Primary nucleation and spherulite growth rate in isotactic polypropylene–polystyrene blends

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The morphology, primary nucleation of spherulites and their growth rate in immiscible blends of isotactic polypropylene (iPP) and atactic polystyrene (aPS) were studied. It was found that PS inclusions are dispersed in an iPP matrix and their size depends on the mixing conditions. During crystallization of iPP aPS inclusions are engulfed by growing spherulites without any pushing or deformation before engulfing. The spherulite growth rate in the blends does not depend on either concentration of aPS in the blend or time of mixing. The spherulite number per iPP volume unit in the blend increases with increasing concentration of aPS and also with increasing mixing time. It was found that additional nuclei which appear in iPP/aPS blends are of two types: heterogeneous and self-seeded primary nuclei. It was demonstrated that the reasons for the increase in primary nucleation are the migration of impurities from aPS melt to iPP melt during mixing and the nucleation of a fraction of spherulites by the iPP–aPS interface. It is suggested that the driving force for the migration process is the interfacial free energy of an impurity with respect to the iPP melt and the analogous energy with respect to the aPS melt.

(Keywords: crystallization; primary nucleation; blends; nuclei migration; growth rate; polypropylene; polystyrene)

INTRODUCTION

In polymer blends in which one of the components is crystallizable the presence of another component strongly disturbs the crystallization process. Both the crystallization kinetics and the final crystal morphology are different in blends and in plain crystallizing component. Such changes were found in blends of compatible polymers as well as in blends of immiscible or partially miscible polymers[1].

In our previous studies we have investigated the primary nucleation behaviour of the crystallizable component in blends of miscible poly(ethylene oxide) and poly(methyl methacrylate) (PEO/PMMA)[2] and systems thought to be partially miscible (iPP/polyethylene[3,4] and iPP/ethylene–propylene copolymer[5]. We have found[2] that in compatible PEO/PMMA blend the non-crystallizing PMMA, acting as a diluent for PEO, causes a decrease in the number of spherulites in comparison to plain PEO.

In the blends exhibiting phase separation of components the migration of impurities (causing heterogeneous nucleation at the crystallization temperature) from one component to the other is observed. The driving force for this migration is the difference between the interfacial free energies of impurities with respect to both blend components[3]. Because of nucleation activity of impurities such migration causes extensive changes in primary nucleation behaviour of the crystallizing component in the blend. Depending on the direction of migration the crystallizing component is richer or poorer in heterogeneous centres and consequently the number of nuclei increases[5] or decreases[3,4] in comparison to the polymer alone. On the other hand the partial miscibility of polymers used in those studies influences the efficiency of migration of heterogeneities, and moreover it disturbs the homogeneous and self-seeding nucleation modes[5], so the nucleation behaviour in partially miscible blends is even more complex. Hence, it would be helpful for complete understanding to study the primary nucleation process in blends of immiscible polymers.

Also the spherulite growth rate in blends is influenced by the presence of the second component. The miscibility (complete or even partial) of polymers causes changes in the secondary nucleation process[1,6]. If the blend is phase-separated the growing spherulites of the matrix reject or engulf the separated inclusions of the second component (depending on the interfacial energy relations)[7]. These phenomena, causing energy dissipation, can induce depression in the spherulite growth rate.

Isotactic polypropylene (iPP) and polystyrene (aPS) are claimed to be incompatible at any concentration[8]. Blends of iPP and aPS constitute completely component-separated systems with low bonding forces between the components[9]. Because of this we have chosen this polymer pair for the studies of the crystallization process in immiscible blends. The present paper reports the results of investigations of primary nucleation and spherulite growth rate in iPP/aPS blends.

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EXPERIMENTAL

Materials and blend preparation

The polymers used were isotactic polypropylene (Montedison, Moplen C 30 G, density 0.91 g cm^{-3}, melt flow index 1.7 g/10 min) and atactic polystyrene (Polish product, Polistyren SC, density 1.08 g cm^{-3}, melt flow index 0.7 g/10 min). Blends containing 0, 10, 20, 30 and 40 wt % of PS were blended by extrusion in a single-screw extruder ($L/D = 25$) at 190°C. In order to improve the dispersion of PS and to study the influence of the duration of blending on crystallization behaviour the extrusion process was repeated for each composition up to three times. After each blending cycle a small sample of the blend was taken for further investigations.

In order to study the migration phenomena blends containing a small amount of magnesium sulphate (chosen as a nucleating agent) were prepared in the following way: The fine powder of magnesium sulphate (mean particle size 3 μm) was premixed in desired proportions with iPP, and separately with PS. Then the nucleated iPP was mixed with pure aPS (blend code iPP*/aPS) and in a separate blend the plain iPP was mixed with aPS already containing nucleating agent (blend code iPP/aPS*). The ratios of components in both blends were 79.8:20:0.2 by weight of iPP, aPS and magnesium sulphate respectively. The mixing process was repeated up to five times for both blends in order to study the primary nucleation behaviour *versus* mixing time and thus to observe the migration of nucleating agent. All mixing processes in this set of experiments were carried out in a laboratory mixing extruder (Custom Sci. Inc. miniextruder) at 190°C.

Sample preparation and techniques

After blending in the extruder the samples were obtained in a form of cylindrical filaments (~ 5 mm in diameter) by quenching the extrudates in iced water. The quenching was performed in order to preserve the initial dispersion of components. In order to study the crystallization by optical polarizing microscopy 5 μm thick sections were microtomed from the filaments by means of an ultramicrotome (Tesla BS490A). Sections were placed on microscopic support glasses and covered with a small piece of coverglass. Care was taken to avoid accidental shear and flow of the sample during its melting. Sample thickness was measured with an accuracy of 1 μm.

