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Processing and property improvement in isotactic polypropylene by heterogeneous nucleation*)

Summary — Crystallization temperature (T_m) was measured for poly-(ethylene-*b*-propylene) copolymer in relation to 0—0.5 wt.% of a single-component nucleating agent (NA) (natrium benzoate, talc, or sorbitol derivatives) (Fig. 1) and the content of the pseudohexagonal β-phase in PP-i (tacticity 95.6%, 97.1%; MWD 3.9, 6.3, resp.) was studied in relation to 0—0.2 wt. % of pimelic acid—calcium stearate used as a two-component NA (Fig. 3). Starting with ~ 0.2 wt % NA, the T_m leveled out. Thus, upwards of 0.15—0.25 wt.%, NA failed to raise T_m. However, even low amounts of NA gave rise to homogeneous morphology, regardless of the processing conditions (*cf.* Figs. 4—6). β-phase orientation was studied in relation to position along flow path at mold temperatures of 45°C and 90°C (Fig. 7). Heterogeneous-nucleated PP-i revealed somehow "frozen" flow-elongated and flow-sheared macromolecular chains, *i.e.*, a higher level of macromolecular orientation. Nucleators, β-phase formation, heterogeneous nucleation and like problems are reviewed (44 refs.).

Key words: isotactic polypropylene, heterogeneous nucleation, structure, morphology, molecular orientation.

Isotactic polypropylene (PP-i) exhibits a relatively low impact resistance. This drawback reduces automotive, household and like applications of this polymer. Numerous technologies have been suggested to modify the mechanical properties of PP-i, including formation of (ethylene-propylene) copolymers, polymer blends and mixtures, *etc.* A significant process-induced modification may be introduced, if prior to processing, heterogeneous nucleation is applied.

This work is intended to investigate the modifications of processing, structure and properties in the isotactic polypropylene matrix as a consequence of addition of various nucleating agents at low concentrations.

Modification of semi-crystalline polymers by heterogeneous nucleation has been extensively studied in the past thirty years. In the pioneer works of Binsbergen *et al.* [1—6] and in subsequent studies [7—16], a wide number of additives have been tested and analyzed. Heterogeneous nucleation has been considered to be a way to modify the structure of polymers and to create specific crystalline forms characterized by different elementary units. To explain the formation of specific α and β structures in PP-i, the hypotheses based on thermal effects [10—12], molecular mechanics (energy-dependent chain rotation) [13, 14] and intermolecular effects (epitaxy effect) [7—9] have been suggested.

For the modification of certain mechanical properties [17—22], the formation of the pseudo-hexagonal β-form of polypropylene has been found to be very advantageous.

FORMATION OF THE β-PHASE

The pseudo-hexagonal crystalline form of PP-i is well known to be formed under special processing conditions or by using specific additives. The shear flow induced α/β-phase transition has been observed in the PP-i processed in the molten state [23—25]. Shear stresses are predominant in the near-wall layers and this fact allows to observe the structural effect of the forming β-phase in this part of the sample by an optical technique [25—29]. The structure gradients usually appearing in the crystallized product can be detected by microscopy and/or by wide angle X-ray scattering (WAXS). As the distance from the die wall is increased, characteristic changes in the β-phase content can be seen as observed in poly-(ethylene-*b*-propylene) copolymer [30].

If isothermal crystallization is applied, a separate production of one PP-i crystal phase (α and or β) is usually observed. A clear temperature limit, $T_{\alpha,\beta}$ equal to 143°C, was proposed by Varga [10—12], to separate the formation of a well-defined crystalline structure of PP-i.

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Isothermal crystallization at a temperature $T > T_{\alpha,\beta}$ generally yields the α-phase only; on the contrary, at the lower crystallization temperatures ($T < T_{\alpha,\beta}$), the type of the crystal structure depends on thermal and strain histories, as well as on the composition of additives.

Addition of specific additives at low concentrations is a popular method used to produce the β-structure with a controlled content of the pseudo-hexagonal phase. Beside γ-quinacridone, the most popular seed of the β-phase of PP-i [3, 14], a series of crystalline substances like 2-mercaptobenzimidazole, triphenodithiacine, phenithiazin, anthracene and phenanthrene have been reported to nucleate this crystallographic form of polypropylene [13]. In the 1980s, a mixture of pimelic acid and calcium stearate [31—34] was published as a new and very efficient β-phase nucleator.

