

Polymorphism of Polypropylene in PP-PA-6 Blends

Abstract

In this paper, the structure and kinetic parameters of isotactic polypropylene in PP/PA-6 blends have been studied as a function of the component content as well as of the presence of compatibilising agent. For this purpose, the styrene-ethylene-butylene-styrene (SEBS) copolymer modified by succinic anhydride was used. Blends containing 10%, 20% and 30% of PA-6 were prepared by extrusion and formed by injection procedures. The samples obtained by the WAXS and DSC methods were analysed. X-ray diffraction analysis showed that in the cases of the 10% or 20% polyamide component in blends, the formation of the beta phase of PP to the amount of 30% was registered. However, the increase in content of PA-6 up to 30% contributed to the decrease of the α -PP phase to 15%. The presence in blends of SEBS agent significantly reduces the induction ability of the beta form of PP for each amount of polyamide. Increasing the content of PA6 to 30% leads to the crystallisation temperature of iPP diminishing, and the half-time of crystallisation lengthening in comparison to materials containing 10% and 20% of PA-6. When the PP/PA-6 system contained SEBS, then an increase in the half-time of crystallisation and a decrease in crystallisation temperature was noted.

Key words: polypropylene, polyamide-6, polymorphism, crystallisation kinetic, WAXS.

Introduction

The essential problem in the formation of polypropylene-polyamide-6 (iPP-PA6) blends is immiscibility, because of the difference in chemical structure of both components. Therefore, to promote interfacial interactions and obtain material, which guarantees good mechanical properties, a compatibilising agent should be applied. Much effort has been made to ensure the compatibilisation of iPP/PA6 blends by using polypropylene grafted with maleic anhydride, or some other compatibiliser such as functionalised styrene block copolymers (styrene-ethylene-butylene-styrene (SEBS)) [3,4].

Moreover, another important factor during the formation of polymer-blends is the

mixing conditions [5,6]. During the solidification of the molten, the PA-6 crystallised first, because the temperature of this component's crystallisation is of the order of 190-180°C, and that of iPP is 130-115°C. Therefore, the surface of polyamide can act as a nucleant of the iPP, and simultaneously influence the kinetic parameters of crystallisation as well as the morphology of the components. Furthermore, the added compatibilising agent should be considered as an additional factor governing the crystallisation process of iPP and PA6 [7,8].

This work is related to our previous studies [8] of the crystallisation of polypropylene in the presence of PA-6. The objective of this work is to evaluate the influences of the PA-6 and the compatibi-

lising agent on selected kinetic parameters of crystallisation, as well as on the formation of the crystal structure of the polypropylene matrix.

Experimental

Materials

For the preparation of the polymer blends, the following polymers were used:

- polypropylene Malen F-401 (Orlen Plock),
- polyamide-6 Tarnamid T-27 (ZAM Tarnow),
- styrene-ethylene-butylene-styrene copolymer (SEBS) Kraton FG 1901X (Shell) to the amount of 10% was used as a compatibilising agent.

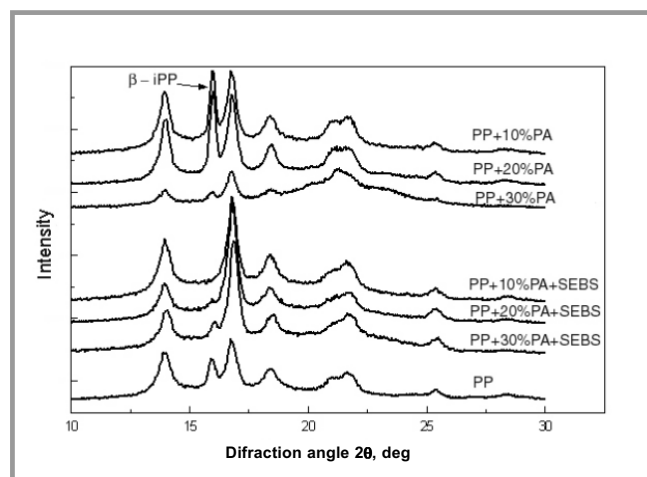


Figure 1. X-ray diffraction pattern of blends, MS side.