The samples were crystallized isothermally on a microscopic hot stage. Before crystallization the samples were melted and melt annealed for 5 min at 190°C or 220°C. Isothermal crystallizations were conducted at temperatures in the range 119–133°C.

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

The radial growth rates of spherulites were determined from the radii of spherulites measured as a function of time during the isothermal crystallization which was carried out on the microscopic hot stage.

In order to study the nucleation activity of the iPP–aPS interface sandwich-like samples were prepared from 2 mm thick iPP sheet pressed against a similar sheet of aPS (plain or containing nucleating agent). The sandwiches were melted at 220°C and then crystallized isothermally at 125°C. After completion of crystallization sections were cut out from the samples perpendicularly to the iPP–aPS interface and examined by means of a polarizing microscope.

The non-isothermal crystallization at cooling rate 5°C min^{-1} was carried out on a Mettler DSC 30 apparatus. The morphology of the blends was studied by means of an optical polarizing microscope (Opton) and a scanning electron microscope (JSM 35).

RESULTS AND DISCUSSION

Morphology

The morphology of the blends of iPP with PS has been studied in detail by several authors[10–13]. The use of different mixing devices (single-screw extruder, single-screw extruder with static mixer, double-screw extruder) has a drastic influence on the state of dispersion of the blend components[10]. In the present investigations we have used the single-screw extruder to obtain the blends. Our observations of phase structure in iPP/aPS blends agree with those described in the literature[10–13]; thus only a brief report on our studies of phase structure is presented.

Examination of thin sections by optical microscopy and of fracture surface by SEM indicate that the iPP/aPS blends show phase separation (see *Figures 1* and *2*). In the composition range studied polypropylene constitutes the continuous phase (the matrix) in which the polystyrene inclusions are dispersed. The inclusions often have elongated shapes and tend to form fibrils, especially for greater concentrations of aPS and shorter mixing times. The distribution of inclusions sizes is broad (for instance in 9:1 iPP/aPS blend the aPS droplets have sizes ranging approximately from 2 to 30 μm). The dispersion of aPS becomes finer with increasing mixing time (i.e. in our studies with repeating the mixing process).

The iPP spherulites growing in the blends engulf the aPS inclusions. Any pushing or deformation of aPS droplets by growing iPP spherulites before engulfing was not observed. The radial orientation of lamellae within spherulites is disturbed by the presence of aPS inclusions since some of the lamellae have to bypass the aPS inclusions in order to continue their growth.

Spherulite growth rate

The measurement of spherulite radii as a function of time during isothermal crystallization in plain iPP as well as in its blends with aPS showed that the growth of spherulites for all concentrations studied is linear with time.

Figure 3 shows the dependence of spherulite growth rate on composition of the blends at two crystallization temperatures. The growth rates were measured for each blend composition and temperature in samples mixed twice and three times in the extruder. The results show that the growth rate of spherulites is constant (within the limits of experimental error) at a given temperature and does not depend on either the concentration of aPS in the blend or the mixing time. Such results are in agreement with the theoretical predictions of spherulite growth rate for the case of engulfing of inclusions by the growing spherulite[7,14]. Similar results were previously reported for blends of iPP with low-[14] and high-[4] density

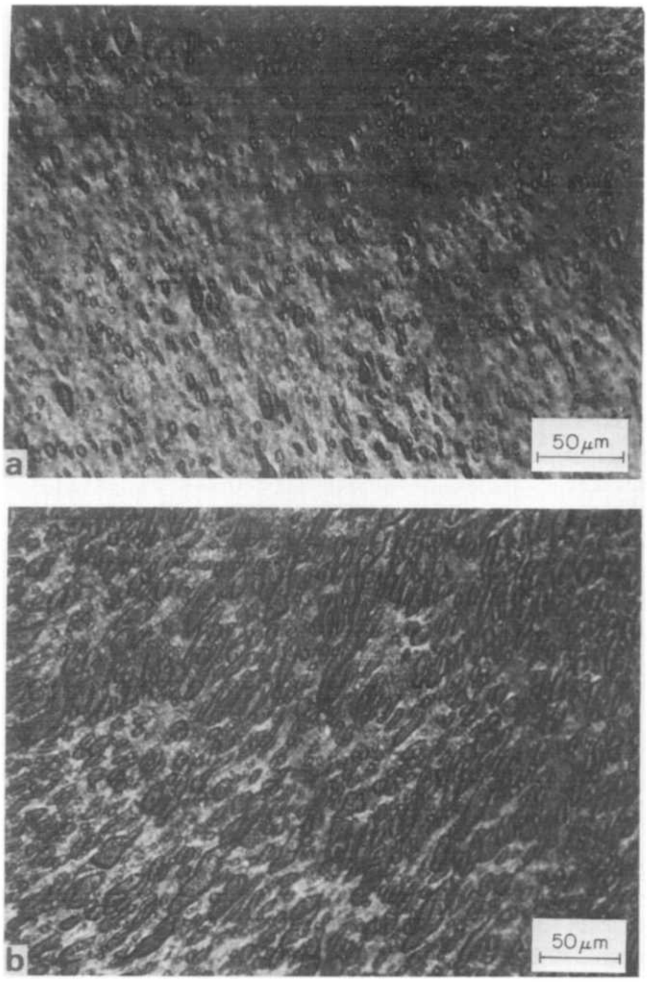

Figure 1 Optical micrographs of the phase structure in molten thin films of (a) 9:1 and (b) 6:4 iPP/aPS blends

polyethylene (in those systems polyethylene inclusions are also engulfed without any rejection and deformation by growing iPP spherulites).

