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The Influence of Processing Parameters on the Supermolecular Structure of Isotactic Polypropylene in PP/LDPE Blends

Abstract
In order to analyse the effect of the addition of low-density polyethylene (LD-PE) on the polymorphic transformation in isotactic polypropylene (iPP), structure studies of iPP/LD-PE blends have been carried out. In this work, iPP/LD-PE blends (100/0, 90/10, 80/20 and 70/30 w/w) were prepared by injection moulding under various injection speeds. The supermolecular structure of the blends by means of wide-angle X-ray scattering (WAXS) was analysed. The results have shown that polymorphs of polypropylene developed due to melt-shearing in the mould strongly depend on the injection speed as well as the content of LD-PE in the blends. The polypropylene (without the PE component) was characterized by the highest amount of the hexagonal form. The addition of polyethylene to iPP importantly depressed the formation of β-iPP. Moreover, an increase in the amount of polyethylene caused a significant decrease in the content of the hexagonal phase of polypropylene. The polymorphs of the polypropylene matrix strongly depend on the technological parameters of the processing. At a higher speed of injection, the amount of the hexagonal form of polypropylene slightly increases.

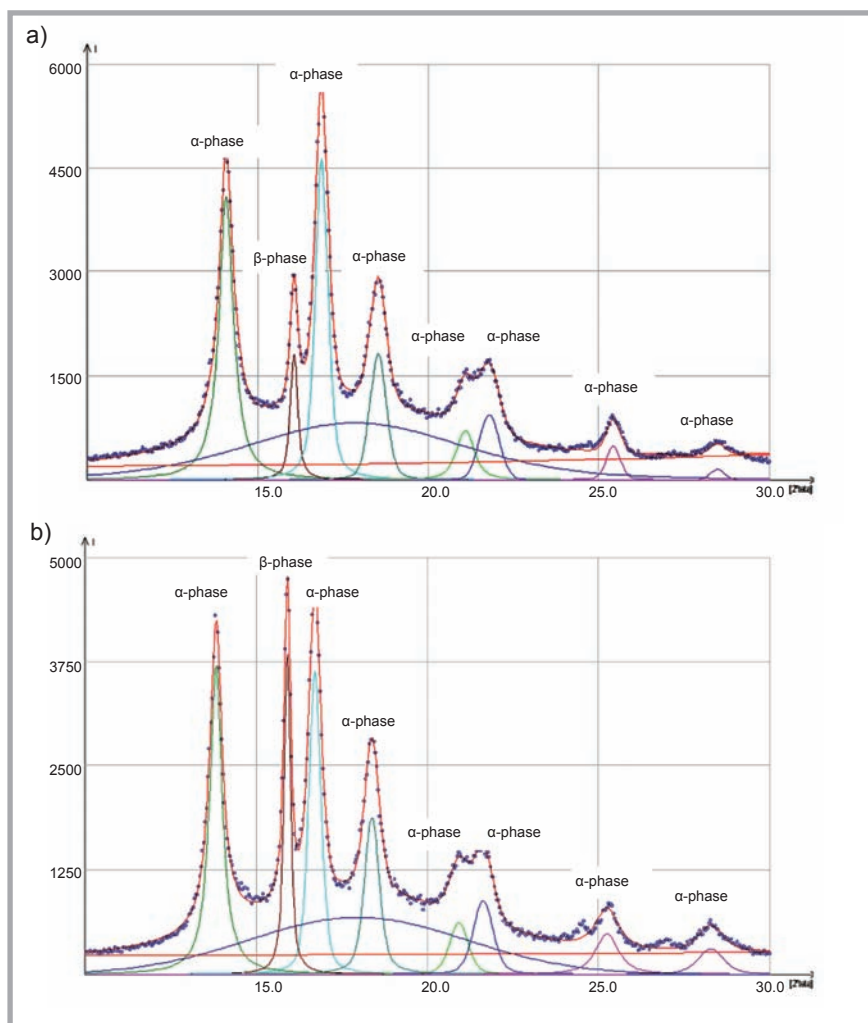**Key words:** *isotactic polypropylene, polymorphs, blends, processing.*

■ Introduction

Polymer blends have received much attention for many decades. Polymer blending is a way of tailoring product properties to specific applications as an alternative to the direct synthesis of new polymeric materials. Much research has been focused on the semicrystalline polymer blend system, isotactic polypropylene (iPP) and polyethylene [1-14]. Blends of iPP and low-density polyethylene (LD-PE) are usually used for the purpose of improving the impact strength and processability of iPP and improving the environmental stress cracking resistance and heat resistance of LD-PE. To date, the most important aspects of iPP/PE blends that have been investigated are related to the influence of their composition on the morphology, mechanical behaviour, melting temperature, crystallinity degree and crystallization rate of components in the melt state [1-14].

