Primary nucleation behaviour in isotactic polypropylene/ethylene–propylene random copolymer blends

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Primary nucleation of spherulites in blends of isotactic polypropylene (iPP) with ethylene–propylene random copolymer (EPM) has been investigated using optical microscopy. The number of spherulites generally increases with increasing EPM content. It is shown that this increase is caused by migration of heterogeneous nuclei across interface boundaries from EPM to iPP during melt-mixing. The migration was observed in the blends with the nucleating agent initially added to EPM before blending with iPP. It is suggested that the interfacial free energy difference between nuclei and the molten components of the blend is responsible for the migration of nuclei. It is also shown that self-seeded nucleation becomes damped in the blends due to partial solubility of the components and that the degradation of the blends during melt-annealing depresses the primary nucleation.

(Keywords: blends; crystallization; primary nucleation; nuclei migration; self-seeding; polypropylene; ethylene–propylene copolymer)

INTRODUCTION

In the rapidly growing literature on polymer blends (see e.g. the reviews 1 or 2) there are relatively few papers devoted to the crystallization behaviour of crystallizable polymer blends, and only some of them report the results of studies on primary nucleation[3–9].

In a previous paper[7] we have described the change of the primary nucleation of isotactic polypropylene (iPP) in binary blends with low density polyethylene (LDPE). We have found that the presence of LDPE causes a drastic depression of the density of nucleation of iPP in the blend. The depression is brought about by the migration from iPP to LDPE during the melt-mixing process of those particulate impurities which are able to induce heterogeneous nucleation.

In the case of iPP blended with various rubbers such as ethylene–propylene random copolymers (EPM), ethylene–propylene diene terpolymers (EPDM), and poly(isobutylene) (PiB) it was found[4,8,9] that the presence of rubber causes an increase in the number of primary nuclei of iPP in the blends.

The iPP/EPM blends generally form heterogeneous systems in which EPM inclusions are incorporated within the iPP matrix[4,8,9]. However, the melting behaviour and crystallinity of these blends point to a partial miscibility of the components. It has been shown[4] that EPM is able to dissolve during blending a number of iPP molecules with relatively higher concentrations of chemical defects (steric defects) as well as molecules of lower molecular mass.

The aim of the study reported here was to investigate primary nucleation behaviour in iPP/EPM rubber blends especially the phenomena occurring in the course of blend preparation.

EXPERIMENTAL

Materials

The materials employed were isotactic polypropylene (Montedison, Moplen S 30 S, density 0.910 g/cm^3, melt flow index 1.7 g/10 min) and ethylene–propylene random copolymer (Montedison, Dutral Co 54, $M_w = 1.8 \times 10^5$, density 0.865 g/cm^3, ethylene:propylene ratio 6:4). Sodium benzoate obtained from Carlo-Erba (Italy) was employed as the nucleating agent for polypropylene.

Preparation of blends

Blends containing 0, 10, 20, 30 wt% of EPM were prepared in the following way:

Powders of iPP and EPM were obtained by precipitation from xylene solution with methanol and were dried under vacuum. The powders were premixed in desired proportions and blended by extrusion in a laboratory mixing extruder at 190°C (Custom Scientific Inc. mini-extruder). The extrusion process was repeated for part of each species to study the influence of the duration of blending.

In order to study the effect of the nucleating agent a quantity of finely powdered crystalline sodium benzoate

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was premixed in the extruder separately with iPP and EPM and the following blends were then prepared: (iPP + sodium benzoate) + EPM (blend code iPP*/EPM) and iPP + (EPM + sodium benzoate) (blend code iPP/EPM*). (The asterisk refers to the polymer to which the nucleating agent was added.) The ratio of the components was 79.8:20:0.2 of iPP, EPM and sodium benzoate respectively. The number of spherulites in isothermally crystallized films of those blends was studied as a function of the number of mixing passes in a single-screw extruder ($L/D = 25$) at 200°C.

In order to observe the influence of the presence of EPM on self-seeded nucleation, a blend containing 0.2 wt% of EPM and 99.8 wt% of iPP was prepared by dissolving both components in xylene followed by precipitation and drying. The powder was mixed in a Brabender-type apparatus (Rheocord EC, Haake Inc.) at 190°C with a residence time of 2 min at a roller speed of 2 rpm followed by 10 min at 32 rpm. The blend was then additionally mixed three times in a miniextruder.

