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Morphology of a melt crystallized iPP/HDPE/hydrogenated hydrocarbon resin blend

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Abstract

The structure, phase structure, morphology, crystallization and melting behavior of isotactic polypropylene (iPP) blended with a master batch (MB), formed by high density polyethylene and hydrogenated hydrocarbon resin (iPP/MB), have been in details investigated by using X-ray diffraction, optical microscopy and differential scanning calorimetry. It was found that the structure and morphology depend on crystallization conditions. A new family of α spherulites of iPP (type I spherulites) can be activated using appropriate crystallization conditions. Nucleation of these spherulites has been explained by using the approach of nucleus migration in polymer blends. Type I spherulites present specific morphological, kinetic and thermal behaviors. In particular it was found that the growth rate of type I spherulites, at a given T_c, is higher than the growth rate of spherulites grown from plain iPP.

Keywords: Spherulites; Hydrogenated hydrocarbon resin; Isotactic polypropylene (iPP)

1. Introduction

Isotactic polypropylene (iPP) is a material with several crystal modifications [1–5], α, β, γ and a modification with intermediate crystalline order. The different polymorphs are distinct for the different chain packing geometries of the helices. The appearance of these structures is critically dependent on crystallization condition and pressure.

The monoclinic α-modification occurs most frequently. In melt crystallization of conventional iPP grades, α-modification is essentially formed and, at high undercooling, may be accompanied by a certain amount of hexagonal β-modification. Under special crystallization conditions, however, when 'temperature gradient methods' are used or when selective β-nucleating agents are present, the product is quite rich in β-modifications [5–6]. The γ-modification forms in degraded, low molecular mass ($M_w = 1000-3000$) iPP samples or in samples crystallized under high pressure [7]. It was also found that the γ-modification occurs also in the case of melt crystallization of random copolymers of propene with other olefins [8].

The quench of the molten iPP leads to a material with an intermediate crystalline order, indicated by two diffuse X-ray diffraction peaks, which are different from those exhibited by both crystalline and amorphous states. This modification was described by Natta as 'smectic' [9].

From microscopy observations of melt crystallized iPP, it was stated that the crystalline morphology of iPP is dominated by a highly characteristic lamellar branching (cross-hatching), with radial and tangential lamellae (chains perpendicular and parallel to spherulitic radius, respectively). This branching has no counterpart in other crystalline polymers [10–15].

Early studies by Padden and Keith [10] suggested the formation of five different types of spherulites consisting of crystals in α and β-modifications (α and β spherulites) during melt crystallization. In particular they demonstrated that three types of α spherulites might be formed depending on crystallization temperature: positive (α_I) below 134 °C, negative above 137 °C (α_{II}), and mixed-type spherulites in the intermediate temperature range (α_{III}).

Several authors supported the observations of Padden and Keith, even if they report different temperature ranges for the formation of the particular types of spherulites, presumably due to the variability in molecular characteristics of used iPP.

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The different optical characteristics of α spherulites have been linked to lamellar morphology through the balance of cross-hatched radial and tangential lamellae. In this way, negatively birefringent α_{II} spherulites are dominated by radial lamellae, whereas α_I positively birefringent spherulites contain increased quantities of tangential lamellae. Raising temperature of crystallization leads to a reduction in the proportion of tangential lamellae and, simultaneously, to a transformation of the birefringence from positive to negative. The transition between negative and positive birefringence occurs when approximately one-third of lamellae is tangential [15]. No tangential fibrils form above 155 °C. It was also revealed that the thickness of tangential fibrils was lower than that of radial ones.

Formation of other types of spherulites was also detected. Awaya [16] observed several new types of α-spherulites, designated as pseudo-positive, pseudo-negative, neo-mixed, high-temperature positive, and flower-like ones. Recently, studying the properties of films of iPP blended with a master batch (MB), formed by 50% of high density polyethylene (HDPE) and 50% of a hydrocarbon resin (HR), the formation of a new kind of α iPP spherulite, characterized by its own morphology, melting behavior and crystallization kinetics [17,18] was observed.

In this paper, the structure, morphology, crystallization and melting behavior of this new kind of spherulites are reported and compared with spherulites obtained by crystallization of plain iPP and iPP blended only with HR (iPP/HR blend).

2. Experimental part

2.1. Materials

The materials used were a commercial iPP, Moplen X30S produced by Montell, $M_w = 3.5 \times 10^5$ g/mol, $M_n = 4.69 \times 10^4$ g/mol, $M_z = 2.06 \times 10^6$ g/mol, M.F.I. (190 °C, 2.16 kg) = 9 g/10 min, density = 0.9 g/cm^3, and a master batch (MB) composed by 50% in weight of hydrogenated hydrocarbon resin (HR), MBG 273 produced by EASTMAN Chemical Co. (The Netherlands), and 50% in weight of HDPE M-6580 produced by Alathon.

