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Structural characterization of α- and β-nucleated isotactic polypropylene

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Abstract: Modification of isotactic polypropylene (iPP) with two nucleation agents, namely 1,3:24-bis(3,4-dimethylobenzylideno) sorbitol (DMDBS) (α-nucleator) and N,N'-dicyclohexylo-2,6-naphthaleno dicarboxy amide (NJ) (β-nucleator), leads to significant changes of the structure, morphology and properties. Both nucleating agents cause an increase in the crystallization temperature. The efficiency determined in a self-nucleation test is 73.4 % for DMDBS and 55.9 % for NJ. The modification with NJ induces the creation of the hexagonal β-form of iPP. The addition of DMDBS lowers the haze of iPP while the presence of NJ increases the haze.

Keywords: α and β isotactic polypropylene; heterogenous nucleation; nucleating agents

INTRODUCTION

Isotactic polypropylene (iPP) is one of the most important commercial polymers because of its relatively low cost, versatility, recyclability and good mechanical performance in engineering applications.[1–7] iPP crystallizes essentially into a monoclinic α-phase (α-iPP) although sporadic occurrence of the hexagonal β-phase (β-iPP) is possible. A high content of the β-phase can be achieved under special conditions such as crystallization under a temperature gradient,[8,9] under shear[10,11] or in the presence of specific β-nucleators.[12–26]

Nucleating agents are low molecular mass organic or inorganic substances added to polymers, before or during processing, in very low quantities. Results of the addition of nucleating agents are usually: an increase in the crystallization rate, more uniform morphology, and sometimes an improvement in mechanical properties including increased transparency. Derivatives of sorbitol (known as DBS, MDBS and EDBS) are the most effective known nucleating agents of iPP, leading exclusively to the creation of the monoclinic α-form.[27–29] The best-known β-nucleating agents are the *trans*-quinacridone Permanent Red E3B[14,16,17,21,23] and mixtures of pimelic acid and calcium stearate.[15,18–20,25,26] The amount of the β-phase in iPP depends on the concentration of the additives and on the cooling conditions during crystallization from the melt. The β content in the iPP (and thus the efficiency of β-nucleators) can be quantified by wide angle X-ray scattering (WAXS) or qualitatively detected by differential scanning calorimetry (DSC) and polarized light microscopy (PLM).

One of the major goals of nucleation is to modify the crystallization kinetics and the crystallization temperature T_c; the latter is quite important in processing. An increase in the crystallization temperature due to nucleation enables shortening of the process cycle time, with obvious advantages for extrusion and injection molding processes.

The specific structural α- and/or β-form modification of an iPP may lead to significant changes in the end-use properties. There is particular interest in adjustment of the optical properties, a so-called clarifying effect achieved by the use of derivatives of sorbitol.[17,30] One can also affect mechanical properties, namely enhance the impact strength and lower the stiffness for β-nucleated iPP.[2]

Fillon *et al*[9,31,32] have suggested that macromolecules of the same polymer are the most effective nucleating agents. Such a situation occurs if the crystallization takes place in partly molten semi-crystalline polymers, a process called self-nucleation. The process allows the highest possible crystallization temperature for a given polymer to be achieved. This situation is the starting point of the present work. Our objective is the characterization of the consequences of the heterogeneous nucleation of an iPP and comparison of

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the efficiencies of selected nucleating agents with the results of self-nucleation.

EXPERIMENTAL

Materials

A commercial iPP, NOVOLEN 1100H, produced by Basell was used. Its density was 910 kg m^{-3} and the melt flow rate (MFI 230 °C, 2.16 kg) was 2.4 cm^3 (10 min)$^{-1}$.

The following nucleating agents were applied: 1,3:24-bis(3,4-dimethylobenzylideno) sorbitol (DMDBS) with melting temperature $T_m = 277\,°C$ and crystallization temperature $T_c = 214\,°C$ as the specific α-phase nucleator; and *N*,*N*′-dicyclohexylo-2,6-naphthaleno dicarboxy amide (NJ) with $T_m = 387\,°C$ and $T_c = 137\,°C$ as the β-phase nucleator.

Sample preparation

The α- and β-phase nucleating agents were combined at concentrations between 0.001 and 0.5 wt% with iPP granulates. The nucleators were mixed with the pellets *via* powder deposition on the surface of the granules, followed by melt homogenization in a single screw extruder, with the screw diameter 30 mm and length to diameter ratio 25. The temperatures of the barrel were 25 °C, 140 °C, 180 °C and 185 °C, and of the extrusion die 195 °C and 190 °C. The screw rotation speed was 30 rpm. Master batches containing 0.5 wt% of the nucleating agents were prepared at first. Other concentrations were produced by mixing the master batch with pure iPP, under the same extrusion conditions, followed by pelletizing.