According to the theoretical estimations the depression of spherulite growth rate induced by energy dissipation due to engulfment of the inclusions by the growing spherulite is negligibly small[7]. On the other hand, the inclusions constitute spatial obstacles for spherulite growth[14]. Geometrical considerations lead to the conclusion that this should cause a decrease of the spherulite growth rate. However, this decrease should also be small, not greater than several per cent. The growth rate for a three-dimensional spherulite in the 5:5 blend is decreased only by 4%[14]. Thus, because of experimental error, the depression of growth rate in the iPP/aPS blends may not be experimentally observed.

Primary nucleation of spherulites (*heterogeneous mode*)

Before each isothermal crystallization the samples were melted and melt annealed for 5 min at 190°C or 220°C. When the sample containing iPP is melt annealed prior to crystallization at lower temperature the self-seeded nuclei remain active during the crystallization process. Samples melt annealed at 220°C do not show self-seeded nuclei because this temperature is sufficient to destroy all traces of crystal ordering in iPP.

On the other hand at the crystallization temperature applied in our studies the homogeneous nuclei in iPP appear seldom, if at all, which is due to too low undercooling than needed for homogeneous nucleation[15,16]. Thus, that mode of nucleation will not be

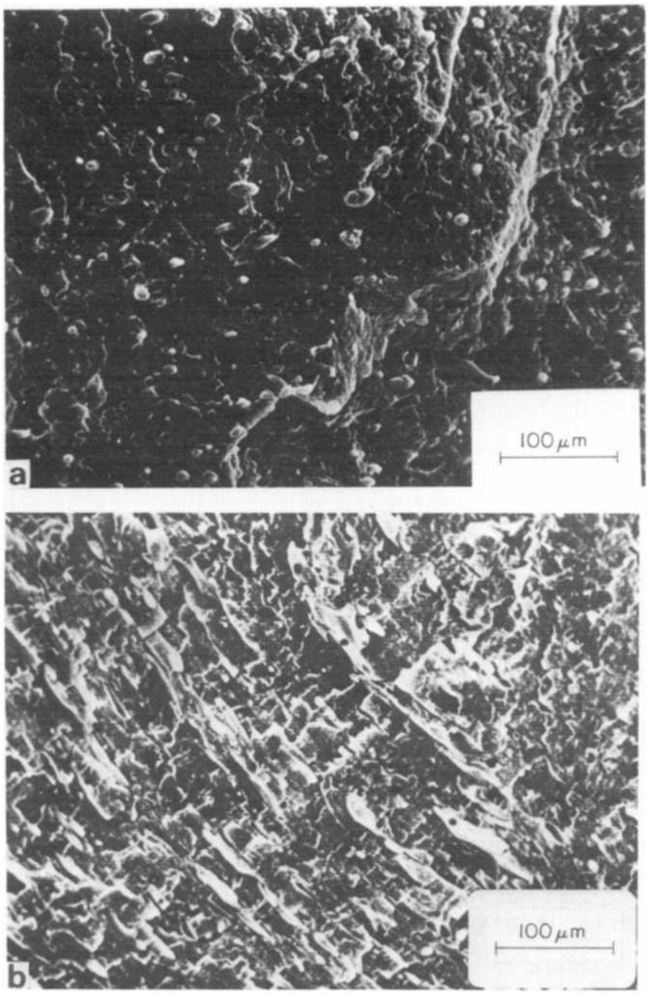

Figure 2 SEM micrographs of the fracture surface in (a) 9:1 and (b) 6:4 iPP/aPS blends

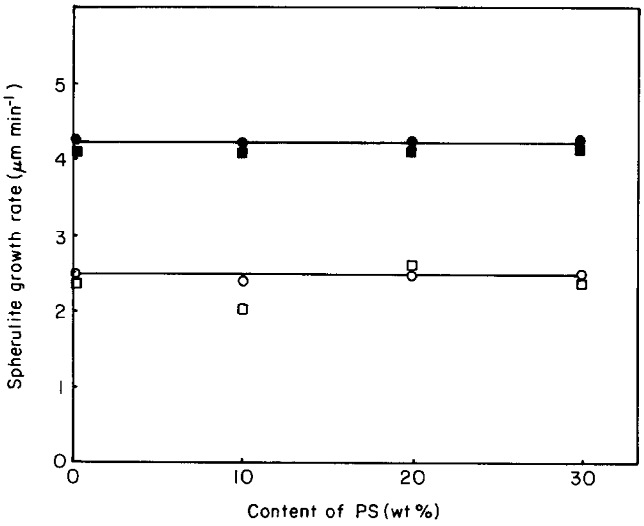

Figure 3 Dependence of spherulite growth rate on blend composition. Temperature of crystallization was 131°C (filled symbols) and 133°C (open symbols); ○, ●, samples mixed twice; □, ■, samples mixed three times