The morphology and mechanical properties strongly depend on the miscibility between the components of the blend. The compatibility of the iPP/PE system is quite different depending on the type of PE chain structure. It is known that HD-PE is able to penetrate the iPP phase sufficiently at low HD-PE contents to reduce the number and size of high segment-density regions, delaying the nucleation and crystallization of the iPP phase [15]. In these blends, there was a certain degree of interaction between the components at an HD-PE concentration below 20%. In the iPP/LD-PE system, the miscibility is noted when the iPP content is below 15% [16]. Another study on PP/LD-PE blends has shown that a small addition of LD-PE (10%) caused the depression of the spherulite growth rate of PP and increased the chain folding energy in PP crystallization [7].

The mechanical properties of multiphase materials depend not only on the level of adhesion, but also on the condition of the processing process. The research into the effect of the processing conditions, during the preparation of the blends, on the structure of the polymer is a focal issue because polymorphic changes of polypropylene can take place as a consequence of the temperature of processing and the shear forces. The isotactic polypropylene can exist in several structural modifications [17-19]: monoclinic (α), pseudo-hexagonal (β) and triclinic or orthorhombic (γ). Polymer processing technologies (e.g. injection moulding, extrusion) impose intense shearing flows and have prompted investigation into the crystallization of polymers induced by shearing. Many authors [20-21] have observed that, during shear treatment, crystalline polymer chains are oriented in the melt and can crystallize with both nucleation and growth differently from under quiescent conditions. The main effect of shear is to assist the formation of nuclei by the alignment of polymer chains in the supercooled melt along the shear direction. This alignment may act as a precursor for the formation of stable primary nuclei [20, 23-25]. Kalay and Bevis [25] noted that the difference in the relative proportions of the α, β and γ phases

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93

Figure 1. *X-ray diffraction patterns of the polypropylene obtained during injection speed: a) 40 mm/s, b) 110 mm/s.*

is dependent on the processing conditions and the moulding method. They observed that the core regions of mouldings of iPP are composed mainly of small α-phase spherolites with sporadic β-phase spherolites. The tendency for the formation of hexagonal-phase spherolites was increased with lower melt temperatures. Recently, the composites of iPP with unmodified fibres as well as those modified by acetic anhydride obtained by extrusion and then reprocessed by injection methods were analysed [26]. It was found that, after extrusion in the polypropylene matrix, the monoclinic (α-iPP) and hexagonal (β-iPP) crystal phases were present. The content of the β form was order 25% and depended on the temperature of the extruder die and the content of the fibres.

Thus, a fundamental understanding of the relation between the processing parameters and the supermolecular structure of components in the blend is crucial for the end applications.

Another reason for the interest in studying PP/PE blends is due to the fact that complete separation of post-consumer PP and PE is very difficult: it is necessary to have a good understanding of the behaviour of PP/PE blends.

In this work, the WAXS method was used to determine the polymorphic structure of isotactic polypropylene dependent on the processing parameters in the semicrystalline iPP/LD-PE blend system.

■ Experimental

Materials

Isotactic polypropylene and low-density polyethylene were used in this study as components of the blend system.

Isotactic polypropylene Malen F-401 was supplied by Basell Orlen Polyolefins Plock Poland with an $MFI_{230/2.16}$ – 2.4-3.2 g/10 min, isotacticity – 95% and T_m = 163-164 ºC.

Low-density polyethylene Malen E FABS, 23-D022 (Basell Orlen Polyolefins Plock Poland) had an $MFI_{190/5}$ – 1.6-2.5 g/10 min and T_m = 105–107 ºC.

Sample preparation

In this work, the iPP/PE-LD (10%, 20% and 30% wt. of the PE phase) were compounded by the extrusion method. The blends were mixed in a Fairex single screw extruder (McNeil Akron Repiquet, France) with a screw diameter of 25 mm and a length to diameter ratio of 25:1, operating at a screw speed of 40 rpm. The temperatures for the feeding zone, melting zone, compression zone and die were 140, 180, 200 and 200 °C, respectively. The blends were extruded with a strand die and pelletized prior to sampling.