The hydrogenated hydrocarbon resin [19] is an oligomer obtained in three steps: polymerization of monomers like styrene, α-methyl-styrene, vinyl-toluene and indene to form the aromatic precursor resin; weak hydrogenation reaction to saturate back bone along the chain; strong hydrogenation reaction to destroy the aromaticity of ring and to create a fully alicyclic resin.

The hydrogenated hydrocarbon resin has the following characteristic: $M_w = 1.47 \times 10^3$ g/mol, $M_n = 9.0 \times 10^2 \times$ g/mol, $M_z = 2.4 \times 10^3$ g/mol.

The HDPE has the following characteristics: $M_w = 3.0 \times 10^5$ g/mol, $M_n = 3.5 \times 10^4$ g/mol, $M_z = 2.0 \times 10^6 \times$ g/mol, M.F.I. = 8 g/10 min, density = 0.965 g/cm^3.

2.2. Blend preparation

The iPP and MB components were mixed in a Brabender-like apparatus (Rheocord EC of HAAKE Inc.) at 210 °C and 32 rpm for 10 min. The composition of the iPP/MB blend was 80:20 (wt/wt).

2.3. Preparation of compression-molded samples

The mixed material was compression-molded in a press at 200 °C for 5 min without pressure to allow complete melting. After this, 50 bar of pressure was applied for 5 min. Then the pressure was released and the mold containing the 1 mm × 60 mm × 120 mm sample was removed from the press and quenched by immersion in water at room temperature. After this treatment the sample was used for the analysis.

2.4. Optical microscopy

Thin slices were cut from the compression-molded samples, inserted between two microscope cover-glasses, melted and squeezed to obtain thin films. The thickness of the squeezed samples was about 10 μm.

Crystal growth rates of pure iPP and iPP/MB 80:20 blend were investigated by optical microscopy with a Zeiss Axioscop polarizing optical microscope equipped with a Linkam TH600 hot stage. A thin film, obtained as described before, was sandwiched between a microscope slide and a cover glass, then inserted in the hot stage.

Each sample was heated from 30 to 200 °C at rate of 30 °C/min, kept at this temperature for 10 min to allow complete melting, then cooled to room temperature at constant scanning rates, ranging from 0.5 to 8 °C/min.

Dry nitrogen gas was purged through the hot stage. The radius of growing crystals was monitored during crystallization by taking photomicrographs at appropriate intervals of time, using a JVC TK-1085E Video Camera. Spherulite radii were measured with the software Image-Pro Plus 3.0.

Spherulite growth rates, G, were measured using the procedure suggested by Chen and Chung [20] for solidification performed during cooling at a constant cooling rate and subsequently modified by Silvestre et al. [21]. According to this procedure, G can be estimated by taking the first derivative of the plot of spherulite radius, r, vs. temperature, T, at each experimental point:

$$\frac{dr}{dT} = \frac{dr}{dt}\frac{dt}{dT} \quad (1)$$

where dt/dT is the reciprocal of the cooling rate, and dr/dt is the radial growth rate, G.

2.5. Thermal analysis

Calorimetric properties of the compression-molded sample blends were measured with a differential scanning

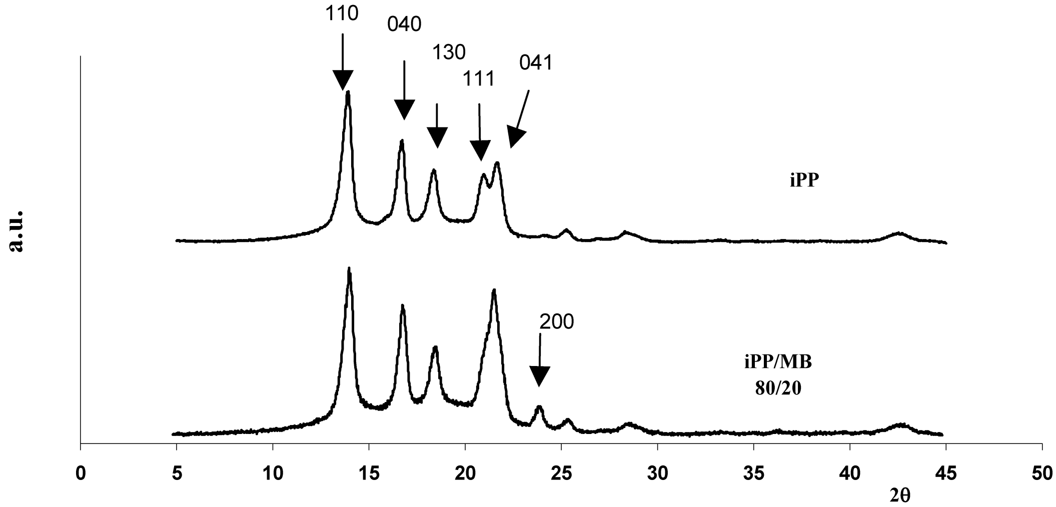

Fig. 1. WAXS profile of film of iPP and iPP/MB 80:20 blend isothermally crystallized at $T_c = 130$ °C.

calorimeter Mettler DSC-30. The sample (about 10 mg) was heated from − 150 to 250 °C at a rate of 10 °C/min.