The samples for the haze measurements were prepared in the form of plates in a compression procedure using a hydraulic press at the constant temperature of 200 °C for 10 min. After pressing the samples to a thickness of about 0.5 mm, they were cooled at the rate of 10 °C min^{-1} in a press to room temperature while maintaining constant pressure.

Differential scanning calorimetry

The DSC measurements were performed by means of a DSC Netzsch 200 thermal analysis system using samples with an average weight of 5–8 mg. The following temperature program was applied: first heating from 30 °C to 200 °C at the rate of 10 °C min^{-1}; maintaining this temperature for 5 min; cooling to 40 °C at the rate of 5 °C min^{-1}; holding for 5 min at 40 °C; and finally second heating to 200 °C at the rate of 10 °C min^{-1}.

For all specific nucleated and 'pure' iPP samples, T_m and T_c were determined from the DSC curves as the maxima of the relevant peaks.

The self-nucleation test for 'pure' iPP was carried out using a DSC program described elsewhere[31,33]. The polymer was heated to 200 °C, cooled to 60 °C, heated to partially molten state, and finally crystallized. The final DSC run was used to determine again a T_c in the self-nucleation testing procedure.

Wide angle X-ray scattering

WAXS measurements were performed using a horizontal TURM62 diffractometer with a HZG3 goniometer operating at 25 mA and 30 kV. A monochromatic X-ray radiation CuK$_\alpha$. ($\lambda = 0.15418$ nm) was used.

The following crystallographic planes for the monoclinic α-phase of iPP were analyzed: (110), (040), (130), (111) and (130), corresponding respectively to the diffraction angles $2\theta = 14.1°$, $16.9°$, $18.5°$, $21.2°$ and $22°$. For the hexagonal β-form the crystallographic planes (300) and (301) characterized by diffraction maxima at the diffraction angles $2\theta = 16.2°$ and $21.2°$ were examined. The β-phase content in crystalline iPP, the so called *k* value, was estimated using the formula proposed by Turner-Jones and coworkers[13]:

$$k = \frac{I_\beta}{I_{\partial 1} + I_{\alpha 2} + I_{\alpha 3} + I_\beta} \times 100\ \% \qquad (1)$$

where k is the percentage content of the β-phase in crystalline iPP, I_β is the intensity of the diffraction of the (300) plane characteristic for the β-phase, $I_{\alpha 1}$ is the diffraction intensity of the (110) plane of the α-phase, $I_{\alpha 2}$ is the intensity of the (040) plane of the α-phase, and $I_{\alpha 3}$ is the intensity of the (130) plane of the α-phase.

Optical microscopy

The morphology was observed using an interference–polarization microscope Labophot-2 (Nikon, Japan) with a Panasonic video camera GP-KR222E. Observations were performed for thin films of iPP with and without nucleating agents.

Haze and transparency factor

Haze and transmission was determined using a Hazemeter M57 (London, UK) spherical spectrophotometer. This instrument is designed for polymeric samples. The total and diffuse transmission was determined. The unit was provided with a 12 V 20 W tungsten halogen lamp and was corrected for C source emission by a glass filter. The measurement of haze involves the separation of scattered light from directly transmitted light. The percentage of transmitted light, which deviates more then 2.5 ° from the forward scattering incident beam, is considered haze. We used samples with diameters no less than 3 cm.

CRYSTAL STRUCTURES

The WAXS patterns of the α- and β-form of iPP are shown in Fig 1. The amounts of the hexagonal form represented by the *k* value from Eqn (1) for iPP with varying concentrations of the NJ nucleating agents are shown in Fig 2. An increase in the *k* value for increasing content of this nucleator is observed. The maximum of the β-form content ($k = 99\ \%$) is found for the NJ concentration of 0.5 wt%. The addition of