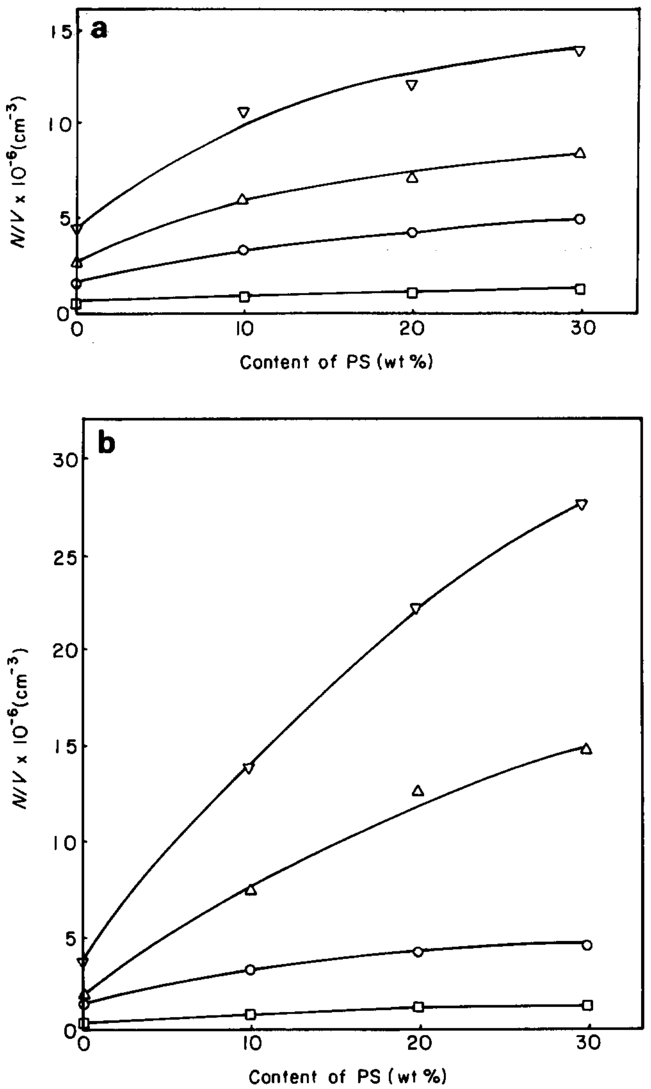

Figure 4 Dependence of number of primary nuclei per iPP volume unit in the blend on blend composition for samples mixed (a) twice and (b) three times in the extruder. Temperature of melt annealing prior to crystallization for all samples was 220°C. Temperature of crystallization: ▽, 119°C; △, 123°C; ○, 125°C; □, 130°C

considered in further analysis of experimental data. It follows then that in samples annealed prior to crystallization at 220°C one can observe practically only heterogeneous nucleation, while in those annealed at 190°C heterogeneous together with self-seeded nucleation can be observed.

Figure 4 shows the dependence of the number of primary nuclei per volume unit of iPP in the blend plotted against blend composition for various crystallization temperatures. *Figure 4a* illustrates the results obtained for the blends mixed twice in the extruder whereas *Figure 4b* shows the results for the blends mixed three times. The melt annealing temperature of all samples was 220°C, so as discussed above the main mode of primary nucleation present in this set of experiments was heterogeneous nucleation.

It is seen that the number of heterogeneous nuclei per iPP volume unit increases with increasing content of aPS in the blend. Moreover, the nucleation density increases also with increasing duration of blending, except for the plain iPP in which the nucleation density slightly decreases with increasing mixing time (compare *Figures 4a* and *4b*).

Morphological observations of crystallized blends show that a considerable number of iPP spherulites (up to 35% in 7:3 iPP/aPS blend) contain the PS inclusions in their very centres. *Figure 5* shows a micrograph of a thin film of an iPP/aPS 8:2 blend crystallized between microscopic glasses. It is seen that many spherulites are nucleated on surfaces of aPS inclusions. This observation indicates the possibility of some nucleation activity of aPS droplets, or rather iPP–aPS interfaces. Such a phenomenon could explain the increase of the nucleation density with increasing concentration of PS in the blend. Also the further increase of this density with increasing mixing time can be explained in this way since the mixing process causes an increase in the total area of iPP–aPS interfaces. This, in turn, increases the possibility of nucleation of iPP spherulites at these interfaces. However, nucleation at interfaces alone cannot explain the large increase of nucleation density observed experimentally since morphology examination reveals that only up to 35% of spherulites contain PS inclusions in their very centres.

In our previous investigations of primary nucleation behaviour in polypropylene-based blends[3–5] we have observed the migration of impurities constituting potential heterogeneous nuclei from one blend component to the other. The migration takes place during mixing of the blend in the molten state. The driving force for it is the difference in the interfacial free energies of the impurity with respect to molten components of the blend[3]. If the interfacial free energy of such a potential nucleus with respect to molten iPP is lower than that with respect to the second component, then the nucleus passes across the interface to iPP when it finds itself near the interface during mixing. Thus, the polypropylene phase becomes richer in heterogeneous nuclei. If the interfacial energy of the impurity with respect to the second component is lower than that with respect to iPP, the migration direction is the opposite, which causes the decrease of the nucleation density in the blend. The yield of the migration depends, among other parameters, on mixing time. With increasing mixing time the increase (or decrease) of nucleation density in the blend becomes more pronounced. Such nucleation behaviour has been observed in blends of iPP with polyethylene[3,4] as well as

