Spherulite nucleation in blends of isotactic polypropylene with high-density polyethylene

Z. Bartczak and A. Gałeski
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-362 Łódź, Poland

and M. Pracella
Centro Studi Processi Ionici di Polimerizzazione, CNR, 56-100 Pisa, Italy

(*Received 4 February 1985; revised 1 April 1985*)

Primary nucleation of spherulites in blends of isotactic polypropylene (iPP) with high-density polyethylene (HDPE) has been investigated by means of differential scanning calorimetry and optical microscopy. The number of iPP nuclei in blends crystallized isothermally at temperatures greater than 127°C decreases with increasing HDPE concentration to a much greater extent than follows from the decreasing amount of iPP, whereas in blends crystallized below 127°C this number increases strongly. The shapes of the spherulite size distributions indicate that athermal (heterogeneous) nucleation is disturbed. Experiments with nucleating agents demonstrate that heterogeneous nuclei migrate across interphase boundaries from iPP melt to HDPE melt during mixing due to the difference in interfacial energy between the nuclei and the molten components of the blend. At temperatures below 127°C the HDPE crystals growing in the blend cause additional heterogeneous nucleation of iPP spherulites. This nucleating activity of HDPE crystals is responsible for the increase in nucleation density of the blend in spite of migration.

(Keywords: crystallization; primary nucleation; blends; nuclei migration; polypropylene; polyethylene)

INTRODUCTION

The properties of a polymer can be modified by changing its chemical structure. Another attractive and simpler method is to blend two or more polymers in a melt or in solution. The properties of polymer blends depend not only on the composition and processing but also on the physical state of each component at the temperature used. Most of the theoretical and empirical investigations of properties of polymer blends have been concerned with blends of amorphous polymers[1]. Blends of crystalline polymers have received relatively little attention.

The properties of blends of polymers that can crystallize depend strongly on their crystallinity, crystalline morphology and degree of dispersion[2–7]. The presence of dispersed particles might cause large changes not only in the morphology of the continuous phase but also in the overall kinetics of crystallization and spherulite growth rate[2–4,8–10].

Blends of isotactic polypropylene (iPP) with low-density or high-density polyethylene (LDPE, HDPE) have been investigated by several authors[2–6,8–10]. It has been found that iPP is not miscible with polyethylene, and the blend forms a heterogeneous system. Polyethylene inclusions in the iPP matrix constitute geometrical obstacles to spherulitic growth and cause large changes in their morphology, but they have very little effect on the growth rate[9]. On the other hand, large changes have been reported in the overall kinetics of crystallization[2] and in spherulite nucleation in blends compared to pure polypropylene[3,4,6,10].

In our previous work[10] we reported the results of a study on spherulitic nucleation in blends of iPP with LDPE crystallized from the melt. It was shown that the decrease in the number of primary iPP nuclei is caused by the migration of heterogeneous nuclei from iPP melt to LDPE melt during melt-mixing of the blend.

This report is devoted to the study of the crystallization behaviour and primary nucleation phenomena in iPP/HDPE blends crystallized from the melt.

EXPERIMENTAL

The polymers employed in the present work were isotactic polypropylene (RAPRA, $M_w = 307\,000$, $M_n = 15\,600$, $M_w/M_n = 20$, density 0.906 g cm^{-3}, melt flow index 3.9 g/10 min) and high-density polyethylene (RAPRA, $M_w = 166\,000$, $M_n = 10\,200$, $M_w/M_n = 16$, density 0.960 g cm^{-3}, melt flow index 3.7 g/10 min).

Blends containing 0, 10, 20, 30 and 50 wt% HDPE were prepared as follows: First, the two components were dissolved together in xylene at 120°C in the desired proportion, then rapidly precipitated with methanol, and the resulting powders dried under vacuum. The powders were blended several times using a laboratory miniextruder (Custom Scientific Inc.) at 190°C.

Samples in the form of films 10–20 μm thick obtained from the blends by compression moulding at 190°C were crystallized isothermally on the microscope hot stage in the 123–135°C temperature range. The temperature of the hot stage was maintained at a constant level by a

0032-3861/86/040537-07$03.00

temperature controller with accuracy ±0.05°C. Before crystallization the samples were melted at 220°C for 10 min in order to destroy all self-seeding nuclei.

Primary nucleation of spherulites was studied by means of a polarizing microscope. The number of spherulites was counted after completion of crystallization, and then used to calculate the number of primary nuclei per unit volume of iPP in the blend (thickness of the sample and area occupied by counted spherulites were measured).

The radial growth rates of spherulites were obtained from measurements of the diameters of spherulites as a function of time during the isothermal crystallization process carried out on the microscope hot stage.

In order to study the effect of nucleating agents (sodium benzoate and magnesium sulphate), fine powder of a nucleating agent was premixed in the miniextruder separately with iPP and with HDPE powder and the following blends were then prepared: (iPP + sodium benzoate) + HDPE (blend code iPP*/HDPE), iPP + (HDPE + sodium benzoate) (blend code iPP/HDPE*), (iPP + magnesium sulphate) + HDPE (blend code iPP**/HDPE), iPP + (HDPE + magnesium sulphate) (blend code iPP/HDPE**). In all blends the brackets indicate the pair of components that were mixed in the first step of blend preparation. The ratio of the components was 79.8:20:0.2 wt% for iPP, HDPE and nucleating agent, respectively, for each blend. The blends were mixed several times in the miniextruder. After each mixing pass a small specimen of the blend was taken in order to study the nucleation behaviour. The specimens were crystallized isothermally in a d.s.c. apparatus (Perkin–Elmer DSC2). Before crystallization the samples were melt-annealed at 220°C for 5 min in order to destroy self-seeding nuclei. The numbers of nuclei per unit volume were calculated on the basis of the Avrami equation from the overall kinetic rate constant K_n.