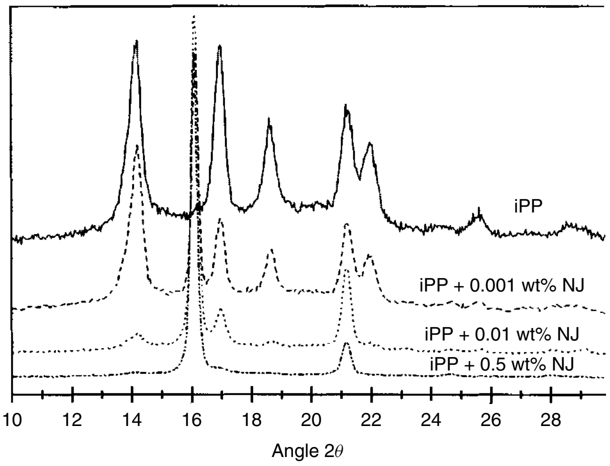

Figure 1. WAXS diffractograms for pure iPP and for iPP with various contents of NJ.

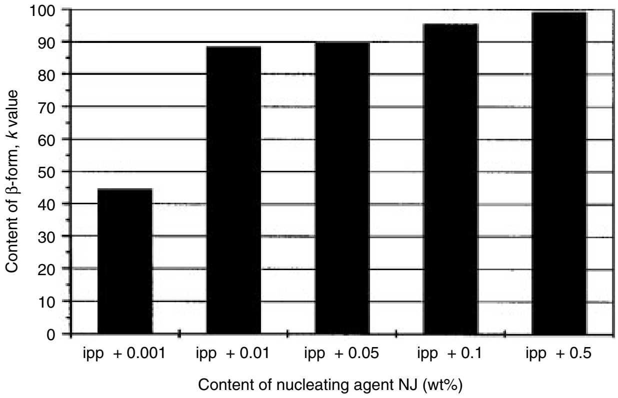

Figure 2. β-phase contents (k value) as a function of the NJ content.

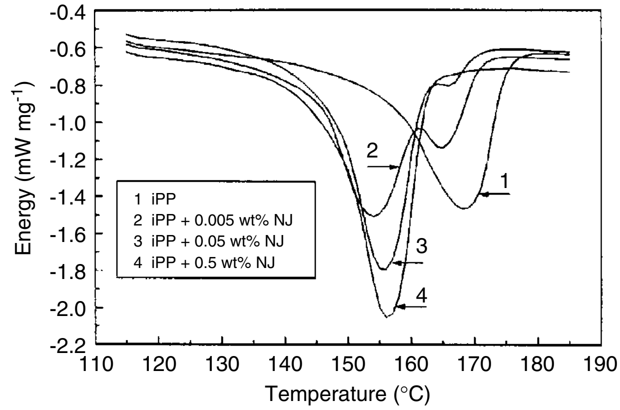

Figure 3. DSC melting curves for iPP with various contents of the NJ nucleating agent.

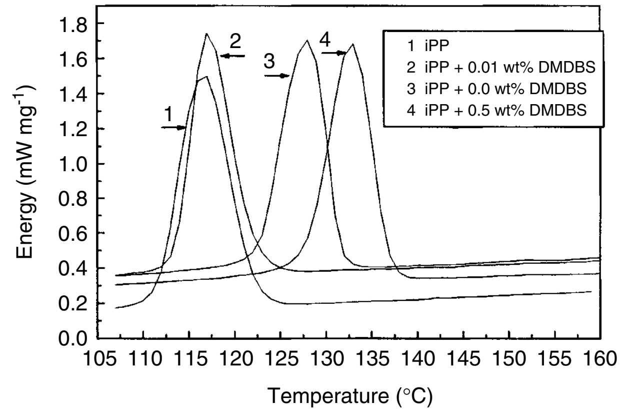

Figure 4. DSC crystallization curves of pure iPP and iPP with various contents of DMDBS.

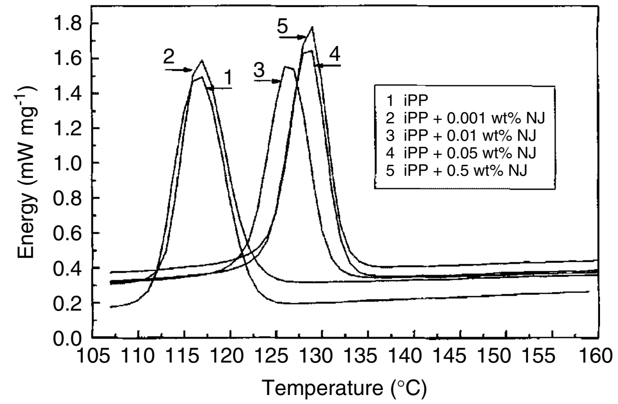

Figure 5. DSC crystallization curves of pure iPP and iPP with various contents of NJ.