To investigate the overall non-isothermal crystallization of the samples, the following procedure was used: each sample was heated from 30 to 200 °C, kept at this temperature for 10 min to allow complete melting and then cooled to room temperature at different scanning rates.

Each experiment was repeated three times to ensure reproducibility. Dry nitrogen gas with a flow rate of 20 ml/min was purged through the cell.

2.6. WAXS measurements

Wide-angle X-ray scattering measurements were carried out using a Philips (PW 1050 model) powder diffractometer (CuNi-filtered radiation) equipped with a rotative sample holder device.

3. Results and discussion

3.1. Structure, phase structure and morphology

The WAXS profiles of iPP and iPP/MB 80:20 films isothermally crystallized at $T_c = 130$ °C are shown in Fig. 1. It is clearly evident that the iPP crystallizes in monoclinic α-form. In fact the peak characteristic of the α-form, between the angles 18–19°, corresponding to the (130) peak of the α-form, is always present. In the profile of the blend (Fig. 1(b)), a peak centered at 2θ about 24°, corresponding to the (200) peak of characteristic of the HDPE crystals is also evident. The patterns of non-isothermal crystallized samples are similar to those shown in Fig. 1, indicating that different crystallization conditions and simultaneous presence of HDPE and HR do not cause variation in the polypropylene structure.

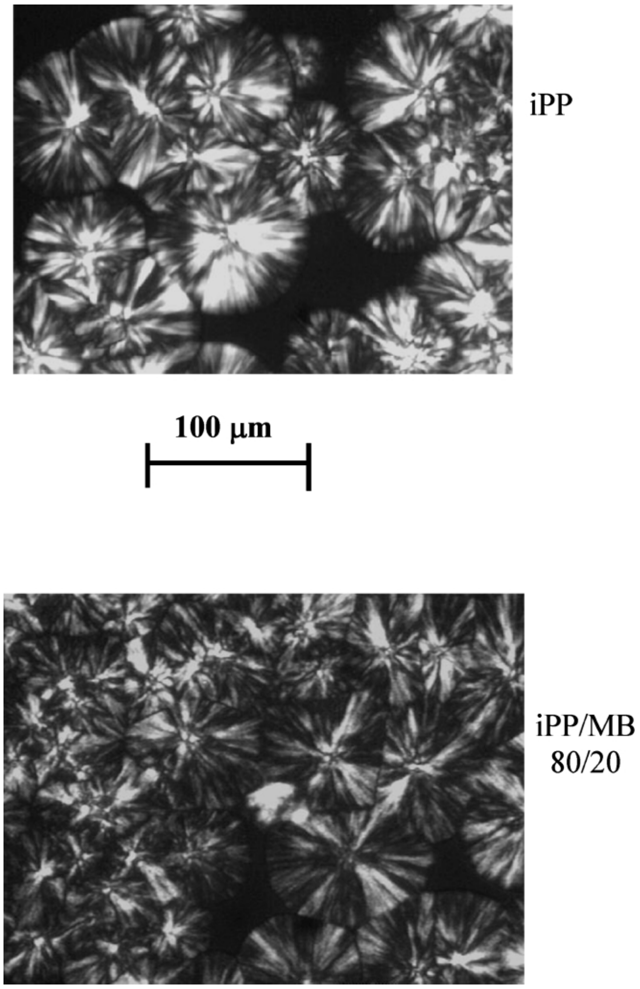

Fig. 2. Optical micrographs of isothermally crystallized ($T_c = 130$ °C) samples: (a) iPP; (b) iPP/MB 80:20 blend.