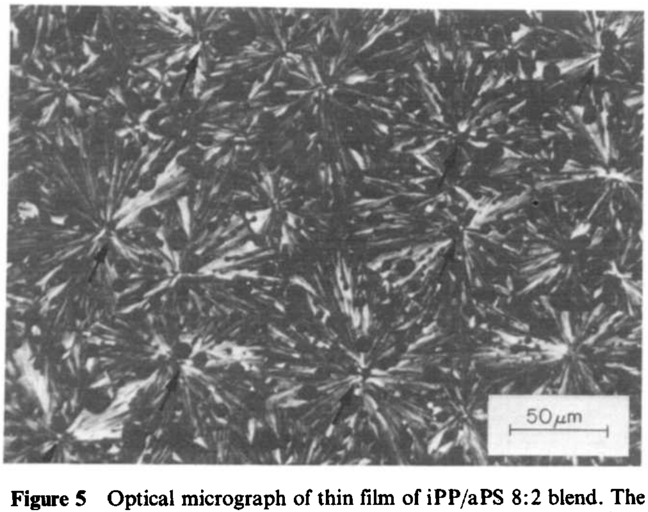

Figure 5 Optical micrograph of thin film of iPP/aPS 8:2 blend. The arrows indicate centres of those spherulites which were nucleated on aPS inclusions

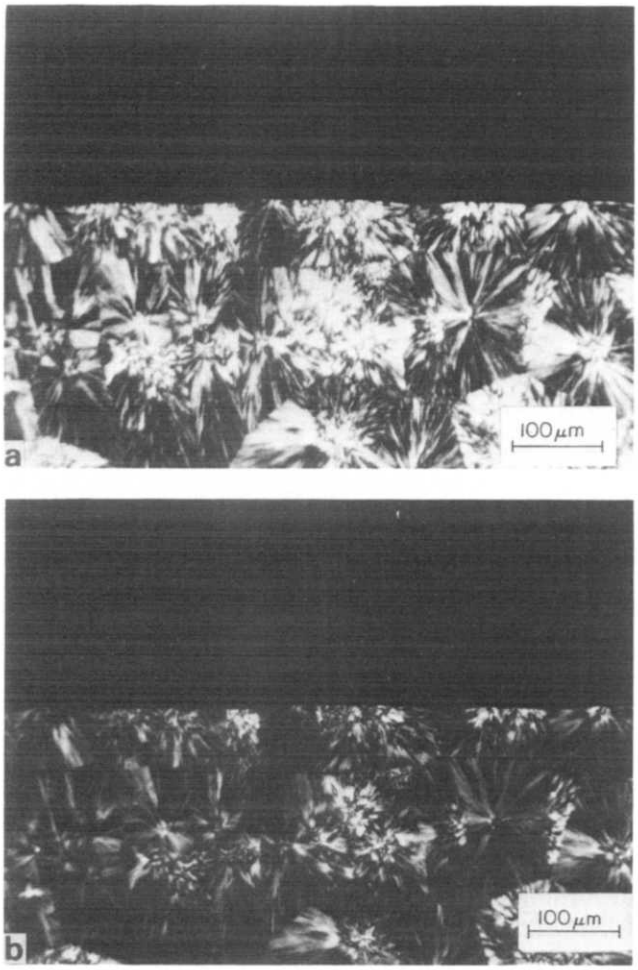

Figure 6 Micrographs of the sections cut from the iPP–aPS sandwich perpendicular to the interface surface between polymers after isothermal crystallization of iPP: (a) the interface of iPP with aPS (the boundary between the dark and filled by spherulites regions on the photograph is the interface between iPP and aPS); (b) the interface of iPP with metal plate (opposite side of the same sample which was in contact with metal plate surface during crystallization)

with ethylene–propylene copolymer . It seems possible that a similar migration phenomenon also takes place in blends of iPP with aPS.

According to the above considerations there are two hypotheses which could explain the increase of the number of heterogeneous nuclei in the iPP/aPS blends with increasing content of aPS and for fixed composition with increasing mixing time: (i) the activity of interfacial surface of aPS droplets as nucleation centres for iPP and/or (ii) the migration of impurities (i.e. potential nuclei) from aPS to iPP during the mixing process.

In order to test the first hypothesis we have crystallized isothermally the sheet of iPP being in contact during melting and crystallization with aPS sheet. The procedure for this experiment was described in the experimental section of this paper. Special care was taken during sample preparation to prevent the contamination of the interface surface by accidental impurities, so the nucleation of spherulites by impurities can be excluded. *Figure 6a* shows the optical micrograph of a thin section transverse to the iPP–aPS interface. It is seen that the majority of spherulites contacting with the interface plane have their centres located on it. More quantitative analysis showed that in the 5 μm thick crosssection there are on average 16 spherulites contacting the interface per 1 mm of the interface length, from which 11 clearly have their centres located on the interface.

The crosssection of the interface iPP–metal plate (the same sample but other surface) exhibits on average 10 spherulites contacting the interface per 1 mm of the interface length, from which only 3 have their centres on the interface (see *Figure 6b*).

In the bulk of iPP there are approximately 9 spherulites per 1 mm of a straight line drawn in the section.

These numbers indicate that the iPP–aPS interface has some nucleating activity for iPP spherulites. The shapes of the boundaries between spherulites contacting the interface indicate also that the nucleation of those spherulites was instantaneous[17].

The interfacial tension between polypropylene and polystyrene is very high, being 5.1 erg cm^{-2} at 140°C (ref. 18). Moreover, the interface between iPP and aPS is very sharp due to their immiscibility. The thickness of the interface layer between iPP and aPS melts calculated on the basis of Helfand theory[19,20] is less than 14 Å. According to the heterogeneous nucleation theory[21] a nucleation event on the surface with high interfacial tension is much more probable than one in the polymer volume. On the other hand the temperature of crystallization used here is higher than T_g of polystyrene, so the shape of the interface between iPP and aPS as a boundary of two liquids is not fixed at the microscopic level. This, in turn, does not favour the nucleation in spite of good energetic conditions. In summary, the interface can induce some limited number of nucleation events but does not cause transcrystallinity as some crystal surfaces do. The aPS droplet surfaces in iPP/aPS blends appear to act as a weak nucleating agent.