DMDBS does not lead to formation of the hexagonal form of iPP; in this case only the monoclinic α-form of polypropylene is observed, which is in agreement with earlier results.[27]

Taking into consideration the higher crystallization rate of the α-iPP at temperatures above $T_{\beta,\alpha} = 140\,°\mathrm{C}$,[8,24] if both nucleating agents are used in a combination, the growth of the monoclinic form will always predominate. This has been shown before by one of the present authors for other nucleating systems.[34]

DIFFERENTIAL SCANNING CALORIMETRY RESULTS

Melting

DSC melting curves for iPP with varying NJ content are shown in Fig 3. The iPP modified with 0.5 wt% of NJ presents only one melting peak, at 158 °C, ie at the melting temperature of the hexagonal β-phase of iPP. For iPP with lower concentrations of the specific β-nucleators two melting peaks, clearly corresponding to the α- and β-forms, may be seen. In contrast, for 'pure' iPP only one melting peak, at 167 °C, is seen, which is characteristic for the melting of α-iPP. Thus, the calorimetric results are in a good agreement with the WAXS structure determinations.

Crystallization curves for iPP with varying NJ and DMDBS content are shown in Figs 4 and 5. iPP without nucleating agents has a T_c of 116 °C. With increasing content of both nucleators, a shift of the crystallization curves towards higher temperatures is seen. Figure 6 presents the crystallization temperature as a function of concentration of each of the nucleating agents. In the case of iPP modified with DMDBS, for

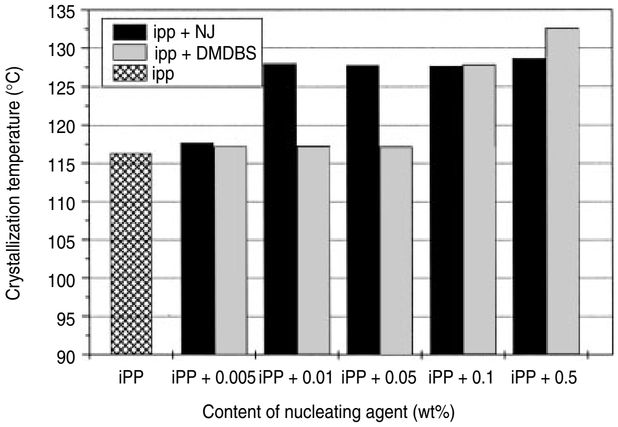

Figure 6. Crystallization temperature T_c as a function of the content of the nucleating agents.

lower content of the nucleator no changes in the T_c are observed: only from a concentration of 0.1 wt% does a significant increase in T_c occur. In contrast, for NJ an increase in T_c may be noted even from the addition of 0.01 wt%. The highest values of T_c of 128 °C for NJ and 132 °C for DMDBS are observed upon addition of 0.5 wt% nucleating agent. We infer that the NJ has a higher efficiency at low concentrations than the DMDBS. On the other hand, the addition of DMDBS allows higher T_c values to be achieved than for NJ.

Although the β-form in iPP is known to be less stable than the α-form, after multiple heating and cooling in a DSC machine a maximum contents of the hexagonal form is reached and does not undergo further changes. Re-crystallization in a hexagonal β-form during cooling from the melt was also confirmed by synchrotron radiation experiments reported elsewhere.[21]

Nucleation efficiency

The efficiency of nucleating agents was determined by means of a self-nucleation test, a procedure described in detail previously.[33] One takes into account the fact that the macromolecular chains of the same polymer are the most effective nucleating agents. Our polymer is only partly melted during the DSC test; small crystalline domains which remain act as nucleating centers in the molten matrix. This way the highest possible crystallization temperature for a given polymer may be determined.

The partly melted polymer was crystallized and the T_c was determined by DSC. The highest T_c found in our experiments was 150.3 °C, but the exact position of the maximum for this very large crystallization peak was not easy to define. We have taken the value of $T_c = 138.5\,°C$ as the maximum on the crystallization curve. The efficiency of nucleation E was evaluated as:

$$E = \frac{T_{\mathrm{cnuc}} - T_{\mathrm{cpure}}}{T_{\mathrm{c\,max}} - T_{\mathrm{cpure}}} \times 100\ \% \qquad (2)$$

where T_{cnuc} is the crystallization temperature of iPP with 0.5 wt% of the nucleating agent (132.6 °C for iPP + DMDBS and 128.7 °C for iPP + NJ), T_{cpure} is the crystallization temperature of 'pure' iPP = 116.3 °C, and T_{cmax} is the crystallization temperature established in the self-nucleation test = 138.5 °C.