The compositions of the investigated blends are shown in *Table 1*.

Sample preparation and techniques

After mixing the blends were in the form of cylindrical filaments (about 2 mm in diameter). In order to study the nucleation behaviour by optical microscopy sections 20 μm thick were cut out from the filaments by means of a microtome (LKB). The sections were placed on microscopic support glasses and covered by pieces of cover glass with no immersion medium. The cover glasses were approximately the same size as the samples. Sample thickness was measured with an accuracy of 1 μm before and after crystallization. The density of primary nucleation was calculated from mean values. The samples were crystallized isothermally on a microscopic hot stage (Mettler FP 5). Before crystallization the samples were melted and annealed for 5 min at 190°C, 230°C or 250°C. Isothermal crystallization was conducted at 119°–135°C.

The number of spherulites was determined from micrographs taken by means of a polarizing microscope and recalculated to the number of nuclei per unit volume of iPP in the blend.

The d.s.c. measurements were carried out using a Mettler DSC 30 apparatus.

RESULTS AND DISCUSSION

It is well known that the nucleation behaviour of polymers depends on the temperature and time of melt-annealing of the sample before crystallization[10,11].

In our studies the time of melt-annealing was 5 min for all samples, whereas the temperature was in the range 190°–250°C.

If the sample is melted and annealed at 190°C, all modes of primary nucleation (homogeneous, heterogeneous and self-seeding) of polypropylene are allowed. At higher annealing temperature (230°C and 250°C) self-seeded nuclei disappear because the annealing temperature is higher than the equilibrium melting temperature of polypropylene (the highest estimation of T_m° is 220°C[12,13]).

At crystallization temperatures above 112°–117°C practically only heterogeneous nucleation is possible, but if the crystallization temperature is lower, homogeneous nucleation may also take place. By changing the annealing and crystallization temperatures it is possible to investigate the separate modes of nucleation.

In *Figure 1* the numbers of nuclei recalculated per unit volume of polypropylene in the blend as a function of EPM concentration are plotted for various mixing conditions, melt-annealing and crystallization temperatures. As can be seen, the number of nuclei per unit volume increases with increasing concentration of EPM in the blend for all conditions of sample treatment, except for the blends mixed once and annealed before isothermal crystallization at 190°C.

The most representative of this behaviour are the blends melt-annealed before crystallization at 230°C. At that temperature self-seeded nucleation is eliminated and the degradation process is not very intensive. The number of nuclei in samples crystallized isothermally after such annealing increases not only with increasing EPM content but also with increasing number of mixing passes (see *Figure 1c* and *1d*). In the explored range of crystallization temperatures in the absence of self-seeding the main mode of nucleation is the heterogeneous nucleation (homo-

Table 1 Blends investigated in the study

Blend code	iPP (wt%)	EPM (wt%)	Sodium benzoate (wt%)	Number of mixing passes	Temperature of melt-annealing (°C)	Temperature of crystallization (°C)
100:0/1 ×	100	0	0	1	190, 230, 250	119, 125, 135
90:10/1 ×	90	10	0	1		
80:20/1 ×	80	20	0	1		
70:30/1 ×	70	30	0	1		
100:0/2 ×	100	0	0	2	190, 230, 250	119, 125, 135
90:10/2 ×	90	10	0	2		
80:20/2 ×	80	20	0	2		
70:30/2 ×	70	30	0	2		
100:0/1 ×	100	0	0	1	190, 220	129, 131
100:0/3 ×	100	0	0	3		
99.8:0.2/1 ×	99.8	0.2	0	1		
99.8:0.2/3 ×	99.8	0.2	0	3		
iPP*/EPM[a]	79.8	20	0.2	1–7	220	132
iPP/EPM*[b]	79.8	20	0.2	1–7		