In the melt from 200 °C down to T_c, the blend samples,

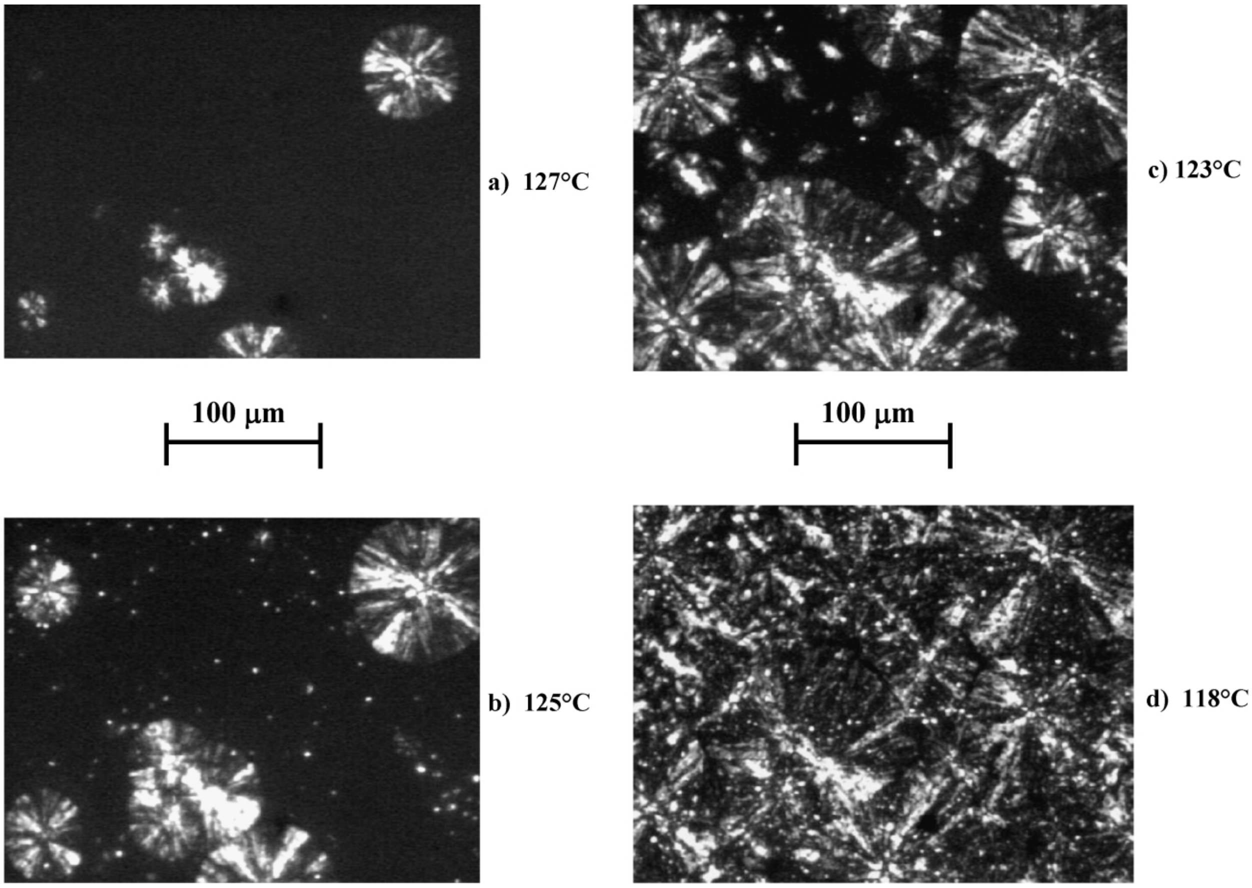

Fig. 3. Optical micrographs of iPP/MB 80:20 blend taken during cooling from the melt at different temperature T (cooling rate 2 °C/min).

observed through an optical microscope, look homogeneous. This homogeneity is not real and it is due to the similarity of the refractive indices of iPP and HDPE in the melt. In fact, when iPP crystallizes, changing drastically its refractive index, spherical domains dispersed in the matrix are soon evident.

In a future work [17,18] it will be reported that the MB presents two main transitions, at -93 and 65 °C: the transition at -90 °C is due to plain amorphous HDPE, whereas that at 65 °C is mainly due to HR phase, containing probably a small amount of HDPE. Moreover, it will be also reported that for the iPP/MB blend two glass transitions are detected at -93 and 20 °C, attributed to plain HDPE and to a homogeneous amorphous phase formed by iPP and HR, indicating that after the mixing all the HR is completely transmigrated to iPP.

The morphological results are therefore in agreement with those obtained studying the glass transition behavior and lead to the conclusion that the melt of the iPP/MB blend is constituted by two phases: an homogeneous iPP/HR phase and a HDPE phase.

During crystallization different phase structures can be generated depending on crystallization conditions.

The morphology of samples crystallized from the melt is always spherulitic, see Fig. 2. The spherulites present positive birefringence.

For isothermal crystallization above 126 °C, after solidification, three phases are present, keeping the sample at T_c : an iPP crystalline phase, an iPP/HR amorphous phase and a HDPE melt phase. For isothermal crystallization below 126 °C, after solidification the system presents four phases: an iPP crystalline phase, an HDPE crystalline phase, a homogeneous iPP/HR amorphous phase and an amorphous HDPE phase.

The morphology of the samples during non-isothermal crystallization is more complex and depends on the cooling rate.

For cooling rates higher than 5 °C/min, the crystallized blend sample is constituted by small spherulites. Comparing the dimensions of spherulites of the blend with those related to pure iPP and to binary iPP/HR 80:20 blends [18], it can be supposed that, in these crystallization conditions, the HDPE acts as a nucleating agent for the polypropylene.