RESULTS AND DISCUSSION

In the temperature range 127–135°C iPP is able to crystallize while HDPE is near to its melting point and remains molten[2]. At temperatures below 127°C HDPE can also crystallize in the same timescale as does iPP. Blends of iPP with HDPE show iPP spherulites with a grain-like structure constituted by polyethylene inclusions even for a large concentration of HDPE. The drop-like morphology does not change while varying the temperature of crystallization (*Figure 1*). Morphological observation during crystallization of the blends shows that HDPE inclusions are not rejected by the growing spherulite into the interspherulitic regions. Spherulites engulf the inclusions and in some cases deform them in the process. No pushing of HDPE particles before their engulfing was observed.

Measurements of spherulite radius as a function of time during isothermal crystallization indicate that for each sample the radial growth rate $G = dR/dt$ is constant throughout the entire crystallization time. The spherulite growth rate does not depend on composition and mixing history. The values of G for samples having different composition and/or mixing history but crystallized at the same temperature are equal within experimental error (see *Figure 2*). Such behaviour is similar to that of blends of iPP with LDPE[9] and is in agreement with theoretical predictions[9,11].

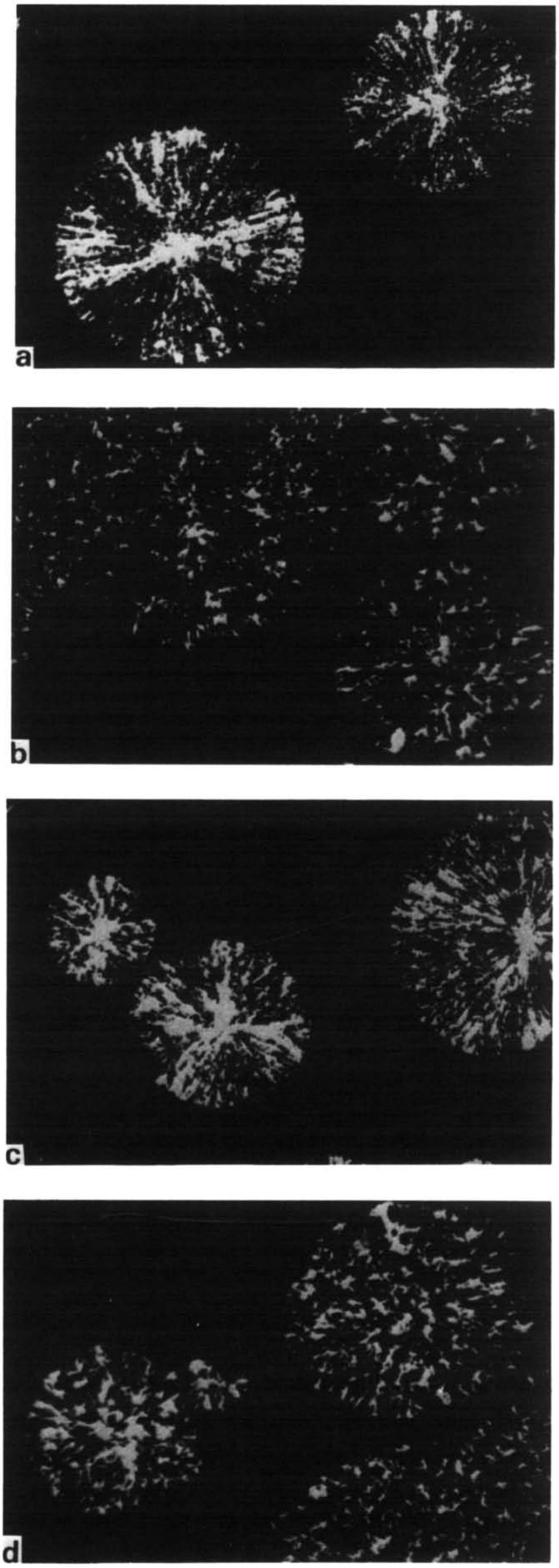


Figure 1 Micrographs of growing spherulites in iPP/HDPE blends: (a) 7:3 iPP/HDPE blend, crystallization temperature $T_c = 127°C$; (b) 5:5 iPP/HDPE, $T_c = 127°C$; (c) 7:3 iPP/HDPE blend, $T_c = 135°C$; (d) 5:5 iPP/HDPE blend, $T_c = 135°C$