The efficiencies thus calculated are $E = 73.4\ \%$ for the DMDBS and $E = 55.9\ \%$ for the NJ.

Crystallization rate

The crystallization half time, corresponding to 50 % of the crystal conversion, is used as a measure of the crystallization rate. As expected, a considerable influence of the concentration (Fig 7) and type of nucleating agent on the rate is observed. The addition of only 0.01 wt% of any nucleating agent leads to a reduction in the half time of about 12 % relative to 'pure' iPP (from 120 s to 105 s). Further increases in the nucleator content cause larger changes in the crystallization rate of the iPP. In iPP with 0.5 wt% of DMDBS or NJ the half time was, respectively, 37 % and 18 % shorter than for the polymer without nucleating agents.

MORPHOLOGY

Optical microscopy using polarized light reveals a significant decrease in the size of the spherulites of iPP with either nucleating agent. In Fig 8 the morphology of large spherulites for the non-nucleated iPP, with a radius in the range 10–90 µm, is clearly visible. In the case of iPP with 0.001 wt% of NJ (Fig 9), there is no significant change in the spherulite size. However, as seen in Figs 10 and 11, the addition of 0.01 wt% of NJ or 0.1 wt% of DMDBS results in a significant decrease of the spherulite dimensions. Similar results are obtained for iPP with higher content of nucleating agent. A very fine morphology does not allow us to determine precisely the size of the spherulites. It may be assumed that instead of well developed spherulites only randomly distributed lamellae create the morphology of highly nucleated iPP. On the other hand, it has to be noted that the increase of the nucleation density leads to more uniform morphology

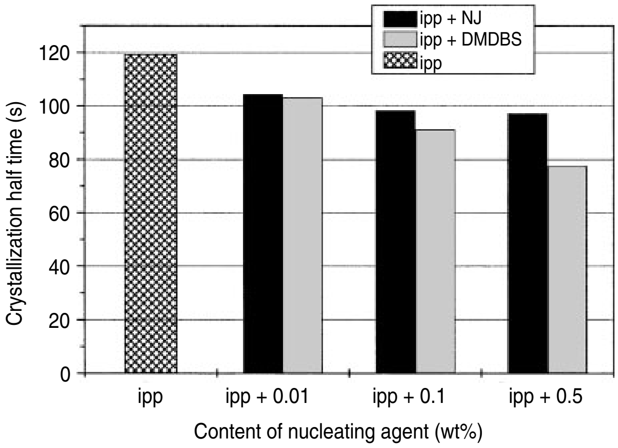

Figure 7. Crystallization half time as a function of the content of the nucleating agents.

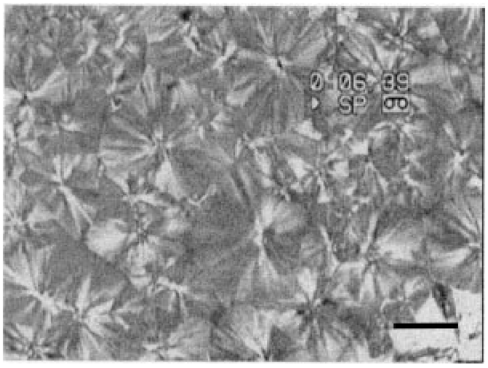

Figure 8. Morphology of non-nucleated iPP.

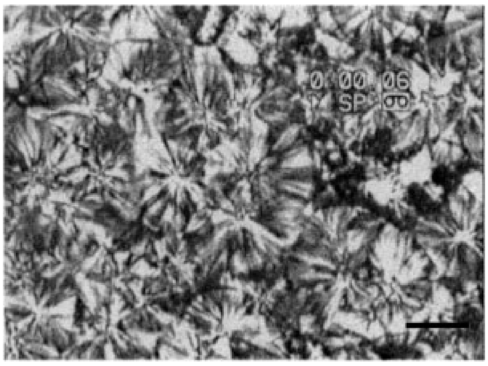

Figure 9. Morphology of iPP with 0.001 wt% NJ.