The second hypothesis is that the increase in the number of heterogeneous nuclei in the iPP matrix is related to the migration of impurities (causing heterogeneous nucleation) from aPS to iPP during the mixing process. In order to test this hypothesis, we have carried out experiments with blend samples containing nucleating agent. We intended to observe the migration of heterogeneous nuclei (more precisely, the migration of nucleation agent particles causing heterogeneous nucleation). Magnesium sulphate was chosen as a nucleating agent for polypropylene[22]. Two 8:2 iPP/aPS blends containing nucleating agent were prepared according to the procedure described in the 'Experimental' section. The blends differed from one another in that in the blend designated iPP*/aPS the nucleating agent was initially dispersed in the polypropylene phase, whereas in the second blend (iPP/aPS*) it was dispersed initially in the polystyrene. The blends were mixed in a miniextruder five times, and after each mixing pass small samples were taken to allow the study of the effect of mixing time. These samples were crystallized non-isothermally in a d.s.c. cell at a cooling rate of 5°C min^{-1}. Melting of the samples prior to crystallization was performed at 220°C.

The temperatures of the crystallization peaks depend little on the mixing time; however, they are different for different samples: 119°C for iPP*/aPS, 118–119°C for iPP/aPS*, 115°C for iPP/aPS (blend without nucleating agent) and 113–114°C for iPP. The peak temperatures for both nucleated samples are high, which proves the activity of nucleating agent independently of preparation

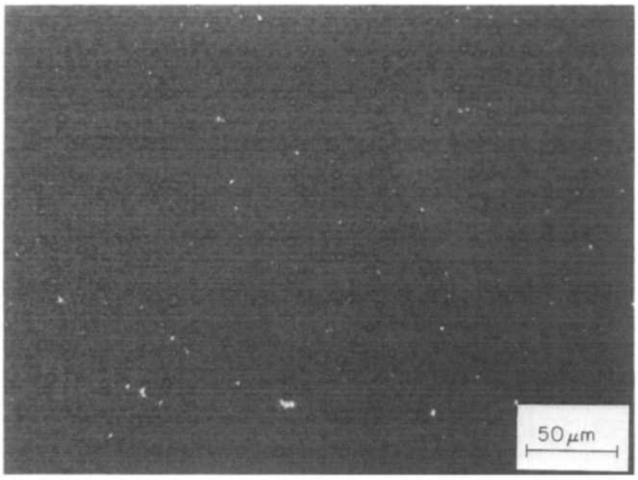

Figure 7 Optical micrograph of the molten sample of 8:2 iPP/aPS blend mixed five times

and mixing history. It should be noted that the crystallization peak in the iPP/aPS* blend is quite high (118°C) just after the first mixing pass, which demonstrates that the migration of magnesium sulphate particles from aPS to iPP is very fast and efficient. In our previous studies with partially compatible blends[3-5] we have not observed such fast migration as in the system studied here. Such a high migration rate in iPP/aPS blends can be attributed to the particularly sharp interface profile between iPP and aPS (less than 14 Å) and to the high difference of interfacial energies of magnesium sulphate with regard to iPP and aPS melts, respectively (the difference being the driving force for migration[3]).

Another direct proof for migration is presented in *Figure 7*. This shows an optical micrograph of a molten 8:2 iPP/aPS* blend (magnesium sulphate introduced to aPS during blend preparation) mixed five times. The micrograph was obtained in the polarizing microscope with the angle between polarizer and analyser axes ~80°, so both phase structure of the blend and birefringent magnesium sulphate particles (the largest) are visible. It is seen that the majority of particles are situated inside the iPP matrix volume, although they were introduced initially to aPS. Such a picture clearly shows that the nucleating agent particles prefer to be situated in the iPP melt rather than in the aPS melt, and migrate during mixing from aPS to iPP.

In view of the results presented above one can suppose that the previously discussed nucleation activity of iPP–aPS interface could be the result of this activity (if at all) but also additionally the result of migration phenomenon—the nucleation events observed to occur at the interface could be involved by the impurities situated inside iPP phase, but close to the interface, which have migrated from aPS in the interface region. In order to test this, the isothermal crystallization of iPP sheet in contact with a sheet of aPS containing sodium benzoate (aPS*) was carried out. Sodium benzoate is known to be a very good nucleating agent for iPP[22]. The sample geometry and experimental procedure were the same as in the experiment described above for crystallization of an iPP–aPS sandwich. If migration across the interface in the absence of mechanical mixing takes place, one should observe a greater number of spherulites nucleating at the iPP–aPS* interface (or even transcrystallinity) than at the interface between iPP and pure aPS, because aPS* containing nucleating agent is richer in potential heterogeneous nuclei for iPP crystallization than plain aPS (which nuclei could migrate to iPP without mixing according to the hypothesis considered here). However, examination of the sections transverse to the iPP–aPS* interface showed that the iPP spherulite morphology near the interface, their number and the position of their centres with respect to the interface do not differ from those observed in iPP–aPS sandwich reported before. Such a result leads to the conclusion that the migration of potential heterogeneous nuclei across the interface does not proceed in the absence of mechanical mixing, so the nucleation events observed at both iPP–aPS* and iPP–aPS interfaces are the result of nucleation activity of the interface alone, as was suggested before.