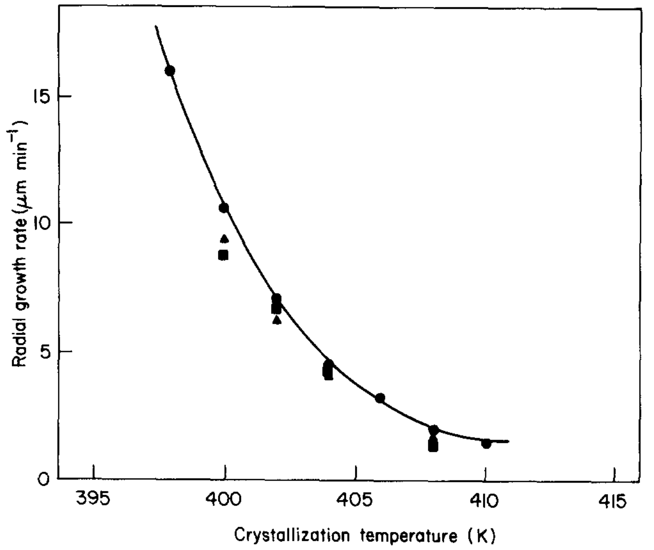


Figure 2 Radial growth rates of iPP spherulites in iPP/HDPE blends as a function of crystallization temperature

It was shown[11–13] that engulfing of the inclusions by the crystallizing front always occurs when the interfacial free energy between inclusion and molten matrix is greater than the corresponding energy between inclusion and solid matrix (the difference in these energies is positive). In the opposite situation, when the energy difference is negative, the smaller particles are rejected, whereas inclusions greater than a certain critical size (depending on growth rate) are pushed some distance and then trapped by the growing front[12]. Rejection of inclusions by the growing spherulite front induces a considerable depression in its growth rate, whereas engulfing does not[9,11].

On the basis of these considerations and the morphological observations and spherulite growth rate data for the iPP/HDPE system mentioned above, it can be concluded that the interfacial free energy between molten HDPE and iPP spherulite is smaller than the corresponding energy between molten HDPE and molten iPP at the crystallization temperature, so that contact of a molten HDPE inclusion with solid iPP is preferred.

Lovinger and Williams[3] have noticed that the average radius of spherulites in blends of iPP with HDPE is less than in pure iPP when the samples were crystallized at a temperature near 100°C. Their observations were confirmed by Gupta *et al.*[4] (d.s.c. measurements of non-isothermal crystallization) and by Teh[6] (microscopic observations).

In *Figures 3a–e* the changes in the number of primary nuclei per unit volume of iPP in blends are plotted as a function of blend composition for various temperatures of isothermal crystallization and mixing times (the nucleation densities for blends mixed once, three and five times in a miniextruder are presented). As can be seen, at crystallization temperatures of up to 127°C the number of primary nuclei increases strongly with increasing content of HDPE in the blend. This result agrees with the data presented in the papers mentioned above[3,4,6]. However, at crystallization temperatures above 127°C the crystallization behaviour of the blends is the opposite: the number of primary nuclei decreases with increasing content of HDPE in the blend. Such behaviour is the same as that observed for iPP/LDPE blends independently of the crystallization temperature[10].

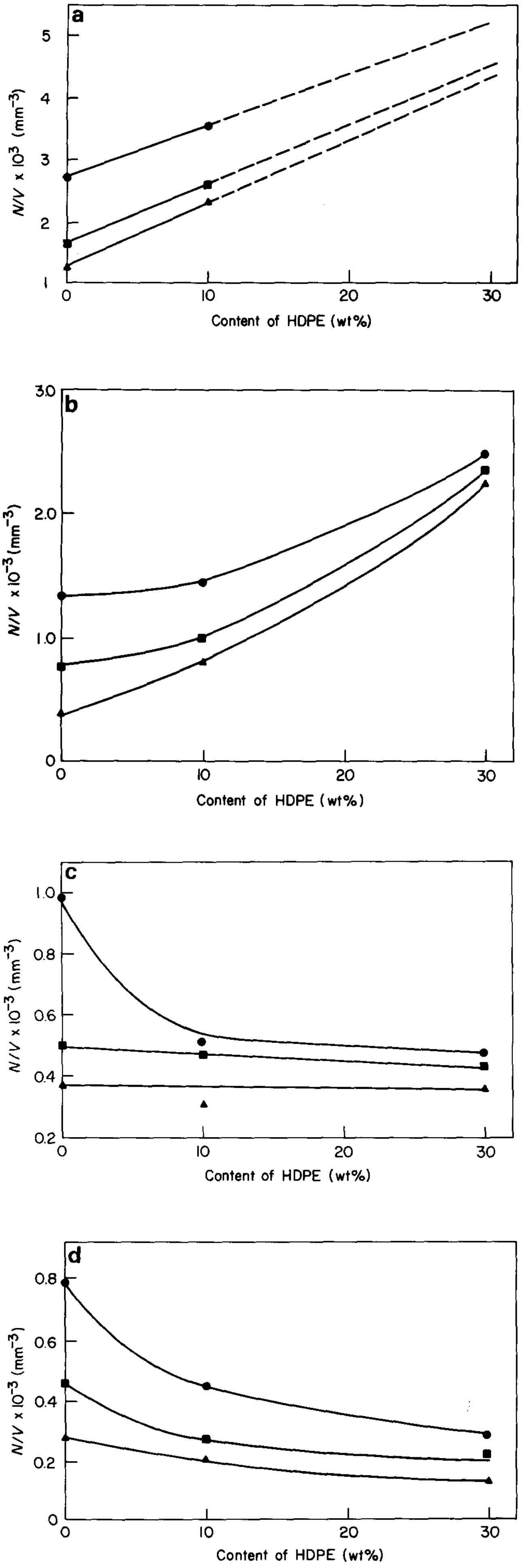
It must be noted that for crystallization temperatures less than 125°C iPP and HDPE have almost the same value of overall crystallization rate in bulk[2]. As a consequence both polymers in the blends crystallize almost simultaneously at that temperature and the d.s.c. crystallization exotherms show a single peak (see Figure 2a in ref. 2). At crystallization temperatures higher than 127°C the overall crystallization rate of HDPE is very low and only iPP is able to crystallize during the experiment. As will be shown below, the change in the crystallizability of HDPE near 127°C is responsible for the mentioned change in the primary nucleation behaviour of iPP in blends with HDPE.