Very interesting morphological results are obtained for cooling rates lower than 5 °C/min. Optical micrographs, taken during non-isothermal crystallization, cooling the samples from 200 °C to room temperature, at a cooling rate of 2 °C/min, are shown in Fig. 3. Different nucleation and crystallization regions can be recognized. Below the

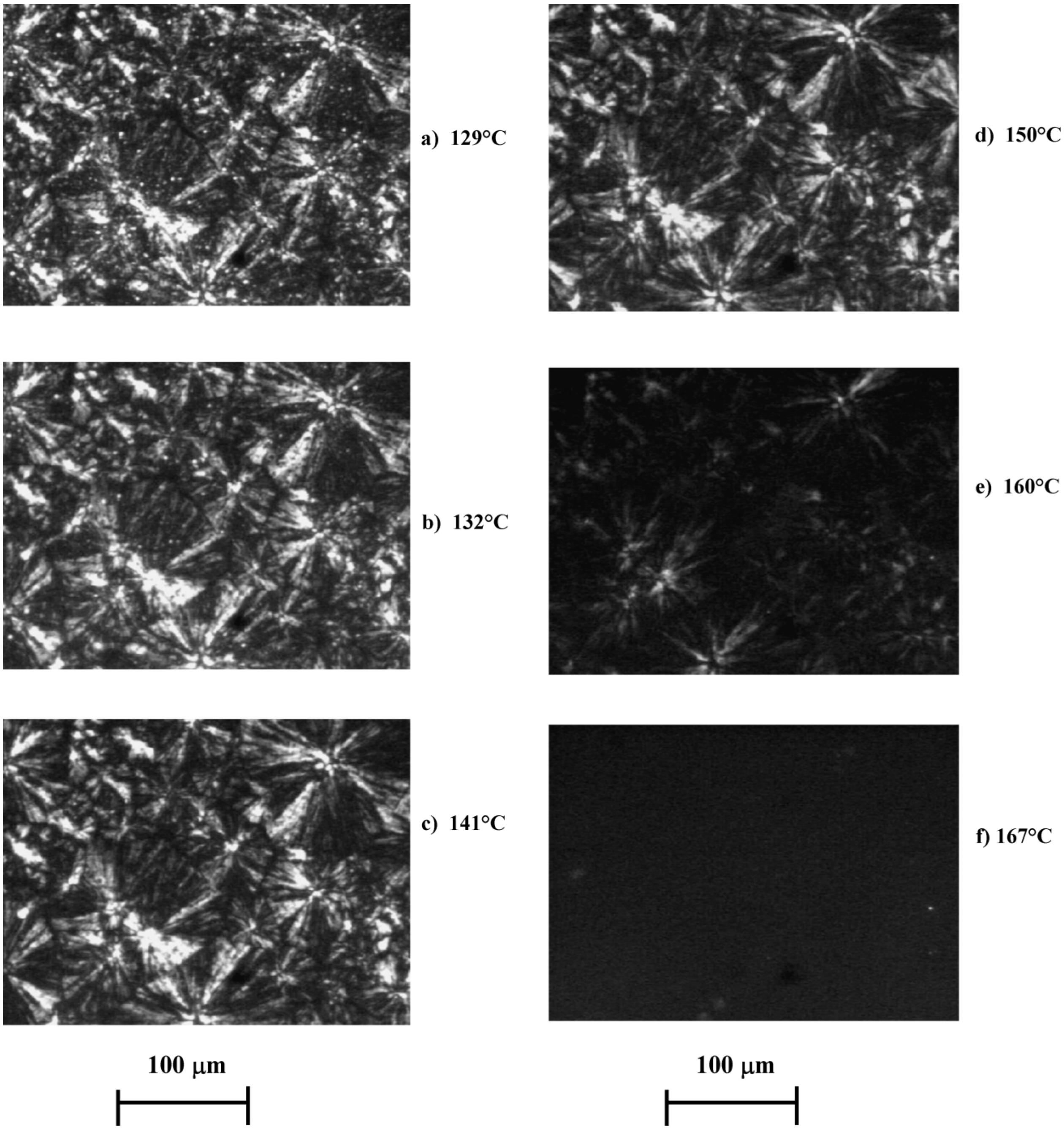

Fig. 4. Optical micrographs of iPP/MB 80:20 blend taken during heating from room temperature to melting temperature at different temperature (heating rate 10 °C/min).