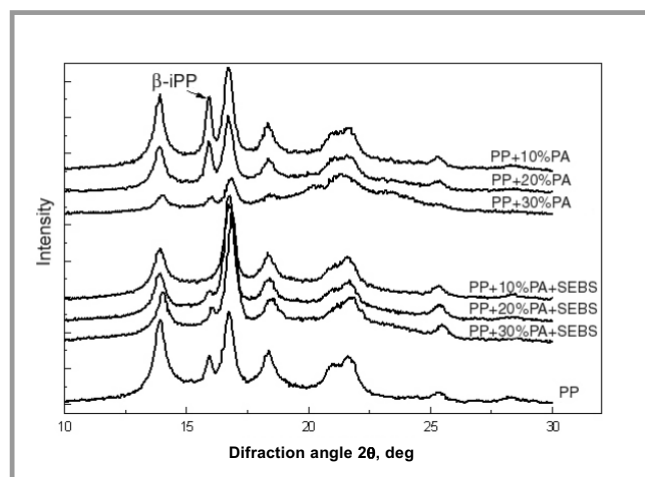


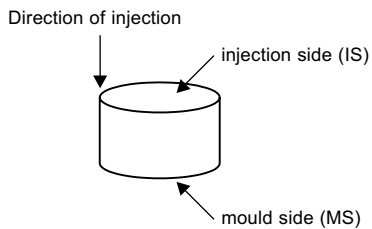
Figure 2. X-ray diffraction pattern of blends, IS side.

Blending

Before processing, all components were dried at 70°C for polypropylene, and at 100°C for PA-6, for 8 h.

The blends of PP/PA-6 (10%, 20% and 30% wt of the PA-6 phase) were prepared by melt-mixing in an extruder. All blends were granulated to injection process for further forming.

The two sides of the moulded piece (injection and mould) in the following measurements were analysed.



X-ray diffraction

The supermolecular structure of blends was analysed by means of wide-angle X-ray scattering (WAXS) using Cu K α radiation. The diffractograms were recorded in an angle range of 10-30° 2 θ . Deconvolution of peaks was performed by the method proposed by Hindeleh & Johnson [9], as improved and programmed by Rabiej [10]. The content of the hexagonal form iPP was determined by the Turner-Jones formula [11].

Calorimetry

The kinetic parameters of non-isothermal crystallisation were carried out using differential scanning calorimetry (NETZSCH). The DSC measurements were realised us-

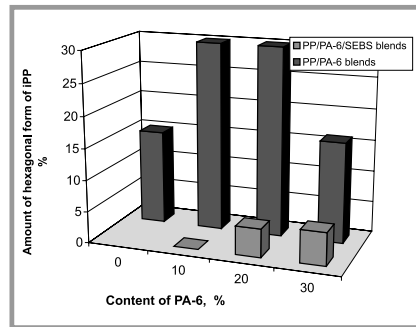


Figure 3. Amount of hexagonal form of iPP vs. content of PA-6 for blends, MS side.

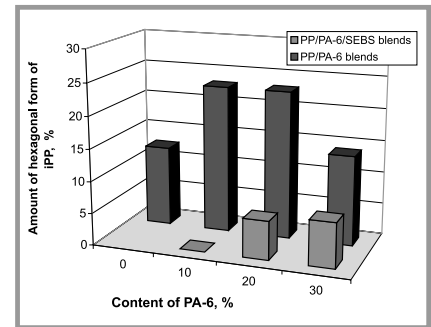


Figure 4. Amount of hexagonal form of iPP vs. content of PA-6 for blend, IS side.

ing the following procedure: a) heating up to 250°C at a rate of 10°C/min; b) maintaining this temperature (250°C) for 5 min; c) cooling to 40°C at a rate 5°C/min. Such a procedure was repeated twice at the same conditions and for all samples.

The degree of crystal conversion, the half-time of crystallisation and the crystallisation temperatures were all determined.

Results and discussion

Figures 1 and 2 show the X-ray diffraction pattern of PP/PA-6 blends with and without the compatibilising agent, obtained by the injection process. The mould side (MS) and injection side (IS) of the samples were analysed. The amount of the hexagonal polymorph as a function of content of PA-6 for the MS and IS samples is shown in Figures 3 and 4.