BENEFITS OF HETEROGENEOUS NUCLEATION

Besides a specific crystal phase formation, the main effects of heterogeneous nucleation of PP-i include:

— higher morphological homogeneity along the cross section, resulting from increased nucleation density;

— increased crystallization temperature T_{cr}, *i.e.*, shorter processing cycle, improving process economy;

— polymer morphology changes, especially reduced size of the spherulites followed by modification of optical, mechanical and electrical properties; and

— changes in polymer crystallinity with an influence on end-use properties.

EXPERIMENTAL

Materials

Isotactic polypropylene and related copolymers were used as matrix polymers; for characteristics of these polymers see [21, 30].

Several nucleating agents were dispersed in the polymer matrix to provoke modification of structure and properties. Natrium benzoate, talc and derivatives of sorbitol were applied as single-component nucleating agents [35, 36] to modify the crystallization temperature. Modification of the crystal structure was produced by red pigment E3B, as a single-component additive, and by a mixture of pimelic acid and calcium stearate as a two-component nucleating system.

Processing

As described elsewhere [21, 30, 36], the polymeric matrix was mixed with the nucleating agents, as a dispersed phase, by extrusion applied to the master batch procedure.

Modification of crystallization temperature (T_{cr})

The crystallisation temperature T_{cr} presents as well an economical parameter directly related to the polymer processing. Due to the increase of the crystallisation temperature, and reduction of the cooling time, the injection molding cycle may be shortened up to 30%; the same effect allows to use much shorter extrusion cooling lines.

Dispersion of a small quantity of nucleating agents (NA) in the polymeric matrix usually results in a great number of nuclei and consequently accelerates the starting point of crystallization, *i.e.*, crystallization occurs at a higher temperature. This physical effect depends strongly on the concentration of the nucleating additives.

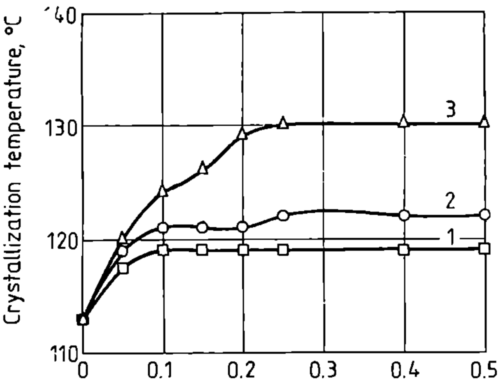

Fig. 1. Crystallization temperature of poly-(ethylene-b-propylene) copolymer vs. nucleating agent content: 1 — natrium benzoate, 2 — talc, 3 — sorbitol derivate

Figure 1 presents crystallization temperatures T_{cr} as a function of NA contents of three types of additives: sodium benzoate, talc, and sorbitol derivatives (MDBS), as determined by differential scanning calorimetry (DSC). Differences in the chemical structure and nucleation efficiency of the additives are seen to result in varying increases of T_{cr}. The following descending order of its nucleation efficiency may be proposed: sorbitol derivatives > talc > natrium benzoate. The very large active surface of sorbitol derivatives associated with the "butterfly-like" shape of the molecule [37], is likely to be responsible for its high efficiency, as discussed elsewhere [35, 36].

Above a certain concentration of the nucleating agent, T_{cr} is seen to level out *i.e.*, a "saturation" effect occurs (Fig. 1). Thus, nucleating agent concentrations higher than about 0.15 do 0.25 wt.% are ineffective, especially when the only intention is to modify T_{cr}. Evidently, the higher concentration of the nucleating agents gives rise to a significant modification of the morphology — an effect to be discussed later.

Nucleation efficiency

The hypothesis that, for the polymers, the own macromolecular chains are the best germination centers, should be taken into account when efficiency of a certain nucleating agent is considered. Therefore, the selfseeding test, allowing to determine the crystallization efficiency of a system composed of a polymeric matrix and nucleating agents, has been proposed by B. Lotz *et al.* [7, 8]. In our case [38, 39], depending on the nucleation system used, the efficiency was between 30 and 60% an indication that significant possibilities still exist in creating new and more efficient nucleating systems for polypropylene.

