX8000 addition on the crystallization processes. Crystallization and melting behavior of pure iPP and of nucleated one were obtained during the first cooling and also during the second heating carrying out non-isothermal differential scanning calorimetry measurements. No considerable influence of the nucleating agent upon the melting temperature of iPP was observed. DSC crystallization curves are presented in Figure 2 a, b. A significant rise of crystallization temperature in a function of increasing content of the NX8000 nucleating agent was denoted. A dependence of T_c on the amount of nucleating agent is presented in Figure 3. The crystallization efficiency is similar to that obtained for other sorbitol based nucleating agents, such as DBS or DMDBS. Characteristic features observed for all sorbitol based NAs are: a strong increase of crystallization temperature for a content of NA equal to 0.25 wt %[7] and a clarifying effect that was observed during a simple visual examination. The values of crystallization temperature determined for samples that contained different amounts of the nucleating agent were measured from peaks occurring in the DSC cooling curves.
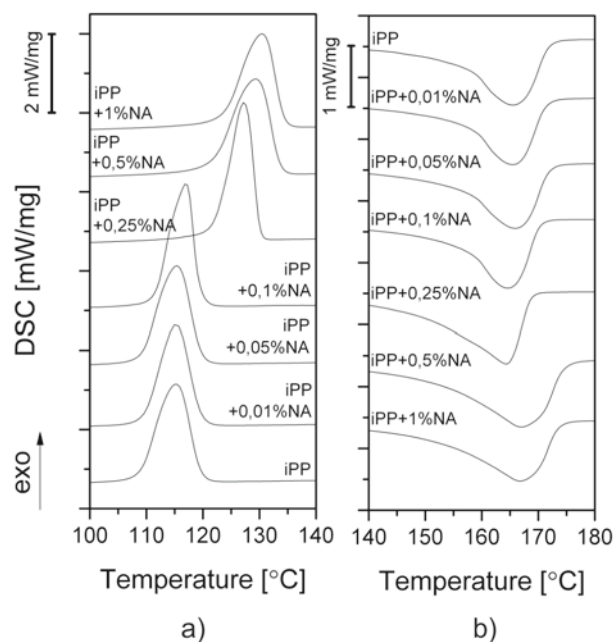

Figure 2. DSC crystallization (a) and melting (b) curves of nucleated iPP

The melting parameters were calculated from thermograms recorded in the course of the second heating of considered samples. The values of temperature at the end of DSC melting process (T_{MP}) (corresponding to a maximum on the melting curve), the melting point determined as an inflexion point of the derivative of DSC melting curve presenting the temperature of the highest efficiency of melting process (T_M), the difference between melting points (T_{MP}-T_M), the melting heat of crystallization (ΔH_m) and the degree of crystallinity are listed in Table 1. The crystallinity degree of nucleated and non-nucleated samples was evaluated using the melting heat of crystallization with the following equation (1):

$$X_C = \frac{\Delta H_M}{\Delta H_O} \qquad (1)$$

where ΔH_o is the melting heat of entirely crystallized iPP, and its value is equal to 207,1 J/g[1, 3, 9, 13, 17].

We have to emphasize that the addition of nucleating agent did not provide a significant increase of melting temperature. However, a difference between two melting points determined in two different ways (i.e. the difference of the melting temperature obtained from a
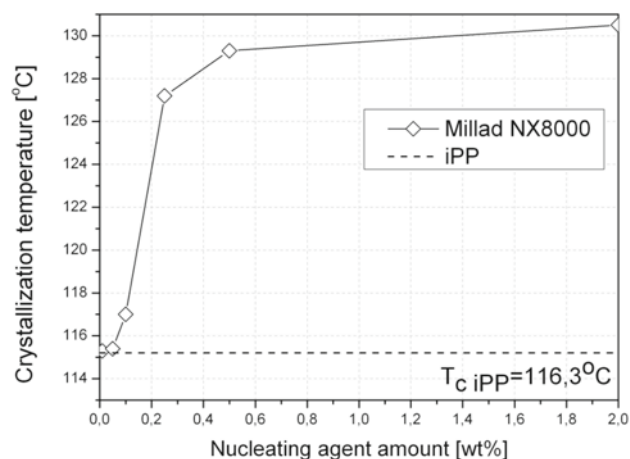

Figure 3. The crystallization temperature versus NX8000-nucleated iPP

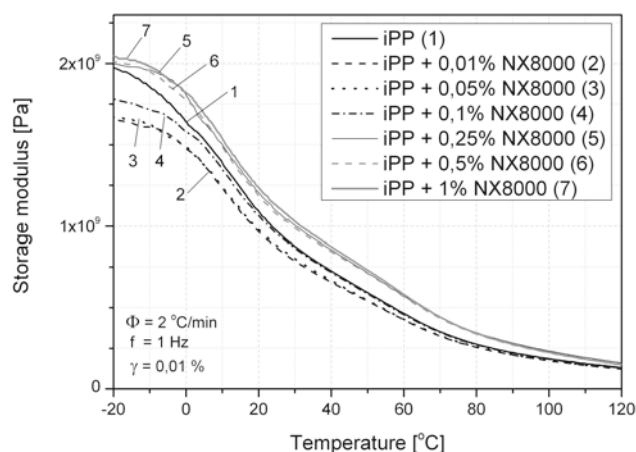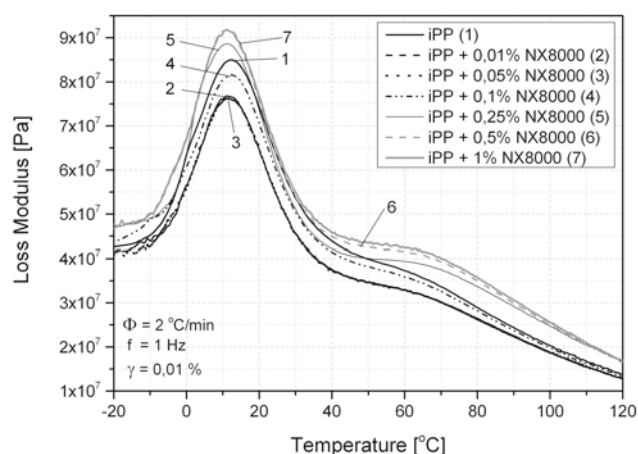**Table 1.** Non-isothermal crystallization parameters of iPP and nucleated iPP in the heating process