On the basis of the experiments reported above one can conclude that the increase in the number of heterogeneous nuclei in blends with increasing content of aPS and increasing mixing time is caused by two separate mechanisms acting simultaneously: the nucleation activity of iPP–aPS interface and the migration of heterogeneous nuclei from aPS to iPP melt during mixing.

Table 1 reports the isothermal crystallization data obtained for blends mixed two and three times. In the first and second columns the blend composition and crystallization temperature T_c are shown respectively. Columns 3 and 5 of the table show relative densities of nucleation normalized to the respective nucleation density at 119°C. In columns 4 and 6 we introduce the difference of nucleation densities in the blend and in plain iPP at the same T_c: $n_{add} = n - n_{PP}$ which represents the additional heterogeneous nucleation resulting from the presence of aPS in the blends. The additional nucleation density is presented here also as the ratio to the entire nucleation density for a given composition and crystallization temperature: n_{add}/n. Examination of the data in *Table 1* shows that the temperature dependence of nucleation density in the blends varies from that for plain iPP. Since the impurities causing the nucleation are most probably of similar origin in iPP and aPS, the relative

Table 1 The relative densities of primary nucleation in iPP/aPS blends

Blend composition	T_c (°C)	Samples mixed twice $n/n(119)$	Samples mixed twice $n_{add}/n(119)$	Samples mixed thrice $n/n(119)$	Samples mixed thrice $n_{add}/n(119)$
100:0	119	1.0	–	1.0	–
	123	0.62	–	0.52	–
	125	0.36	–	0.35	–
	130	0.15	–	0.13	–
90:10	119	1.0	0.57	1.0	0.74
	123	0.57	0.54	0.53	0.74
	125	0.30	0.50	0.23	0.60
	130	0.08	0.19	0.06	0.32
80:20	119	1.0	0.62	1.0	0.84
	123	0.58	0.60	0.56	0.73
	125	0.34	0.60	0.18	0.69
	130	0.07	0.24	0.05	0.62
70:30	119	1.0	0.67	1.0	0.87
	123	0.60	0.66	0.53	0.87
	125	0.34	0.65	0.16	0.72
	130	0.07	0.38	0.05	0.63

changes with crystallization temperature of the number of spherulites nucleated by the impurities in plain iPP and in the blends should also be similar. Thus, taking into consideration the data reported in *Table 1* it can be concluded that the nucleation mechanism by iPP–aPS interface decreases its efficiency with the increasing crystallization temperature. Such a conclusion is confirmed by the morphological observations.

As already noted the number of nuclei induced by the interface does not exceed 35% of the entire number of nuclei in the blends. On the other hand, the ratio n_{add}/n shows that the number of 'new' nuclei in the blend at lower T_c, where nucleation by the interface is still active, constitutes from near 60% to more than 80% of all the nuclei. This indicates that the nuclei created by the migration constitute the majority of the additional nuclei present in the blends, even at low T_c. Of course, at high T_c where the nucleation activity of the interface vanishes, almost all of the additional nuclei are introduced to iPP by migration.

The number of additional nuclei caused by the presence of aPS in the blends increases with increasing content of it in the blend, but not proportionally. This suggests that the creation of additional nuclei is not controlled directly by the concentration of aPS in the blend. Morphological observations show that the surface area of the iPP–aPS interface does not increase as fast as the volume of aPS in the blend increases, because for greater aPS concentrations the inclusions are large and assume a fibrillar shape. Prolonged mixing causes better and finer dispersion of aPS, and thus the area of the interface increases. If we compare the data from columns 4 and 6 in *Table 1* one can see that the number of additional nuclei increases with increasing mixing time, also in samples crystallized at high T_c at which practically only the nuclei introduced by migration are active. Thus, both mechanisms of acquiring nuclei by iPP in blends are controlled by the area of the interface surface. It is obvious that the number of spherulites nucleated by the interface depends directly on its area. The efficiency of migration and consequently the number of additional nuclei also increase with increasing iPP–aPS interface surface area. Of course, the number of nuclei created in this way is still dependent on the volume of aPS in the blend, constituting the reservoir of potential nuclei, but the state of dispersion and thus the interface area have considerable influence on the efficiency of migration.

Self-seeding primary nucleation

We have also carried out the study of self-seeding mode of primary nucleation of iPP in blends with aPS. If the sample is annealed prior to crystallization at 190°C self-seeded and heterogeneous modes of nucleation occur during the crystallization process. The results of nucleation density investigations in blend samples melt annealed at 190°C and then crystallized isothermally are shown in *Figure 8*. For comparison the results for the blends crystallized at the same temperatures but annealed at 220°C (i.e. no self-seeding is expected) are replotted from *Figure 4*. It can be seen that the nucleation density in samples annealed at 190°C is much higher than in those annealed at 220°C prior to crystallization, but the tendencies are similar in both sets of results. The number of nuclei observed is the sum of heterogeneous nuclei and self-seeding. Since the heterogeneous mode of nucleation does not depend on the temperature of melt annealing, the entire gain of nuclei in the blends annealed at 190°C can be ascribed to the increase in self-seeding. The reason for an increase can be explained in the following way: The self-seeded nuclei often persist in the melt due to the presence of some heterogeneities (impurities). The steps, cracks and other irregularities of surfaces of these impurities can stabilize small polymer crystallites, increasing their melting temperature[23]. As was shown in this paper, the iPP melt in the iPP/aPS blends is richer in heterogeneities than the melt of plain iPP due to their migration from aPS melt. Moreover, those impurities