[a] Sodium benzoate added initially to iPP

[b] Sodium benzoate added initially to EPM

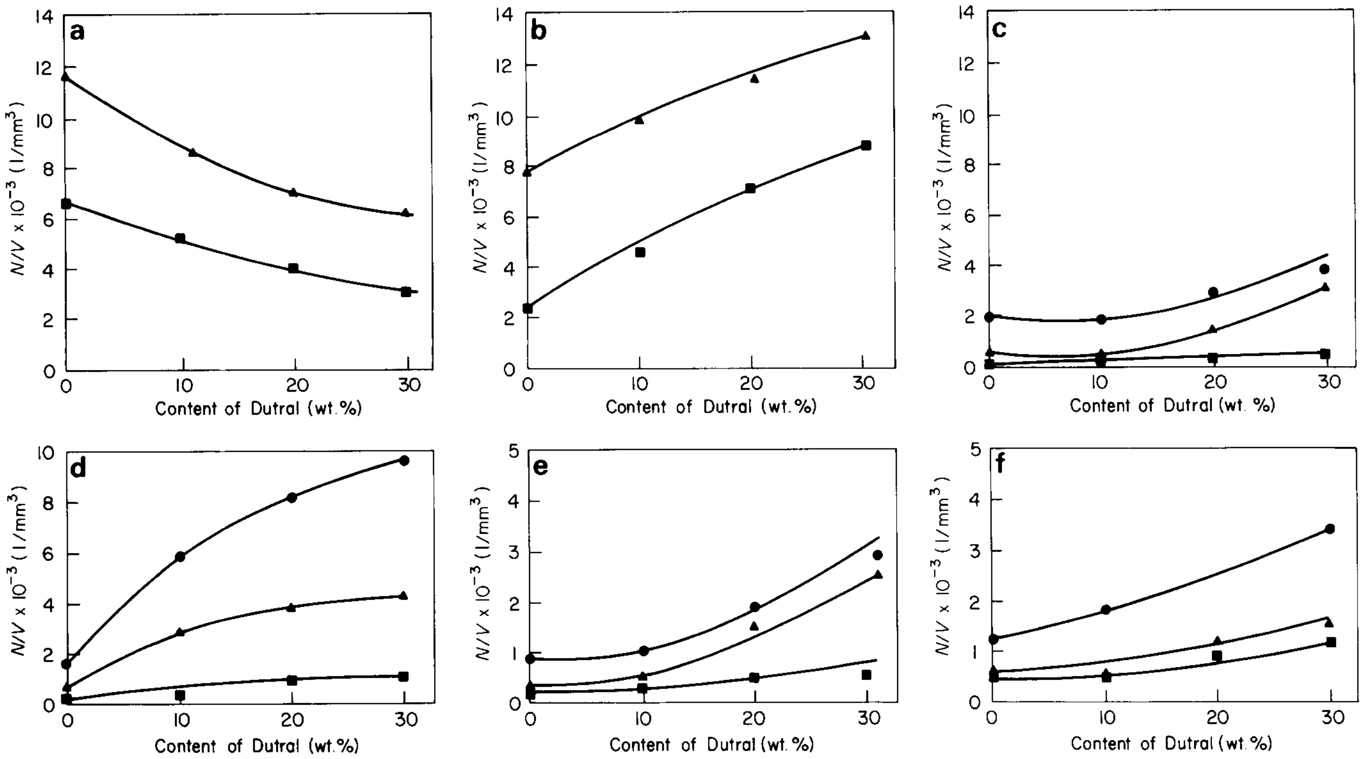

Figure 1 Dependence of the number of primary nuclei per unit of volume of iPP in the blends on the concentration of Dutral-EPM for different temperatures of annealing (T_a) and the number of mixing passes: (a) $T_a = 190°C$, blends mixed once in mini-extruder; (b) $T_a = 190°C$, blends mixed twice; (c) $T_a = 230°C$, blends mixed once; (d) $T_a = 230°C$, blends mixed twice; (e) $T_a = 250°C$, blends mixed once; (f) $T_a = 250°C$, blends mixed twice; (●): $T_c = 119°C$; (▲): $T_c = 125°C$; (■): $T_c = 135°C$

geneous nucleation is relatively small for such undercoolings). Thus, the increase of the nucleation density is due mainly to the increase of the number of heterogeneous nuclei. Our similar studies conducted for iPP/LDPE[7] and iPP/HDPE blends[14] led us also to the conclusion that the main reason for the change of the nucleation density in those blends is a quantitative change of the heterogeneous nucleation.