The samples used for the structure investigation were obtained using injection moulding. The composite materials were prepared using a barrel temperature of 210 °C, injection pressure of 60 bar and a cooling time of the samples in the injection mould of 30 sec. During processing, two different injection speeds of 40 mm/s and 110 mm/s were applied. After moulding, the specimens were immediately sealed in a polyethylene bag and placed in a vacuum desiccator for a minimum of 24 h prior to structural testing.

Structural investigations

The supermolecular structure of the blends was analysed by means of wide-angle X-ray scattering (WAXS) using Cu $K_α$ radiation. The X-ray diffraction pattern was recorded in the angle range of 2Θ = 10-30° in step 0.04°/3 sec. The deconvolution of peaks was performed by the method proposed by Hindeleh and Johnson [27], improved and programmed by Rabiej [28]. After the separation of the X-ray diffraction lines, the contents of the β phase (k) were determined by using the Turner-Jones formula [29]:

$$k = \frac{I_{\beta 1}}{I_{\beta 1} + I_{\alpha 1} + I_{\alpha 2} + I_{\alpha 3}}$$

where:
I – intensities of diffraction peaks from planes: $I_{\beta 1}$ – (300) β phase; $I_{\alpha 1}$ – (110) α-phase; $I_{\alpha 2}$ – (040) α phase; and $I_{\alpha 3}$ – (130) α phase.

The changes in the structure were analysed as a function of the injection speed as well as the content of LD-PE in blends.

Results and discussion

Figures 1a and *1b* illustrate the X-ray diffraction patterns of the polypropylene obtained by the injection technique. The materials were prepared using two different injection speeds (40 mm/s and 110 m/s).

The X-ray diffraction patterns showed that both the applied injection speeds result in the formation of the α and β form. The diffraction patterns in *Figures 1a* and *1b* showed peaks at 2θ = 16.2, which were derived from the β phase of iPP. The amount of β-iPP polymorph depends on the injection speed. In the presence of the higher injection speed, more β phase (29%) is formed than in the case of the lower one (14%).

In the next experiments, we found that the polymorph structure of iPP in blends strongly depends on the injection speed (*Figures 2a* and *2b*).

The X-ray diffraction patterns of iPP/ 10% LD-PE blends show the β phase of iPP beside the α phase. It can also be observed that the peak corresponding to the β phase is more intense on the surface of the sample obtained at the higher injection speed.

Table 1 shows the amount of hexagonal phase vs. content of LD-PE during various injection speeds for all the analysed materials.

From this table, it can be deduced that the polymorphs of the polypropylene matrix strongly depend on the technological parameters of the processing. It should be stressed that the polypropylene had higher values of the hexagonal phase when the higher injection speed was applied. When the blends were obtained at the higher injection speed (110 mm/s), the amount of the β form was higher (about 100%) in comparison with the lower injection speed (40 mm/s).