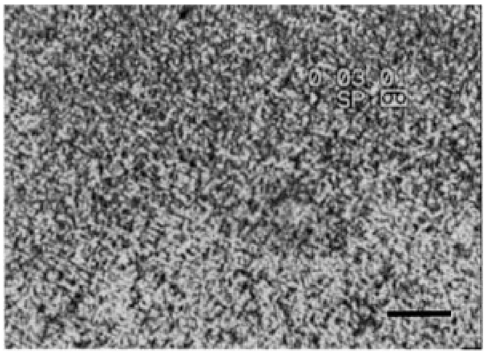

Figure 10. Morphology of iPP with 0.01 wt% NJ.

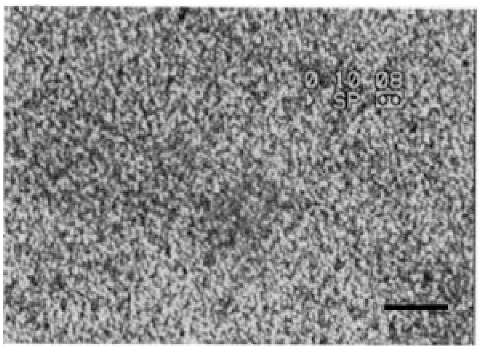

Figure 11. Morphology of iPP with 0.1 wt% DMDBS.

of iPP; this might be the origin of the improvement in properties.

The morphological lamellar arrangements are different for the α- and β-forms. As shown elsewhere,[1,17,26,35,36] in the α spherulites we find both radial and tangential lamellae. In contrast, there are no tangential lamellae in the β-form. The radial-only arrangement of the lamellae in the β spherulites is probably the origin of the higher impact strength of this crystal form of iPP.[2,36]

TRANSPARENCY AND HAZE

Haze is associated with a loss of contrast due to light scattering at large angles. Three dimensionless quantities are commonly measured in order to characterize the transparency of polymeric materials: direct transmittance, total transmittance and haze. The direct transmittance is the portion of the light that passes through the specimen without scattering. The total transmittance is the ratio of transmitted light at all forward angles to the incident light. The haze is the fraction of the transmitted light which deviates from the directly transmitted beam by more than 2.5 °.

In Fig 12 the haze values as a function of the concentration of the nucleating agents are displayed. An increase in haze is seen with increasing concentration of the β-phase nucleating agent (NJ). In contrast, the addition of the DMDBS (the α-phase nucleator) causes a decrease in the haze value. This results in better optical properties of polypropylene crystallized in this form. Although the addition of NJ is accompanied by a decrease in the spherulite size, an increase in the haze and a decrease in the transparency for the β-form iPP may be related to different lamellar organisation of the β spherulites *versus* α spherulites discussed at the end of the previous section and/or to the negative birefringence characteristics of the spherulites.[1,30,35,36]

CONCLUSIONS

The effect of β-formation in iPP by the use of NJ is clearly demonstrated by a double DSC melting peak and also by the characteristic WAXS diffraction maximum for the (300) plane. Depending on the NJ concentration, the β-phase content may even reach a *k* value of 99 %.

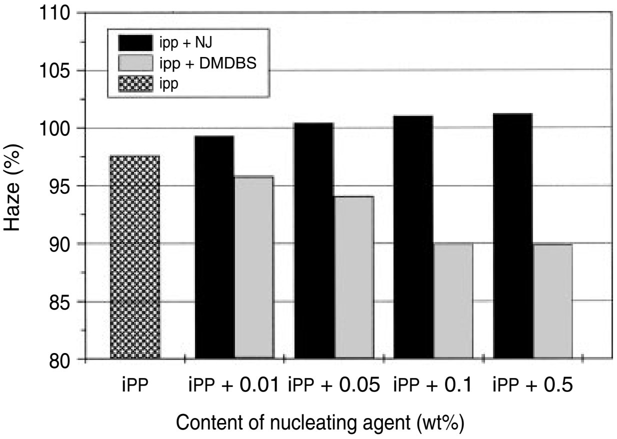

Figure 12. Haze values as a function of the content of the nucleating agents.

Due to the heterogeneous nucleation, a significant increase in the temperature of crystallization and shortening of the crystallization half time was observed. The crystallization efficiency of DMDBS (α-phase nucleating agent) was about 73 % and that of NJ about 56 %. In both cases, significant changes of morphology and optical properties were observed. The addition of the α-phase nucleating agent leads to an improvement of the optical clarity (lower haze); in contrast, the β-phase nucleating agent results in a higher haze, *ie* lower clarity.

The modification of crystallization temperature together with shorter crystallization time and improved properties enable a broadening of the application range of this commercially popular thermoplastic polymer.

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