Another phenomenon observed is the disappearance of part of the nuclei when the mixing time is prolonged (see *Figure 3*). The decrease in the nucleation density is observed not only in the blends (for constant blend composition and crystallization temperature) but also in samples containing only iPP. Thus, these changes do not result from the presence of HDPE in the system, and it is more likely that they are caused by changes in the structure of the iPP melt due to prolonged action of shear forces and temperature during the melt-mixing process. A more detailed study of this phenomenon will be reported elsewhere[14].

In order to explain the nucleation behaviour of the blends, we investigated the changes in spherulites size distributions. The results indicate (see *Figures 4* and *5*) that at the crystallization temperature of the blend above 127°C the athermal (heterogeneous) nuclei disappear from the iPP matrix. This conclusion is based on the shapes of spherulite size distributions for different modes of primary nucleation taken from refs. 15 and 16.

The decrease in the number of heterogeneous nuclei can be accounted for in terms of migration from polypropylene to polyethylene during mixing of those particulate impurities that could induce heterogeneous nucleation of iPP spherulites.

The value of the interfacial free energy of the nucleus is nearly the same as the analogous energy of the iPP crystal[17]. Morphological studies lead to the conclusion that contact of the iPP crystal with HDPE inclusions is preferred—the inclusions are engulfed by the growing spherulite (rejection of inclusions does not occur). Thus, the interfacial free energy of nuclei has a lower value when they are surrounded by HDPE melt[11]. Consequently, potential heterogeneous nuclei can pass across the interfacial boundary during mixing because of energetic conditions: the interfacial free energy of a nucleus in contact with the HDPE melt is smaller than when it is surrounded by the iPP melt, which makes contact of a nucleus with the HDPE melt energetically more profitable. Consequently, if the nucleus is located on the interphase boundary between the components of the blend, it will be swept away by HDPE. Such a situation may frequently occur during melt-mixing of the blend because forces cause both deformation of HDPE inclusions and movement of potential nuclei. The probability of migration increases with increasing time of mixing as well as increasing content of HDPE in the blend. Since a similar phenomenon of heterogeneous nuclei migration had been observed for a mixture of iPP with LDPE[10], we expected the same behaviour in iPP/HDPE blends. In fact, when we compare the shapes of spherulite size distributions for plain iPP and the



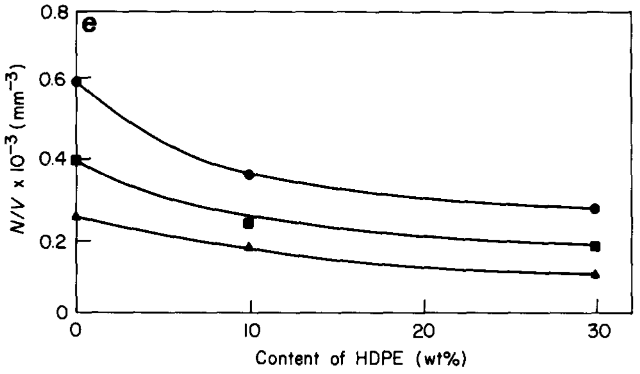


Figure 3 Variation in the number of primary nuclei per iPP unit volume in the blend with composition of the blends for various crystallization temperatures: (a) $T_c = 123°C$; (b) $T_c = 127°C$; (c) $T_c = 129°C$; (d) $T_c = 131°C$; (e) $T_c = 135°C$. ●, Blends mixed once; ■, blends mixed three times; ▲, blends mixed five times

blends (*Figures 4a* and *5a*, *4c* and *5b*) we can conclude that the number of heterogeneous nuclei decreases. Moreover, a further decrease in their number is observed when the blend is mixed for a longer period of time (see *Figure 5*).