melting point, there is a region of about 20 °C, where no crystal growth takes place. Decreasing the temperature at about 140 °C, some nuclei appear and start to grow, giving rise to large spherulites (type I spherulites). The number of these nuclei is limited (see Fig. 3(a)). Decreasing the temperature to around 126 °C, several birefringent spots appear (see Fig. 3(b)). Decreasing furthermore the temperature, some of these spots grow assuming the spherulitic shape (see Fig. 3(c) and (d)). These spherulites (type II spherulites) are smaller than type I spherulites. It is interesting to note that both kinds of iPP spherulites include HDPE domains during their growth. Such domains are not birefringent (dark zones) down to $T = 126$ °C. At this temperature they become birefringent, indicating a crystallization of this phase. After complete crystallization, the temperature was increased up to melting at 10 °C/min. During this heating process, the development of the morphology was also monitored. Optical micrographs are shown in Fig. 4. At 132 °C the birefringent spots start disappearing (compare Fig. 4(a) and (b)). At 141 °C they disappear completely (see Fig. 4(c)). At 160 °C type II spherulites are completely melted (see Fig. 4(e)); at $T = 167$ °

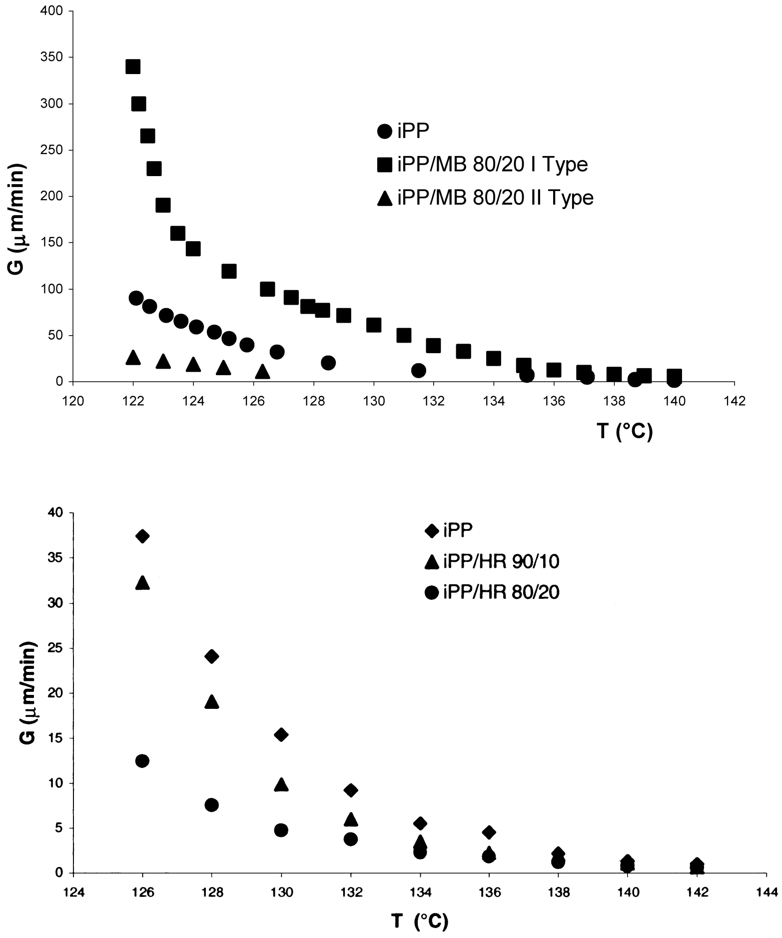

Fig. 5. Spherulite growth rate as a function of temperature for spherulites grown from melt of plain iPP, iPP/MB blend (type I spherulites and type II spherulites) and iPP/HR blends.

C also type I spherulites melt. The morphological analysis clearly shows that the simultaneous presence of HDPE and HR greatly influence the nucleation and crystallization of iPP.

It is to be underlined that for cooling rates <5 °C/min, two families of spherulites are present. These two families have different nucleation temperature and different thermal stability, and as it will be reported in Section 3.2, they present also a different crystallization behavior. Both families of spherulites present positive birefringence and are formed by monoclinic crystals.

3.2. Crystallization behavior

Crystallization behavior was studied in isothermal and non-isothermal conditions following spherulite growth rate and overall crystallization rate, by using optical microscopy and differential scanning calorimetry, respectively.

In Fig. 5(a) spherulite growth rates of iPP and iPP/MB blend, obtained using isothermal and non-isothermal methods, are plotted as a function of temperature. In Fig. 5(b) the isothermal spherulite growth rates of binary iPP/HR 90:10 and 80:20 blends, as a function of temperature, are also reported for comparison.

It is to be underlined that the growth rate of iPP spherulites in iPP/MB blend is followed, where possible (namely for temperatures below 126 °C), both for type I and type II spherulites. It is clearly evident from Fig. 5(a) that, for any T_c, type I spherulites present a growth rate always higher than that of the spherulites obtained by crystallization of plain iPP. Type II spherulites present, at a given T_c, a value of G lower than that of iPP.