Modification of the PP-i crystal structure; formation of the β-phase

The fraction of the β-phase form and its distribution along the cross section of injection molding parts have been widely investigated. Usually the β-phase content is evaluated from the WAXS diffraction intensity determined for both PP-i crystal phases [6]. Figure 2 [40] presents the β-phase content in PP-i samples nucleated with a red pigment Hostaperm E3B (linear *trans*-quinacridone dye), which is a well-known β-phase nucleator.

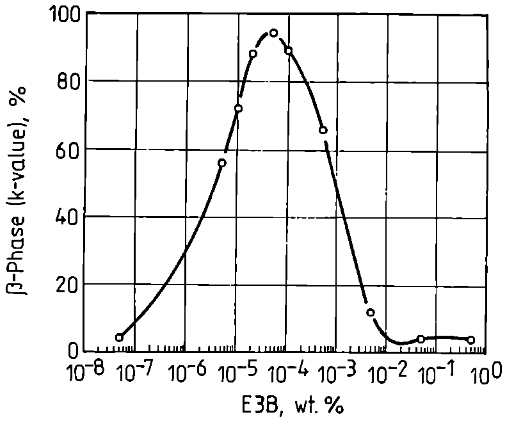

Fig. 2. The pseudo-hexagonal β-phase content in PP-i vs. E3B concentration [40]

This is a planar molecule of five fused rings 1.406 nm x 0.52 nm in size [37]. A characteristic maximum on the β = f(NA%) curve, found for PP-i and for copolymers of propylene [21, 30, 41] , may be attributed to the thermal conditions of germination by specific nuclei and to the growth kinetics of the α/β crystal structure. According to Varga [12], the regions with various growth rates of both crystal structures of polypropylene are split by the characteristic temperature $T_{\alpha,\beta}$. Therefore, the maximum on the β = f(NA%) curve, observed at about 10^{-4} wt.% of NA, may be explained by the synergy of a higher germination density and of a specific thermal crystal growth rate.

Phase modification in relation to chemical structure

To determine the influence of the PP-i chemical structure on the crystal phase modification, we studied two isotactic polypropylenes identical in viscosity (MFR) but different in tacticity and molecular mass distribution. The chemical structure modification was achieved by the so-called visbroken procedure [42]. The two-component nucleation system, pimelic acid—calcium stearate, showed the relationship between the β-phase content and the NA concentration to depend significantly on the chemical structure and the stereo regularity of the polymer (Fig. 3). The PP-i lower in degree of tacticity (and lower in molar weight distribution), was more sensitive to specific nucleation, finally yielding a high value of constant *k* at each NA concentration. On the contrary, the PP-i higher in degree of tacticity showed the *k*-value to be related to the nucleating agent content to the same degree as observed before (see Fig. 2).

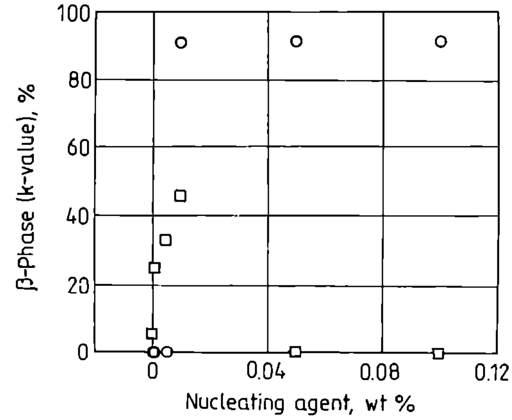

Fig. 3. The pseudo-hexagonal β-phase content vs. two-component nucleating system (pimelic acid + calcium stearate) for PP-i of various tacticity and molecular weight distribution (— tacticity 97,1%, MWD 6.3; ○ — tacticity 95.6% MWD 3.9)

Modification of mechanical properties by specific nucleation

One of the most important limitations on the use of PP-i, is the relatively low impact resistance within the range of T_g (about -15°C). To overcome this problem, neat PP-i is replaced by poly-(ethylene-*b*-propylene) and poly-(ethylene-*co*-propylene) copolymers or by blends of polypropylene with low-modulus polymers. The latter polymeric material has found wide application in the production of automotive bumpers.