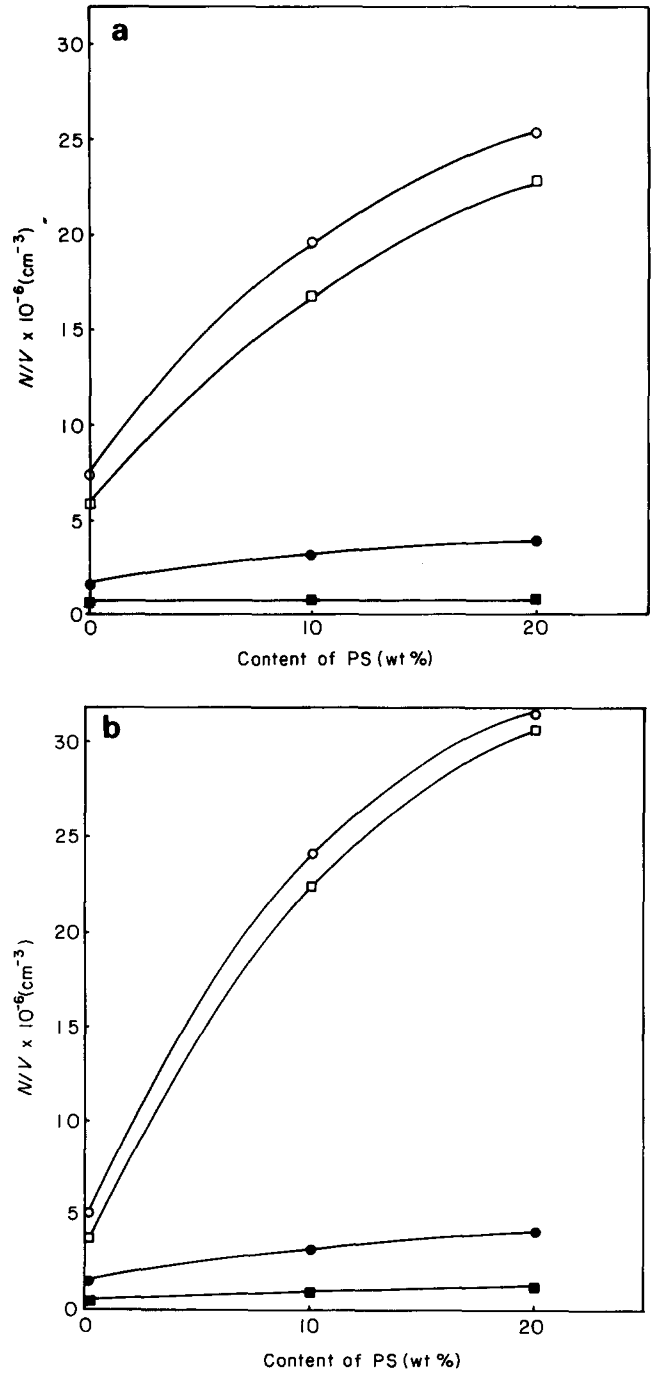

Figure 8 Dependence of number of primary nuclei per iPP volume unit in the blends with aPS on their composition for samples mixed (a) twice and (b) three times in the extruder. Temperature of melt annealing prior to crystallization was 190°C (open symbols) and 220°C (filled symbols). Crystallization temperature: ○, ●, 125°C; □, ■, 130°C

resume a more irregular and defective surface due to mixing in the extruder. In such surface defects the self-seeded nuclei can be preserved over the period of melt annealing at 190°C. It is necessary to note that not all impurities which have migrated to iPP result in heterogeneous nucleation as the energy barrier for further growth is not always overcome. These impurities can, however, participate in self-seeded nucleation, increasing the melting temperature of polypropylene crystallites situated in cracks or other irregularities on their surfaces. According to the above the number of self-seeded nuclei in iPP/aPS blends is quite large and increases with increasing content of aPS in the blend. For the same reason it increases with increasing mixing time.

The described self-seeded nucleation behaviour in iPP/aPS blends is opposite to that previously found in blends of iPP with ethylene–propylene copolymer[5], where the partial miscibility of blend components causes the reduction of a considerable fraction of self-seeded nuclei, although the direction of migration of impurities is the same as in iPP/aPS blends.

CONCLUSIONS

On the basis of the results presented one can conclude that the number of heterogeneous nuclei increases with increasing content of aPS in the blend. The main reason for this increase is the migration of impurities from aPS to iPP during the mixing process. The driving force for the migration is most probably the difference of the interfacial free energies of the impurities with respect to iPP and aPS melts. The migration process in iPP/aPS blends is faster than in other polypropylene-based blends, which is probably caused by immiscibility of components and the sharp interface profile. Moreover, the interface induces additional heterogeneous nucleation. Such ability depends on the temperature of crystallization and decreases with increasing T_c. The number of nuclei induced by the interface is less than the number of nuclei induced by acquiring impurities over the whole temperature range studied. The phenomenon of nucleation activity of the iPP/aPS interface is caused by the high value of interfacial free energy between iPP and aPS and the sharpness of the interface.

Both mechanisms causing the elevation of nucleation density in the blends are controlled by the area of the iPP–aPS interface surface. The interface area depends, in turn, on the concentration of aPS in the blend and mixing conditions—intensity and duration.

As a consequence of the migration of impurities we have observed an increase of both heterogeneous nucleation and self-seeded nucleation. The analysis of the results shows also that the lack of miscibility of components makes the primary nucleation in such blends different than in partially miscible blends.

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