The phenomenon of nuclei migration should occur for all heterogeneous nuclei, but it is the most effective for nuclei active at higher temperatures of crystallization. For such nuclei the difference in interfacial free energies of the nucleus with respect to HDPE and iPP melts is higher than for nuclei active at lower temperatures (nuclei more similar to iPP crystal with regard to surface energy). However, *Figures 3a* and *3b* show that at crystallization temperatures of up to 127°C the number of nuclei per unit volume does not decrease as the HDPE content in the blend increases. In fact, the opposite effect is observed: the number of nuclei increases strongly. Such behaviour is caused by the presence of HDPE crystals, which are able to grow at temperatures below 127°C. It is known from d.s.c. studies[2] that at these temperatures both components of the blend crystallize; hence some polyethylene crystals can be situated on the interfaces. Moreover, it has been previously shown[18] that polyethylene crystals might cause the so-called 'copious nucleation' of polypropylene (i.e. the heterogeneous mode of nucleation[19]). Olley *et al.*[18] have reported that, during crystallization of iPP/PE blends, polypropylene crystals were nucleated on the surfaces of polyethylene crystals. This causes an increase in the nucleation density of iPP in the blends with respect to the case of pure polymer for the same thermal conditions. On the other hand, the migration phenomenon induces a decrease in the number of heterogeneous nuclei, which is not strong for lower temperature. Thus, the presence of crystallizing polyethylene is sufficient to increase the nucleation density in iPP, especially at temperatures lower than 125°C. For higher temperatures the polyethylene phase crystallizes more slowly compared to polypropylene and nucleation via polyethylene crystals decreases to disappear finally above 127°C, as shown in *Figure 3*.

Examination of the shape of spherulite size distributions for samples crystallized at 127°C (see *Figures 6a* and *6b*) indicates that at this temperature the number of heterogeneous nuclei increases. This confirms the conclusion that polyethylene crystals growing inside HDPE inclusions near the boundaries act as a nucleating agent for polypropylene. Moreover, the polyethylene phase is richer in heterogeneous nuclei due to migration

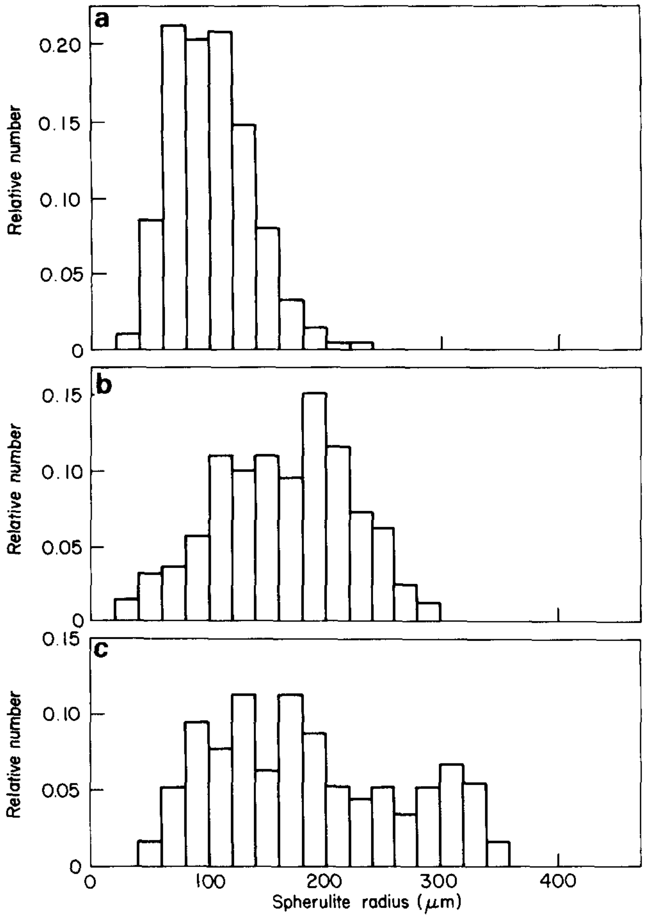


Figure 4 Spherulite size distributions in iPP crystallized isothermally at 135°C: (a) mixed once; (b) mixed three times; (c) mixed five times

from iPP, so the number of HDPE crystals may be larger than usual.

In order to verify directly the hypothesis of migration and its influence on primary nucleation behaviour, experiments were conducted with artificially nucleated blends. Sodium benzoate and magnesium sulphate were chosen as the nucleating agents[20,21]. It is known[20] that sodium benzoate is a very active nucleating agent for polypropylene at high crystallization temperature (it raises the temperature of the maximum rate of non-isothermal crystallization in d.s.c. scans by 24°C), whereas magnesium sulphate is active as a nucleating agent at lower temperatures (it raises the temperature of such a maximum by only 4°C).

In a first set of experiments the blends containing sodium benzoate were examined to show the migration of heterogeneous nuclei active at high crystallization temperature. Two 8:2 iPP/HDPE blends containing 0.2 wt% sodium benzoate were prepared according to the procedure described in the Experimental section of this paper. The first blend had the sodium benzoate introduced initially to iPP (iPP*/HDPE blend) and the second one had it introduced initially to HDPE (iPP/HDPE* blend). The blends were mixed several times in a miniextruder. After each mixing pass part of the blend was taken to study primary nucleation. The samples were crystallized isothermally in a d.s.c. cell at 132°C. For the sake of comparison 8:2 iPP/HDPE blend samples with the same mixing history but without the nucleating agent were also crystallized. From the kinetics of crystallization the Avrami exponent n and overall kinetic rate constant K_n were calculated in the usual manner[22,23].