The diffraction patterns of the MS and IS samples in Figures 1 and 2 showed peaks at $2\theta = 16.2$, which derived from the β -phase of iPP.

In the presence of the 10% or 20% polyamide component in blends (MS), the β -iPP rises in amount to 30%. When PA-6 is 30%, then the content of β -PP drops to 15%. These values are similar to those in the samples of pure polypropylene obtained by the injection method (Figure 3 and 4).

It is worthy of note that the presence of SEBS reduces the amount of the hexagonal form of PP for each amount of polyamide. The content of this polymorphic phase fell within the range of 0 – 6% only.

Moreover, larger contents of β -PP on the mould side were observed in comparison to the injection side (Figure 4). The noted behaviour is most likely an effect of differences in the cooling rate.

Figures 5 and 6 shows the DSC curves for cooling cycles of blends with and without the SEBS compatibiliser. Figure 7 shows the dependence of the crystal conversion of iPP vs. time crystallisation, and Figure 8 shows the half-time values

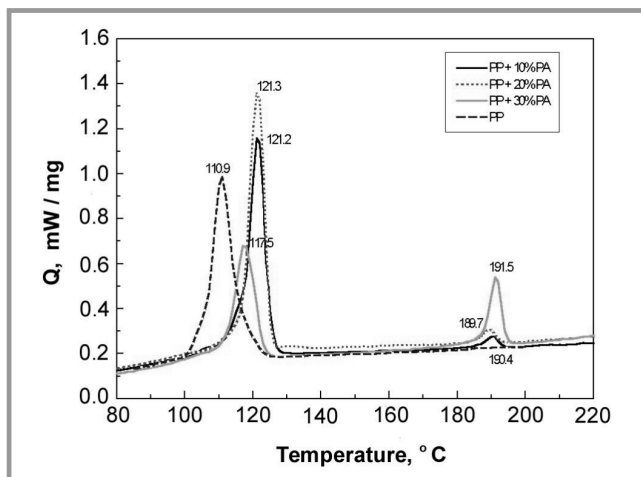


Figure 5. DSC curves for cooling cycles of PP/PA-6 blends without SEBS agent.

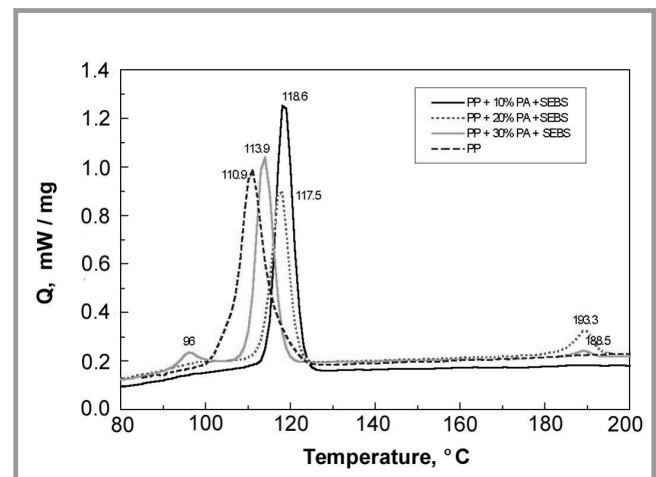


Figure 6. DSC curves for cooling cycles of PP/PA-6 blends with SEBS.

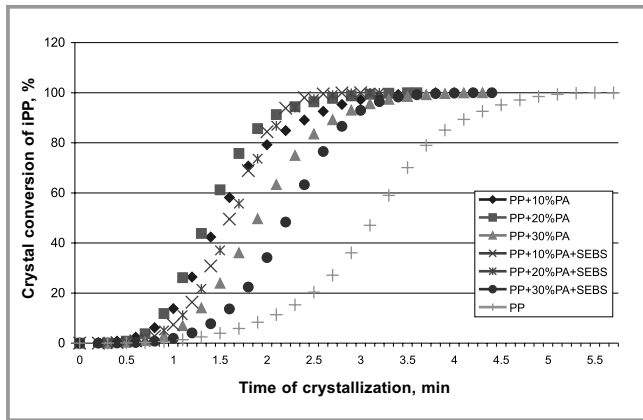


Figure 7. Degree of crystal conversion of iPP in PP/PA-6 blends.