The mechanical properties of PP-i can also be modified by specific nucleation. A transformation from the brittle to ductile type of break in the PP-i with the predominant β-form, has been observed [20]. The break lines were found to follow the boundaries between the β-spherulites; the brittle type of fracture of the α-form PP-i was explained by the break of spherulite boundaries.

Our earlier works [21] have shown the impact strength to be related to spherulitic morphology of PP-i.

The ductile type of break, observed in the dart test, was related to the predominant share of the β-spherulites representing the radial type of lamellar growth. On the contrary, the typical α-spherulites, which besides the radial exhibit also tangential lamellae (Fig. 4) [40], generally produce the brittle type of break.

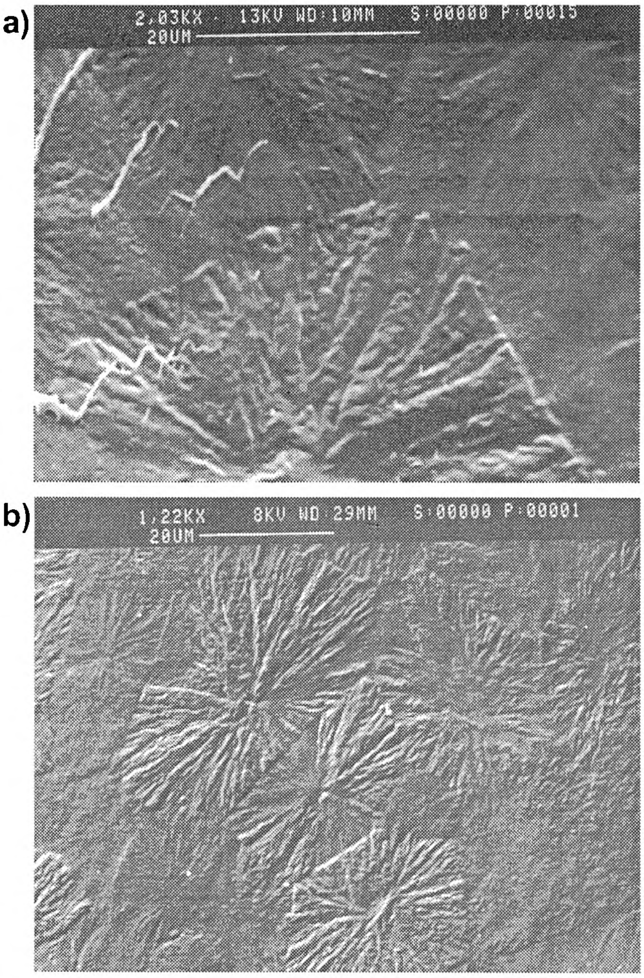

Fig. 4. The scanning electron microphotographs of: a) α — spherulites with well visible radial and tangential lamellae (isotactic polypropylene with 5 x 10^{-5} wt.% of dimethyl quinacridone, a violet pigment), b) β — spherulites characterized by radial growth direction lamellae (isotactic polypropylene with 5 x 10^{-5} wt.% of γ — quinacridone, a red pigment) [40]

Homogeneity of structure and morphology

The distribution of velocities along the cross section of flow of molten polymers in extrusion dies, channels and in injection molds, is known to affect deformations in macromolecular chains, and consequently to give rise to various crystalline structures in the product [43, 44]. The structure and morphology gradients in the polymeric products are also strongly influenced by cooling conditions. The relative low crystallization rate of a pure PP-i, along the cross section of the product gives rise to the formation of a structural-properties gradient on processing. Specific nucleation additives can essentially modify the crystallization kinetics, resulting in highly homogeneous morphologies. Hence the query: "Which effect is predominant: the intrinsic crystallization induced only by external cooling parameter or the nucleation-controlled structure morphology?" remains unsolved by the processing of additive-modified semicrystalline polymers.