Our hypothesis, confirmed for the systems mentioned above, is that the impurities present in the volume of both components of the blend which induce heterogeneous nucleation are able to migrate across the interface from one polymer to the other during the melt-mixing process. It is suggested that the driving force for this phenomenon is the difference in the interfacial free energies of the nuclei surrounded by iPP melt and those surrounded by the melt of the second component of the blend. During melt-mixing the nuclei can move in the volume of the blend and pass across the interface between the components. For energetic reasons, more probable is passing to the polymer, with respect to which the nucleus has lower interfacial free energy. Consequently, after the mixing process the crystallizable component of the blend becomes richer or poorer in heterogeneous nuclei, depending on the sign of the difference in interfacial free energies.

In the case of iPP/EPM blends heterogeneous nuclei tend to migrate from EPM to iPP (negative interfacial free energy difference), so the polypropylene becomes richer in heterogeneous nuclei and, consequently, the overall number of active nuclei in the blend increases. The intensity of migration obviously depends on the content of the second polymer in the blend (constituting a reservoir of potential nuclei) while the efficiency of the process depends on the time (or intensity) of mixing. The number of nuclei in the iPP/EPM blends (when they were melt-annealed at 230°C before crystallization) simply increases with increasing EPM concentration and for samples with fixed concentration it increases with increasing mixing time. Such behaviour confirms the hypothesis of migration.

In order to test the migration of heterogeneous nuclei hypothesis we carried out experiments consisting of blending iPP and EPM which contained a quantity of deliberately introduced nucleating agent. Sodium benzoate was chosen as a very effective nucleating agent for polypropylene[15,16].

Two 8:2 iPP/EPM blends containing 0.2 wt% sodium benzoate were prepared in the way described in the experimental section. In the first blend sodium benzoate particles were initially introduced into iPP before blending with EPM (iPP*/EPM blend) while in the second blend they were initially introduced into EPM before blending with iPP (iPP/EPM* blend). The blends were melt-mixed several times in an extruder. After each mixing pass a sample was taken and it was isothermally crystallized at 132°C (melt-annealing at 220°C for 5 min). For each sample the number of spherulites per unit volume was determined. The results of this experiment are shown in *Figure 2*.

The number of nuclei per unit volume in the blend iPP*/EPM (nucleating agent initially introduced into iPP volume) is practically independent of the number of mixing passes. In contrast, in iPP/EPM* blend (nucleating agent initially introduced into EPM volume) the number of nuclei per unit volume increases with increasing mixing time and finally reaches the value near that for iPP*/EPM blend. The nucleation densities converge to the same value independently of the initial location of the nucleating agent in the sample. This behaviour evidently shows that the heterogeneous nuclei

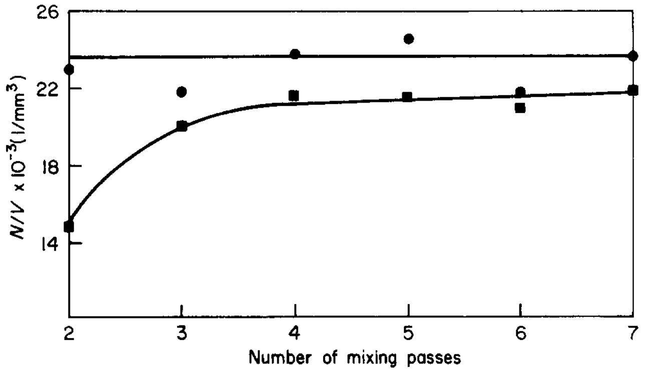

Figure 2 Dependence of the density of primary nucleation on the number of mixing passes for 8:2 iPP/EPM blends containing sodium benzoate particles as the nucleating agent: (●): iPP*/EPM; (■): iPP/EPM* (the asterisk indicates the polymer to which the nucleating agent was initially introduced). All samples were annealed at 220°C for 5 min and crystallized isothermally at 132°C

migrate from EPM to iPP and do not migrate in the opposite direction.