Theoretical predictions give a value of the Avrami exponent n equal to 3 for the heterogeneous mode of nucleation. The Avrami overall kinetic rate constant is then given by following relation:

$$K_3 = \tfrac{4}{3}\pi N G^3 \qquad (1)$$

where N is the density of primary nucleation and G is the spherulite growth rate. However, in most cases the experimental values of n are non-integral due to several experimental factors and errors[24] and the Avrami constant K_n is different from the theoretical value (K_3). In order to estimate the nucleation density using equation (1) it is necessary to know the value of K_3 (and, of course, the value of spherulite growth rate G, which can be measured in a separate experiment). It is possible using dimensional analysis[25] to find with a good accuracy the value K_3 from the experimentally obtained value K_n:

$$K_3 = (K_n)^{3/n} \qquad (2)$$

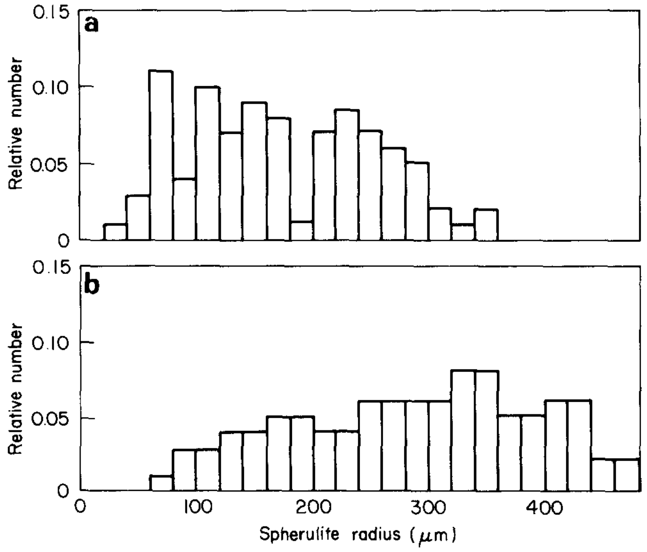


Figure 5 Spherulite size distributions of 9:1 iPP/HDPE blend: (a) mixed once; (b) mixed five times. Crystallization temperature $T_c = 135°C$

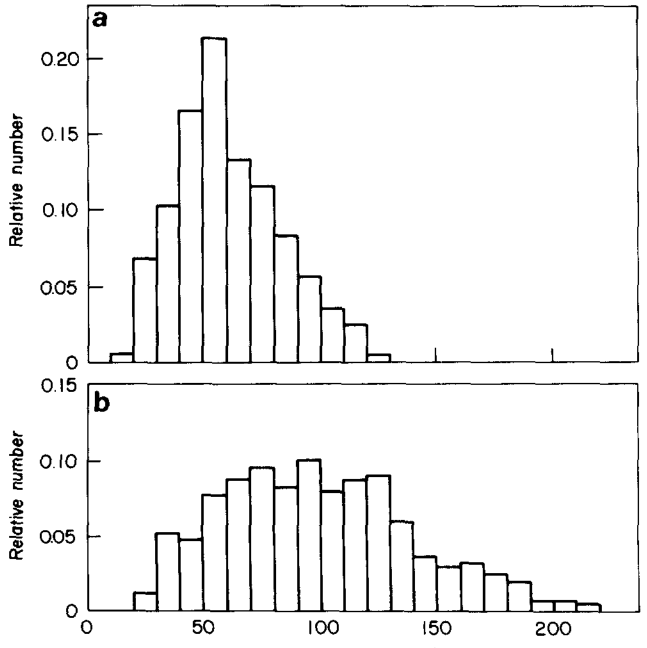


Figure 6 Spherulite size distributions of 9:1 iPP/HDPE blend: (a) mixed once; (b) mixed five times. Crystallization temperature $T_c = 127°C$

Combining relations (1) and (2) we are able to calculate the value of the nucleation density N.

The values of nucleation density obtained in this way for the iPP*/HDPE, iPP/HDPE* and iPP/HDPE blends are presented in *Figure 7*. It is seen that when the nucleating agent was introduced initially to HDPE (iPP/HDPE* blend) the number of primary nuclei is not considerably different from the number of primary nuclei in the iPP/HDPE blend (not artificially nucleated) for all mixing times. This indicates that only a small number of sodium benzoate crystalline particles migrated from HDPE to iPP and could nucleate the spherulites. On the other hand, when sodium benzoate was initially introduced to iPP (iPP*/HDPE blend) the number of primary nuclei was several times greater than in the blend without any nucleating agent in the initial stage of melt-mixing. With increasing mixing time the number of primary nuclei decreases drastically. Such behaviour indicates that almost all nuclei migrate from iPP to HDPE during the mixing process.

It can be concluded from these results that, during melt-mixing of the blend, there is migration from iPP to HDPE of nuclei active at high temperature of crystallization. The migration is very effective – almost all nuclei introduced to iPP move to HDPE and only a few others move in the opposite direction.

In the second set of experiments with artificially nucleated blends we used magnesium sulphate as a nucleating agent in order to study the behaviour of nuclei active at low temperature of crystallization. Magnesium sulphate is not a strong nucleating agent and appears active at temperatures much below 127°C (at which the change in nucleation behaviour in the blends occurs). The aim of this set of experiments was to show that nuclei active at low crystallization temperature also migrate from iPP to HDPE and the increase of nucleation density in blends occurring at low temperature is caused by overwhelming nucleation activity of polyethylene crystals.