The morphology observed in injection molded parts, produced at various mold temperatures should deliver an answer to this question. In this case, samples of neat PP-i and nucleated PP-i were investigated. Neat PP-i samples show always a significant distribution of morphology along the cross section [30]. In Fig. 5, the cross section of PP-i nucleated with 5 x 10^{-5} wt.% of E3B, produced by injection molding at a mold temperature T_m of 45°C is presented. The multilayer structure with the core created by larger spherulites and a fine-grained structure close to the surface is usually observed under these processing conditions. In this case, in the shearing zone near the wall and in the core, bright β-spherulites are seen to occur distributed in the α-spherulite matrix.

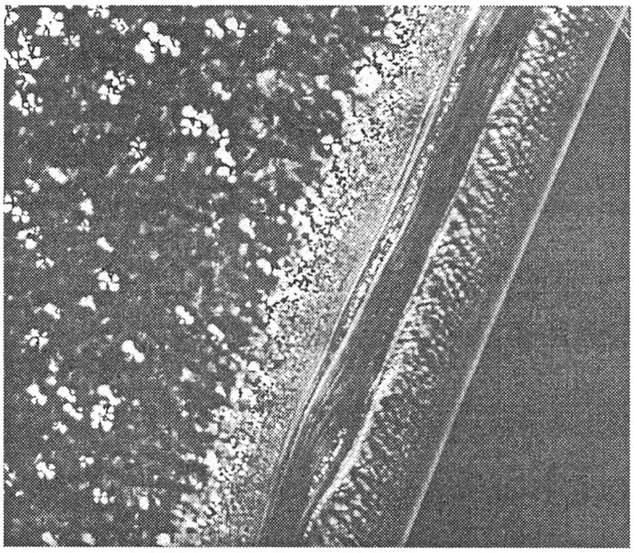

Fig. 5. Morphology across the cross-section of PP-i injection molded samples nucleated with 5 x 10^{-5} wt.% of E3B at mold temperature T_m = 45°C

The higher the mold temperature (T_m) and therefore the lower the induced cooling rate of the product, the thinner is the well visible outer layer (T_m = 90°C) (Fig. 6). The higher mold temperature (T_m = 90°C) combined with even a low quantity of a nucleating agent (5 x 10^{-5} wt.% of E3B), results in a significant homogeneity of morphology across the cross section of the product. Smaller spherulites are formed in the core of the sample, resulting from the higher germination density. The increased crystallization temperature (see Fig. 1), and the lower cooling rate, made the multilayer morphology

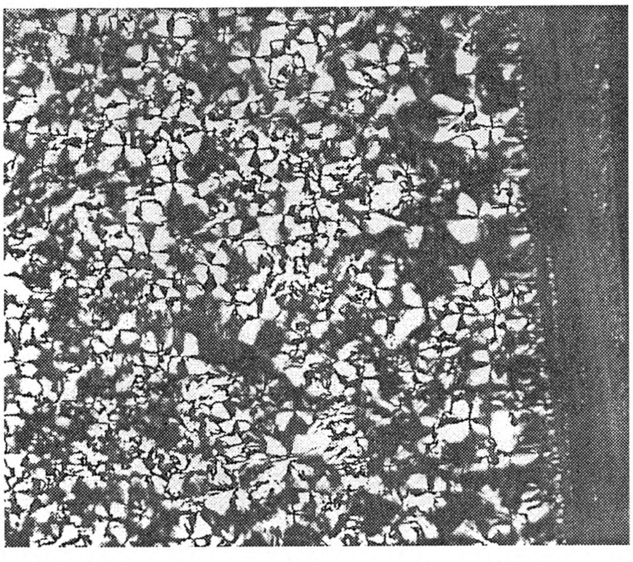

Fig. 6. Morphology across the cross-section of PP-i injection molded samples nucleated with 5 x 10^{-5} wt.% of E3B at mold temperature T_m = 90°C

partly disappear. In this case, almost no fine-grained morphology in the layers near the wall can be observed. It may be expected that such a type of homogeneous morphology gives products of a higher thermal dimensional stability, and more homogeneous in physical and mechanical properties.