It is interesting that the presence of LD-PE reduces the amount of the hexagonal form of iPP for each content of polyethylene during the higher injection speed. Moreover, the polymorphs of the polypropylene matrix developed due to melt-shearing strongly depend on the content of LD-PE. An increase in the amount of this compound caused a significant decrease in the ability to induce the hexagonal phase of iPP.
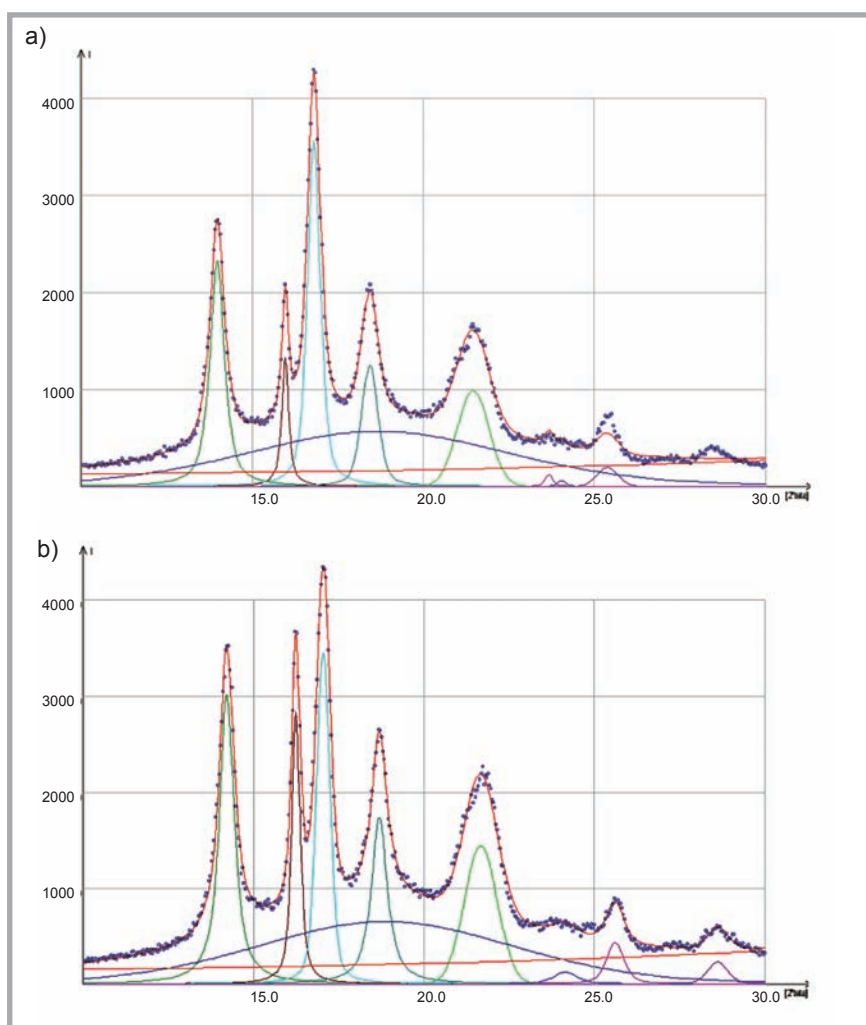
Figure 2. X-ray diffraction patterns of the iPP/10% LD-PE blends obtained during injection speed: a) 40 mm/s, b) 110 mm/s.

Table 1. The amount of hexagonal phase vs. the content of LD-PE during various injection speeds.

Content of LD-PE [%]	Amount of the hexagonal phase of iPP [%]	
	Injection speed – 40 mm/s	Injection speed – 110 mm/s
0	14	29
10	15	26
20	12	21
30	11	16

The explanation of the variability in the amount of the hexagonal form of iPP vs. the content of LD-PE during the higher injection speed may be the kinetic aspect of creation of both polymorphic structures of isotactic polypropylene. The phase transformation from the metastable β phase to the stable α phase has been extensively studied [30-36]. M. Arroyo et al. [7] observed that the growth rate of PP spherulites decreases in the presence of LD-PE particles. Moreover, at LD-PE percentages above 10%, the half crystallization time of the iPP is significant increased. Also, other papers in the literature [37, 38] showed that the iPP spherulite growth rate decreased in the presence of a second component. Our observations suggest that the phase β→α phase transformation is blocked when the content of LD-PE is lower (10%) due to a faster rate of crystallization. In this situation, a larger amount of the hexagonal form is generated. When the rate of crystallization is smaller (in the presence of 30% LD-PE), then the transformation β→α phase is easier and, as a consequence, a decrease in the amount of the β form is observed.

Moreover, it is perfectly visible that, at the lower injection speed (40 mm/s), the content of polyethylene does not influence the values of the hexagonal phase. However, the blends were characterized by similar values in comparison with pure polypropylene. The content of this polymorphic phase was in the range of 11-15%.

The next stage of our investigations will comprise experiments aiming to elucidate the impact of macromolecular orientation as well as other processing parameters on the polypropylene structure in iPP/PE blends.

■ Conclusions

It was found that the polymorphs of polypropylene developed due to melt-shearing in the mould strongly depend on the injection speed as well as the content of LD-PE in the blends. It is very interesting that the polypropylene (without the PE component) was characterized by the highest amount of the hexagonal form. The addition of polyethylene to iPP importantly depressed the formation of β-iPP. The increase in the amount of polyethylene caused a significant decrease in the content of the hexagonal phase of polypropylene. Moreover, the polymorphs of the polypropylene matrix strongly depend on the technological parameters of the processing. At a higher speed of injection, the amount of the hexagonal form of polypropylene slightly increases.

These investigations are very significant because they characterize the influence of real parameters of processing during the injection method on the structure of blends.

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