Specimen	ΔH_m [J/g]	T_{MP} [°C]	T_M [°C]	$T_{MP}-T_M$ [°C]	Xc [%]
iPP	94.97	165.5	160.5	5	45.85
iPP + 0.01% NX8000	92.41	165.6	160.8	4.8	44.62
iPP + 0.05% NX8000	94.69	166	160.7	5.3	45.72
iPP + 0.1% NX8000	91.81	164.7	160.8	3.9	44.33
iPP + 0.25% NX8000	105.9	164.4	161.7	2.7	51.13
iPP + 0.5% NX8000	117.3	166.9	164.8	2.1	56.63
iPP + 1% NX8000	109.9	166.9	163.9	3	49.20

DSC curve peak and the melting temperature obtained from an inflexion of DDSC curve that corresponded to the point of the highest melting process efficiency) showed a downward trend which can be assigned to more uniform structure of nucleated polypropylene due to heterogeneous nucleation. We obtained the highest crystallinity level for the sample that contained 0.5 wt % of NX8000 which was the most suitable amount of nucleating agent. The presence of sorbitol derivatives resulted in a formation of a fibrillar network during crystallization[7]. In the case of a low amount of nucleating agent the density of a fibrillar network did not limit the mobility of iPP during crystallization, therefore, the increase of crystallinity degree was observed. Whereas, the addition of the NX8000 equal to 1 wt % obstructed the mobility of macromolecular chains and suppressed macromolecular segmentation due to a formation of the fibrillar network of the sorbitol nucleating agent.

Thermomechanical properties

The results of thermomechanical investigations conducted by DMTA in a torsion mode, for non-nucleated and nucleated samples, in a form of graphs showing storage and loss modulus in relation to temperature are presented in Figure 4 and 5.

The addition of nucleating agent influenced the sample's behavior which depended on the amount of nucleating agent applied. For samples that contained less than 0.25 wt % of NX8000 the storage modulus (Fig. 4) was lower than for the non-nucleated sample. However, it should be acknowledged that the behavior of 0.1 wt % of NX8000 sample was similar to the pure iPP. The difference between the storage modulus of both materials was decreasing in a function of increasing temperature. The storage modulus for samples that contained more

Figure 5. The loss modulus of non-nucleated and α-nucleated iPP samples as a function of temperature during the DMTA test in a torsion mode

than 0.25 wt % of nucleating agent was higher than for the pure iPP, and their values were similar across the entire temperature range tested. The stiffness of the samples that we investigated slightly raised with the increase of NA amount, up to a maximum of 1 wt % examined herein.

The influence of NX8000 additive on the loss modulus resulted in similar changes in tendency, as we presented in Figure 5. The tests showed that the addition of the nucleating agent in amounts that guarantee high nucleation efficiency (0.25 wt % and more) led to a significant increase of the loss modulus. These samples also exhibited a distinct plateau in a temperature range between 40 and 70°C and remarkable values of the loss modulus in higher temperatures which could lead to limitations in thermoformability of clarified materials.

Despite the tendency in the changes of the storage and loss modulus described above, for all the modified materials with increasing the concentration of the nucleating agent, the temperature peaks in the loss modulus were shifted to a lower temperature range (Fig. 5). Consequently, the nucleation of isotactic polypropylene with the NX8000 α-nucleating agent caused a slight decrease of the glass transition temperature (T_g), which is negligible. It is noteworthy that, in former studies concerning the influence of 1,3:2,4-Bis(3,4-Dimethylbenzylidene) Sorbitol, a contrary effect was observed[15].

CONCLUSIONS

The investigations carried out showed a significant influence of the sorbitol based α-nucleating agent on thermomechanical properties of isotactic polypropylene matrix. The addition of 0.25 wt % and more of the nucleating agent led to changes in crystallization and

Figure 4. The storage modulus of non-nucleated and α-nucleated iPP samples as a function of temperature during the DMTA test in a torsion mode

melting behavior. Increasing crystallization temperature and narrowing melting temperature range resulted from strong heterogeneous nucleation efficiency, as well as uniform structure of crystallized polymeric material.

The addition of the nucleating agent, in amounts greater than 0.25 wt % resulted in an increase of thermomechanical properties intensity, such as the storage and the loss modulus, accompanied by simultaneous and slight decrease of the glass transition temperature.

The thermomechanical behavior of the samples that contained 0.5 and 1 wt % of the NX8000 proved similar. In comparison with nucleation efficiency obtained from DSC thermal analysis, the sample that contained 0.5 wt % of NA should be considered as iPP blend which is the most suitable for manufacturing transparent products. It should be pointed out that the effect of heterogeneous nucleation led to an improvement of mechanical properties and processability during injection molding process. Therefore, a thermoformability of clarified materials might deteriorate by the enhanced stiffness in processing temperatures that occur near the softening point temperature.

ACKNOWLEDGMENT

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