Flow induced macromolecular orientation

The shear stresses predominant in the near-wall layers of flowing molten polymers, are responsible for the creation of highly oriented zones in the product [23—25]. The LDA (Laser Doppler Anemometer), *i.e.* a direct and touchless, optical flow velocity measurement, allows to detect the type of stresses and its distribution across the cross section of flowing molten polymers. The huge flow velocity gradient in the near wall layers is the origin of important shear stresses, resulting in a high level of macromolecular orientation in this zone [26—29, 44]. On the contrary, elongation in the core of the flowing molten polymer, followed by relaxation, leads to lower macromolecular orientation. Therefore, a more homogeneous morphology may be observed in the core, as mentioned already before (see Figs. 5 and 6).

Because crystallization of the heterogeneous-nucleated polymers, *i.e.* solidification, starts at a higher temperature, a higher degree of orientation in the nucleated PP-i samples may be awaited to occur. An increase in the crystallization temperature of even 20°C has been observed [21, 30, 36] and therefore the relaxation time of flow induced stresses is strongly limited. This is probably the origin of the "frozen" orientation state of macromolecules resulting from shearing or elongation flow induced deformation.

The macromolecular orientation in the injection molded samples was measured by the WAXS technique in the transmission mode. The flow induced macromolecular orientation was quantified by the α-phase orientation index, presenting the orientation of the *c*-axis parallel to the direction of flow based on the distribution of the diffraction intensity along the azimuth φ angle. Evaluation of this index is based on the equatorial reflection (110), and makes use of the decrease of intensity of the reflections (111) and (131 + 041), when the crystallites are oriented in the direction of flow (A = 1 for highly oriented α-crystallites) [43].

$$A = [H_{\alpha(110)}]/[H_{\alpha(110)} + H_{\alpha(111)} + H_{\alpha(131)} + H_{\alpha(041)}] \quad (1)$$

where: $H_{\alpha(110)}$, $H_{\alpha(111)}$, $H_{\alpha(131)}$ *and* $H_{\alpha(041)}$ *are the heights of the corresponding crystalline peaks, taken from the amorphous background.*

The orientation distribution along the injection molded samples is presented in Fig. 7. It may be noted that the level of the macromolecular orientation depends on the injection molding conditions (mold temperature), *i.e.* on its crystallization kinetics, and on the position along the injection molded flow path. A higher degree of orientation is evident for the lower mold temperature of 45°C; on the contrary, the higher mold temperature, 90°C, results in a lower degree of overall macromolecular orientation. The highest level of the orientation, observed in the narrow parts of the samples both for mold temperatures of 45°C and 90°C, may be attributed to the synergy of the nucleation effect and the shearing-induced increase in the crystallization rate. Especially the shear stresses during filling of the narrow part of the mold cause both the alignment of the chains and the creation of a three dimensional order, *i.e.*, conditions which encourage the overall crystallization.

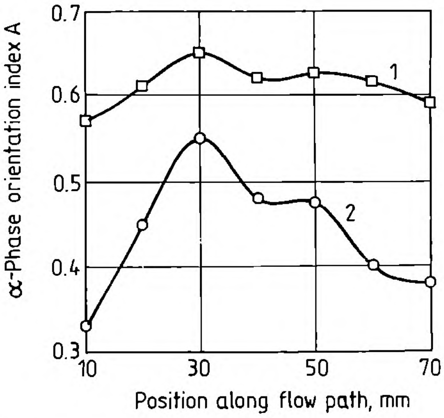

Fig. 7. Distribution of WAXS determined orientation along the flow path of injection molded samples; mold temperature: 1 — 45°C, 2 — 90°C

CONCLUSIONS

Heterogeneous nucleation of isotactic polypropylene is an origin of the higher crystallization temperature, where specific crystallographic forms (α and β) may be created, depending on the composition of the nucleating system. If an appropriate content of the active nucleating additives is applied, the structure-morphology gradient across the cross section of PP-i products almost disappears. Owing to the heterogeneous germination and/or to the shear-induced alignment of the macromolecules in the molten flow, the accelerated crystallization is the origin of the higher level of macromolecular orientation in the PP-i products. Both effects, the heterogeneous nucleation and the processing conditions, influence the structure-properties relationship in the PP-i products.

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