Moreover, it was found that the values of G for type II spherulites are comparable with those of the binary blends iPP/HR 80:20.

In order to explain these interesting results, the theory of nuclei migration phenomena in polymer blends, proposed by Galeski et al. [22], can be invoked. According to this theory, in a polymer blend, the difference in interfacial free energies of the impurities with respect to both molten components is the driving force for the migration across the interface of the nuclei from one component to another. The tendency to minimize the interfacial energies favors, therefore, the migration of the heterogeneities toward that blend component in which their interfacial energies are

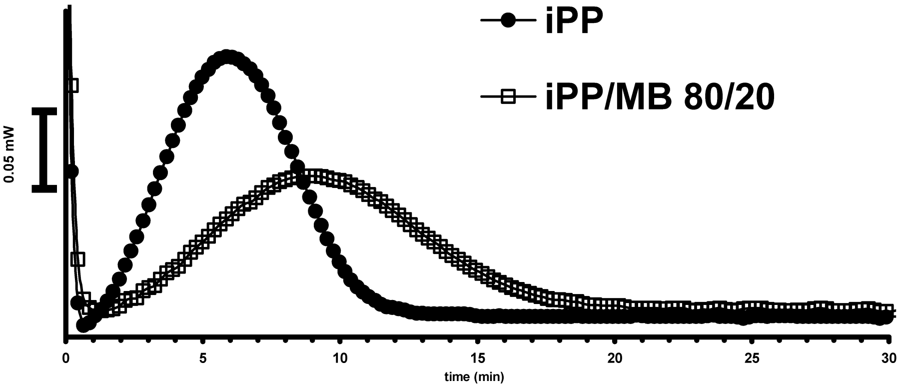

Fig. 6. Thermoanalytic curve of iPP and iPP/MB blend during isothermal crystallization ($T_c = 130$ °C). The half time of crystallization obtained from the curves was 5 and 7.5 min for iPP and iPP/MB blend, respectively.

lower. Probably, during the preparation of the MB, some HDPE heterogeneous nuclei migrate towards the HR phase, that becomes rich of HDPE nuclei. In the subsequent process of iPP/MB blend preparation, the HR phase, enriched by the HDPE nuclei, form a single homogeneous phase with iPP. So in the melt iPP/HR phase, two kinds of heterogeneous nuclei are present: the original iPP nuclei and the HDPE nuclei migrated from HDPE to HR. Probably these last nuclei give rise to type I iPP spherulites with their own morphological, kinetic and thermal behavior.

The presence of the HDPE nuclei activate and facilitate the crystallization of iPP, decreasing the activation energy of the nucleation process.

Type II spherulites are due to the nucleation and growth of the heterogeneous nuclei belonging to iPP.

Different overall crystallization behaviors are obtained changing the crystallization conditions.

The thermoanalytic curves, obtained following the crystallization of iPP and iPP/MB blend in isothermal conditions at 130 °C and during cooling at 2 and 5 °C/min, are reported in Figs. 6–8, respectively.

For isothermal crystallization at 130 °C, a single peak is observed, Fig. 6. From this curve it is possible to observe that, at the used T_c, the addition of MB to iPP decreases the overall crystallization process of iPP. In particular, the half time of crystallization of the blend increases of the 50% with respect to pure iPP, at the same T_c. The morphology and spherulite growth rate analysis has revealed that at 130 °C few large spherulites (type I) nucleate and grow with a rate higher than that of plain iPP spherulites. Taking into account these results and the fact that the overall crystallization rate comprises the nucleation rate plus the spherulite growth rate, it can be concluded that the addition of MB to iPP causes a drastic decrease in the nucleation rate, that overcomes the increase of growth rate.

When the crystallization occurs at a cooling rate lower or equal to 2 °C/min, the presence of two peaks for the blend is detected (Fig. 7), confirming the crystallization of different families of crystals: type I iPP spherulites start to grow first at high T_c, followed by nucleation and grow of HDPE spherulites and type II iPP spherulites. The crystallization of type I iPP spherulites gives rise to the peak at higher temperatures, whereas the crystallization of HDPE together with the crystallization of type II iPP spherulites, give rise to the peak at lower temperatures.