It should be emphasized that the migration occurs during the mixing process; therefore, the increase in the number of heterogeneous nuclei should be observed for all annealing and crystallization temperatures. However, as will be shown below, there are other phenomena overlapping the migration.

The number of nuclei in the blends crystallized after melt-annealing at 250°C also increases with increasing EPM concentration in the blend as for samples melt-annealed at 230°C (see *Figure 1e* and *1f*). However, the increase is not as great as for samples annealed at 230°C. The explanation of that behaviour is that although the nucleation density increases due to migration of heterogeneous nuclei during melt-mixing, annealing at 250°C causes partial degradation of the samples which inactivates some of the nuclei.

In order to find out whether the degradation influences the nucleation, the samples were annealed at 190°C, 230°C and 250°C in a d.s.c. cell in the presence of air. The endotherms plotted against time in *Figure 3* show that when the blends were annealed at 250°C much more intensive degradation took place than at lower temperatures. Moreover, curves C and D in the Figure indicate that almost all of the thermal effect is connected with the degradation of polypropylene. Similar results (not shown here) were obtained for blends mixed twice.

The following experiment illustrates the influence of degradation on the primary nucleation: 90:10 iPP/EPM blends, mixed once and twice, were treated according to the scheme:

melt-annealing at 250°C for 5 min→
non-isothermal crystallization→
melt-annealing at 190°C for 5 min→
isothermal crystallization at 125°C

During the first annealing (250°C) the sample undergoes degradation. It was then crystallized non-isothermally, melted again and annealed at 190°C (the degradation is slow at this temperature) and crystallized isothermally at 125°C. After crystallization the number of spherulites per unit volume was determined. For comparison, a non-degraded (reference) sample, having the same composition and mixing history, was prepared in the following way:

melt-annealing at 190°C for 5 min→
non-isothermal crystallization→
melt-annealing at 190°C for 5 min→
isothermal crystallization at 125°C

The number of spherulites after crystallization at 125°C was also determined for that sample.

Both the degraded and reference sample were annealed for the same time although at different temperatures. Because of non-isothermal crystallization both samples ought to have similar morphology before the second melting and annealing. Thus, they should exhibit similar self-seeding behaviour.

The results of this experiment are presented in *Table 2*. The number of spherulites per unit volume in the degraded sample is much less than that for the reference sample. The treatment of both samples was the same except the temperature of the first melt-annealing. Therefore, only degradation could have evoked the depression of nucleation in the blends. The conclusion following from that experiment is that the observed decrease in the number of nuclei with the temperature of annealing increasing from 230°C to 250°C and for constant blend composition is caused by a degradation process occurring during annealing at 250°C. The degradation reduces mainly the nucleation process involving molecular nucleation, i.e. self-seeding because of the change of molecular chain length. Due to shortening of the

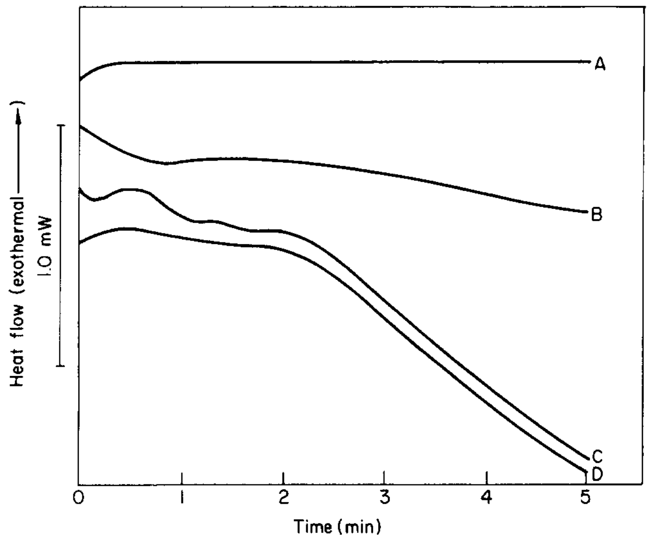

Figure 3 Thermograms of iPP and 7:3 blend annealed in d.s.c. apparatus taken at constant temperature in the presence of air: Curve A: iPP mixed once, $T_a = 190°C$; curve B: iPP mixed once, $T_a = 230°C$; curve C: iPP mixed once, $T_a = 250°C$; curve D: 7:3 blend mixed once, $T_a = 250°C$. All curves recalculated to sample weight of 1 mg