The preparation of the blends, experimental and evaluation procedures were the same as in the experiments with sodium benzoate. The only difference was that the isothermal crystallizations were performed at 119°C. In *Figure 8* the exotherms of crystallization are presented. It is seen that when the nucleating agent was introduced initially to HDPE (iPP/HDPE** blend) the exotherms consist of two separate crystallization peaks: of HDPE (smaller peak) and iPP (greater peak). Magnesium sulphate appears here as a nucleating agent for polyethylene. It causes the crystallization of HDPE faster than the crystallization of iPP. The HDPE crystallization

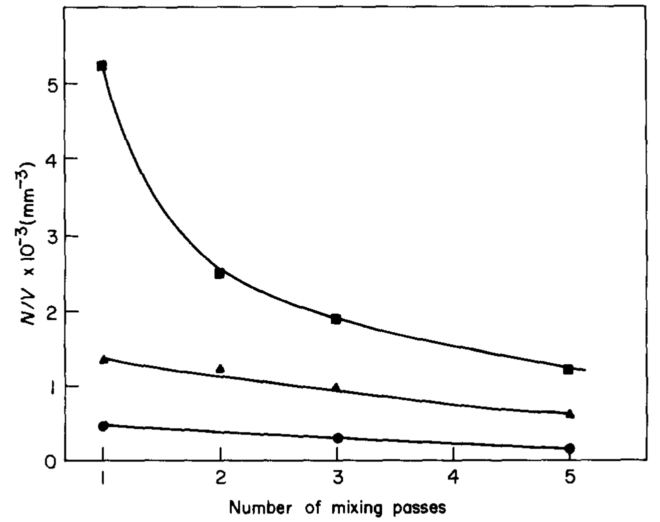


Figure 7 Plots of nucleation density vs. mixing time for 8:2 iPP/HDPE blends containing 0.2 wt% of sodium benzoate crystallized isothermally at 132°C: ■, iPP*/HDPE; ▲, iPP/HDPE*; ●, iPP/HDPE. The asterisk indicates the polymer to which sodium benzoate was initially introduced

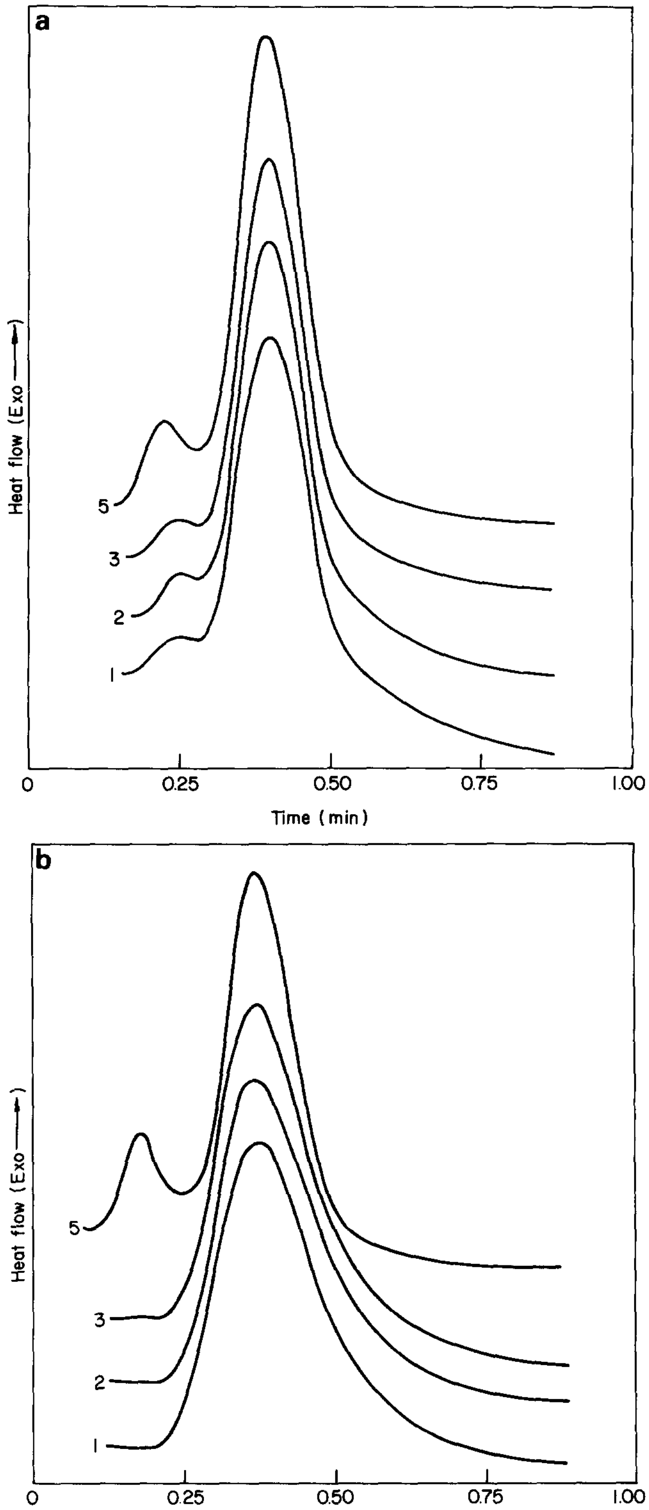


Figure 8 Exotherms of isothermal crystallization at 119°C of the 8:2 iPP/HDPE blends containing 0.2 wt% of magnesium sulphate: (a) iPP/HDPE**; (b) iPP**/HDPE. The asterisks indicate the polymer to which magnesium sulphate was initially introduced. The numbers on curves indicate the number of mixing passes