When the crystallization occurs at a cooling rate equal or higher that 5 °C/min, the crystallization of iPP in blends starts at a temperature higher than that of plain iPP,

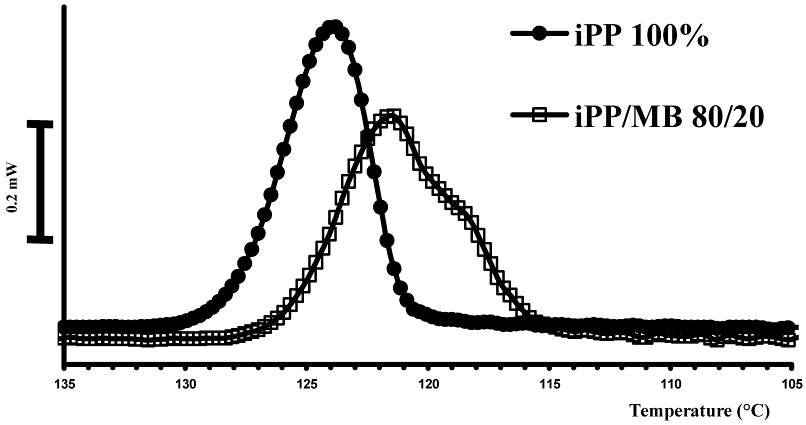

Fig. 7. Thermoanalytic curve of iPP and iPP/MB blend during cooling from the melt (cooling rate = 2 °C/min).

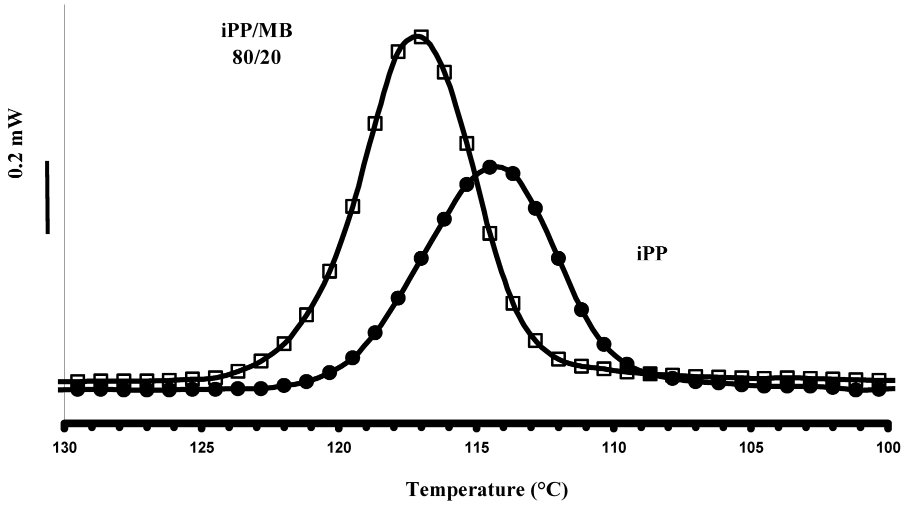

Fig. 8. Thermoanalytic curve of iPP and iPP/MB blend during cooling from the melt (cooling rate = 5 °C/min).

indicating that, in presence of MB, iPP needs a lower undercooling to crystallize, Fig. 8. The presence of crystallized HDPE probably lowers the activation energy required for the formation of stable nuclei, and the crystallization process can start at a lower undercooling. These heterogeneous nuclei are probably formed at the interfaces between HDPE and iPP.

Comparing Figs. 6–8 it is also interesting to note that only for cooling rate = 5 °C/min the curves of the blends shift at higher temperature. This results indicates that the nucleation effect of HDPE is effective only for crystallization performed in non-isothermal conditions with cooling rates not less than 5 °C/min. For these cooling rates, lower temperatures are quickly reached and HDPE can crystallize before nucleation and growth of type I spherulites. Crystalline HDPE inclusions can act as nucleating agents for crystallization of iPP matrix.

The sample, after crystallization, is composed of type II iPP spherulites together with HDPE microspherulites.

4. Conclusion

The principal finding is that, in melt crystallized 80:20 iPP/MB blend, a new family of iPP α spherulites (type I spherulites) can be obtained. The nucleation and grow of this new kind of spherulites can be activated using appropriate crystallization conditions:

- For crystallization temperature higher than 126 °C, the sample is formed exclusively by type I iPP spherulites.
- For isothermal crystallization at T lower than 126 °C and during cooling from the melt at rates lower than 5 °C/min, both kinds of spherulites form. For these crystallization conditions, we suppose that there is a time-dependent sequence of iPP crystallization. As the material is cooled from the melt, at high temperatures (T_c 140–126 °C) few very large spherulites (type I iPP spherulites) nucleate and grow. Cooling this material to temperature lower than 126 °C, new additional material crystallizes, giving rise to several small spherulites (type II iPP spherulites). At the same crystallization temperature $G_{\mathrm{TypeI}} > G_{\mathrm{iPP}} > G_{\mathrm{TypeII}}$. The type I iPP spherulites presents a higher thermal stability with respect to type II.
- Crystallization during cooling at cooling rates ≥ 5 °C/min causes the formation of only type II iPP spherulites.

This paper, moreover, underlines the fundamental role of the crystallization conditions on the morphology and hence on the properties of polymer materials. In fact, changing the cooling rate of only few degrees for minute, dramatic substantial changes in the spherulites dimensions as well as in the resulting phase structure of the blend are observed.

Acknowledgements

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