Table 2 Densities of primary nucleation in 90:10 iPP/EPM blends in crystallization at 125°C ('degradation experiment')

Sample	$N/V \times 10^{-3}$ (mm^{-3})
90:10/1 × (degraded)	0.95
90:10/1 × (reference)	3.97
90:10/2 × (degraded)	0.62
90:10/2 × (reference)	3.42

molecular chains the heterogeneous mode of nucleation should change to only a small extent. This conclusion is in agreement with experimental results.

When the blends were melt-annealed at 190°C before crystallization their nucleation was somewhat different than for higher annealing temperatures. The number of primary nuclei in the blends which had been mixed once decreased with increasing EPM concentration whereas in the blends, which had been mixed twice, it increases (see *Figures 1a* and *1b*).

As has been shown above, migration of heterogeneous nuclei occurs during melt-mixing, so the resulting increase in the number of nuclei should be observed regardless of the temperature of melt-annealing before crystallization. Such a behaviour is in fact observed in the blends mixed twice (*Figure 1b*) although the number of nuclei per unit volume is not as high as it is in the case of melt-annealing at 230°C. However, for blends mixed once, when the migration of nuclei is not as large, the opposite effect is observed (*Figure 1a*). Such behaviour indicates that in blends annealed at 190°C the effect of migration of heterogeneous nuclei is screened by some other effect.

On the other hand, it is known[11] that melt-annealing at 190°C allows self-seeding nucleation in polypropylene during its crystallization. That mode of primary nucleation does not appear in the previously discussed cases. This suggests that it is only self-seeding nucleation that is damped in the presence of EPM and it depresses the overall primary nucleation in the blends as compared with plain iPP.

It has been suggested[4] that iPP and EPM are partially miscible – during mixing EPM dissolves those parts of iPP molecules which have locally higher concentration of chemical defects and molecules with lower molecular weight.

Our suggestion is that partial miscibility of the components of the blend causes a decrease in the number of self-seeding nuclei. In order to test that concept two sets of experiments were carried out:

(i) Two samples containing 99.8 wt% of iPP and 0.2 wt% of EPM (code 99.8:0.2) and 100% of iPP (100:0) were prepared by the method described in the Experimental section. A small amount of EPM in the blend and a long time of mixing were employed in order to achieve a homogeneous blend (partial solubility of the EPM in iPP is probably less than 1%). If the blend is homogeneous, migration of nuclei does not occur, and only the self-seeding primary nucleation can change in the blend. Samples of the blends were crystallized isothermally at two different temperatures after melt-annealing at 190°C (self-seeding nucleation is allowed) or 220°C (most of self-seeding nuclei disappear). Following that the number of nuclei per unit volume was determined. The values of nucleation density are presented in *Table 3*. When the samples were melt-annealed at 220°C (no self-seeding) both the 99.8:0.2 blend and plain iPP exhibit almost the same nucleation density (within experimental error). However, when self-seeding is active (melt-annealing at 190°C) the density of nucleation in the blend is several times lower than in pure iPP conditioned in the same way. Such results are in agreement with our hypothesis of the influence of partial miscibility of EPM with iPP on self-seeding in iPP.

An additional observation was made in this experiment: in the 99.8:0.2 blend many β-form spherulites were observed. Also in blends containing a larger amount of EPM a certain number of β-form spherulites was observed but not as many. On the other hand samples of plain iPP, although prepared in the same way, do not contain an excessive number of β-form spherulites. The explanation might be that EPM which is well dissolved in iPP induces the nucleation and growth of the β-form and not of the α-form. A similar observation for iPP/PE blends is reported in ref. 17.