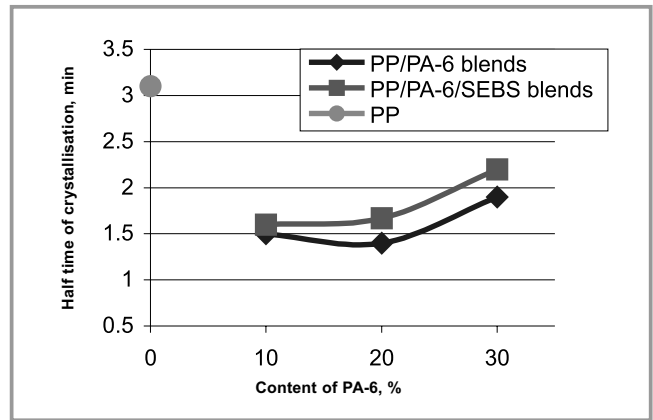


Figure 8. Half-times of crystallisation of iPP in PP/PA-6 blends.

of crystallisation ($\tau_{0.5}$) vs. amount of PA-6 respectively.

The results registered by the DSC method confirmed that the presence of SEBS caused a lowering of the crystallisation temperature of T_c of iPP for each composition of blends (Figures 5, 6). It is interesting that the crystallisation temperature of iPP practically hardly changed at all up to 20% content of PA-6, and fell by about 3°C at 30% content of PA6. However, in the case of blends with 30% PA6 and 10% SEBS, the T_c of polyamide was noted at 90°C. Such a dramatic reduction of T_c of PA6 in the presence of SEBS was also observed by Ohlsson et al. [7].

The curves presented in Figure 7 showed that the courses of the degree of crystal conversion of iPP in blends have a similar character, although significantly differing from those in pure polypropylene.

The half-time of crystallisation vs. the content of blends (Figure 8.) showed that iPP in blends crystallises twice as fast in comparison to pure polypropylene. However, in the presence of SEBS, the $\tau_{0.5}$ was slightly lengthened, and if the content of PA6 in blends increased to 30%, then $\tau_{0.5}$ significantly lengthens. Similar effects have been detected by Compoy et al. [3], who observed that the crystallisation rate

of PP in blends is higher than the corresponding value for pure PP, and crystallisation was faster in blends without compatibilising agents.

Table 1 collects some parameters of crystallisation of iPP and the registered amount of β -PP arising during the processing of iPP/PA6/ blends.

The data presented in Table 1 indicates a certain relationship between the parameters of crystallisation and the amount of beta-polymorphic modification. When $\tau_{0.5}$ is shorter and the crystallisation temperature is higher, then more β -PP is formed.

Conclusions

From the structural study, the following conclusions can be drawn:

- 1) The presence of a 10% or 20% polyamide component in iPP/PA6 blends prepared by the injection method causes the formation of significant amounts of the hexagonal phase of PP (30%). The increase in PA-6 content of up to 30% contributed to the decrease in β -PP phase to 15%.
- 2) The styrene-ethylene-butylene-styrene (SEBS) copolymer modified by succinic anhydride added to the blends

reduces the induction ability of the beta form of PP for each amount of polyamide. The content of this beta polymorphic phase diminishes to only 6%.

- 3) The presence of compatibilising agents in polymer blends causes an increase in the half-time of crystallisation and a reduction in the degree of crystal conversion of polypropylene.
- 4) Blends containing 30% of PA-6 are characterised by a lower crystallisation temperature of iPP and an extended half-time of crystallisation of iPP in comparison to blends with 10% and 20% of PA-6.

□

Acknowledgments

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Table 1. Parameters of crystallisation and amount of β -PP in PP/PA-6 blends.

Content of PA-6 in PP/PA-6 blends, %	Half time of crystallisation of PP, min]	Crystallisation temperature of PP, °C	Amount of β -PP, %
0	3.1	110.9	15
10	1.5	121.2	30
20	1.4	121.3	30
30	1.9	117.5	16

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