(ii) In the second set of experiments we crystallized samples of 80 wt% iPP and 20 wt% EPM, and plain iPP (mixed once and twice) according to the following procedure:

melt-annealing at 190°C for 1 min →
non-isothermal crystallization →
melt-annealing at 190°C for 1 min →
isothermal crystallization at 131°C →
melt-annealing at 190°C for 1 min →
non-isothermal crystallization →
melt-annealing at 190°C for 1 min →
isothermal crystallization at 125°C

and the reference sample:

melt-annealing at 190°C for 3 min →
non-isothermal crystallization →
melt-annealing at 190°C for 1 min →
isothermal crystallization at 125°C

Both samples were annealed together for 4 min at 190°C. Due to non-isothermal crystallization the samples are supposed to possess similar crystal morphologies before the last melting and annealing (important for self-seeding). The only difference was that the first sample was additionally at 131°C at the beginning of the experiment. The purpose of this crystallization was to segregate dissolved EPM from iPP. Crystallization at 131°C is relatively slow so the crystals grow more perfectly and segregation of the components can occur. In this way we intended to obtain samples with exactly the same composition but with different component structure – the first sample possessing more separated components and the reference sample more homogeneous. In the sample of plain iPP we did not expect any changes. They were crystallized only for reference to detect any changes in nucleation behaviour in pure polypropylene caused by the treatment.

Table 3 Number of nuclei per unit volume in iPP and the 99.8:0.2 iPP/EPM blends ('solubility experiment')

Sample	T_c (°C)	$N/V \times 10^{-3}$ (mm^{-3})	
		$T_a = 190$°C	$T_a = 220$°C
100:0/1 ×	129	28.10	1.53
99.8:0.2/1 ×	129	7.00	1.62
100:0/3 ×	129	19.30	1.09
99.8:0.2/3 ×	129	4.13	0.55
100:0/1 ×	131	25.42	1.38
99.8:0.2/1 ×	131	4.39	1.28
100:0/3 ×	131	15.12	0.79
99.8:0.2/3 ×	131	3.56	0.83

Table 4 Number of nuclei per unit volume in the 80:20 blend and plain iPP crystallized at 125°C ('segregation experiment')

Sample	$N/V \times 10^{-3}$ (mm^{-3}) Reference	'Segregated'	Percentage increase
80:20/1 ×	8.29	10.43	25.8
100:0/1 ×	12.26	12.69	3.5
80:20/2 ×	14.92	19.17	28.5
100:0/2 ×	9.03	8.99	−0.4

After crystallization at 125°C the number of spherulites per unit volume was determined in all samples. The results are presented in *Table 4*. The nucleation density in iPP samples does not vary much, so the thermal treatment does not cause any marked changes in the nucleation of iPP. In the samples containing EPM the number of spherulites increased when the sample was initially slowly crystallized (at 131°C). This means that separation of the components due to crystallization restores the ability of iPP to undergo self-seeding.

The results of both experiments ((i) and (ii)) confirm the concept of damping of self-seeded primary nucleation of iPP in blends by the presence of dissolved EPM. Partial solubility of iPP and EPM decreases the number of self-seeded nuclei. Because of the low level of miscibility it should not markedly influence heterogeneous nucleation since it is not very sensitive to the change of concentration.

CONCLUSIONS

On the basis of the experiments carried out the following conclusion can be drawn:

- The nucleation behaviour of iPP is strongly disturbed by the presence of EPM in the blend.
- The main reason for the increase of nucleation density in the blends is the migration of heterogeneous nuclei from EPM to iPP during melt-mixing of the components. It is suggested that the driving force for this phenomenon is the difference of interfacial free energies of the nuclei surrounded by iPP melt and those surrounded by EPM melt. Since the nuclei migrate from EPM to iPP the difference is negative.
- The migration process depends on the mixing time. The number of migrated nuclei increases with increasing mixing time.
- Because of partial miscibility of iPP and EPM the self-seeded primary nucleation in the blend is damped. The dissolved EPM fraction decreases the number of self-seeded nuclei. It should be noticed that prolonged mixing causes also a decrease of self-seeding in iPP due to thermomechanical degradation.
- It may be expected that homogeneous nucleation should be depressed in a similar way as self-seeded nucleation in blends with partial solubility of the components.
- The temperature of preparation of the blends has a significant influence on the nucleation processes. At high temperature degradation occurs resulting in a decrease of the number of primary nuclei.

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