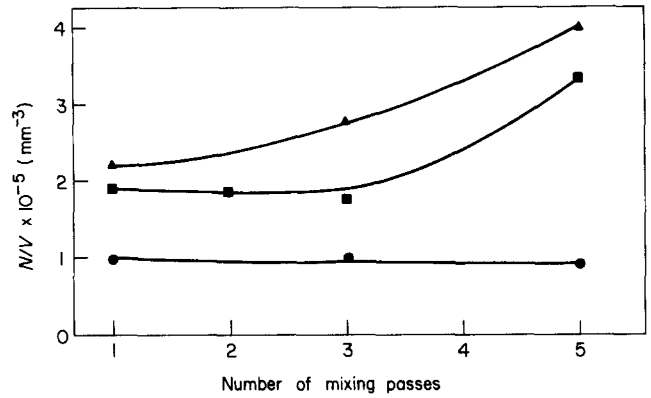


Figure 9 Plots of nucleation density vs. mixing time for 8:2 iPP/HDPE blends containing 0.2 wt% of magnesium sulphate crystallized isothermally at 119°C: ■, iPP**/HDPE; ▲, iPP/HDPE**; ●, iPP/HDPE. The asterisks indicate the polymer to which magnesium sulphate was initially introduced

peak is present in all exotherms for iPP/HDPE** blends independently of the mixing time of the sample. This leads to the conclusion that no migration of magnesium sulphate from HDPE to iPP occurs. In contrast in iPP**/HDPE blend (magnesium sulphate introduced initially to iPP) the peak of HDPE crystallization is absent from samples mixed once and twice (see *Figure 8b*). A small peak appears in the crystallization of the blend mixed three times and, finally, for the blend mixed five times the corresponding peak is as large as in the iPP/HDPE** blend. This means that magnesium sulphate particles migrate to HDPE from iPP during melt-mixing.

The densities of nucleation calculated from the Avrami constant for both artificially nucleated blends and non-nucleated blend are shown in *Figure 9*. The number of primary nuclei increases in both nucleated blends with increasing mixing time, whereas it remains almost constant in the blend with no nucleating agent. Such behaviour can be explained by the nucleation activity of HDPE crystals. The greatest nucleation density in iPP component appears in iPP/HDPE** blend where a number of additional polyethylene crystals arose due to magnesium sulphate nucleating agent. If magnesium sulphate was introduced initially to iPP (iPP**/HDPE blend) the density of nucleation is greater than in a blend that has not been artificially nucleated, but is not as great as in the iPP/HDPE** blend. With increasing mixing time the nucleation density increases independently of the migration of heterogeneous nuclei. However, migration alone is finally responsible for this increase because as a consequence the concentration of magnesium sulphate in HDPE phase increases and then, due to its nucleation ability with respect to HDPE, the number of polyethylene crystals (which in turn nucleate iPP) increases.

The results of this experiment show that HDPE crystals act as a nucleating agent for iPP and appear to be a more active nucleant than magnesium sulphate. The phenomenon of migration of heterogeneous nuclei to HDPE occurs during mixing but induces an increase in the number of nuclei in iPP via more intense nucleation of HDPE.

CONCLUSIONS

The following conclusions can be drawn from the results of this paper:

During the melt-mixing process, migration of all heterogeneous nuclei from iPP to HDPE melt occurs.

The driving force for the migration of heterogeneous nuclei across the interface between components of the blend is the interfacial free energy difference of those nuclei when they are surrounded by iPP melt and by HDPE melt respectively.

The phenomenon leads to a decrease in the number of primary nuclei when the blend is crystallized above 127°C. Thus, the average spherulite size increases.

At crystallization temperature up to 127°C two opposite tendencies are observed. One is the disappearance of heterogeneous nuclei from iPP matrix due to their migration during mixing, and the other is an increase in the number of heterogeneous nuclei due to the presence at the interface of polyethylene crystals growing at these temperatures and acting as a nucleating agent for iPP. Because of migration of nuclei during mixing, the HDPE phase becomes richer in heterogeneous nuclei, and many crystals are formed there (HDPE phase is dispersed in the form of separate inclusions in the iPP matrix). The polyethylene crystals cause heterogeneous nucleation of iPP. Finally the number of spherulites in the blend increases and their average size decreases. In most practical applications, crystallization of the blend occurs at temperatures far below 127°C. This causes an increase in number of spherulites and, consequently, a decrease of spherulite size. This, in turn, may have an influence on the mechanical properties of the blend.

REFERENCES

1 Paul, D. R. and Newman, S. (Eds.) 'Polymer Blends', Academic Press, New York, 1978
2 Martuscelli, E., Pracella, M., Avella, M., Greco, R. and Ragosta, G. *Makromol. Chem.* 1980, **181**, 957
3 Lovinger, A. J. and Williams, M. L. *J. Appl. Polym. Sci.* 1980, **25**, 1703
4 Gupta, A. K., Gupta, V. B., Peteres, R. H., Harland, W. G. and Berry, J. P. *J. Appl. Polym. Sci.* 1982, **27**, 4669
5 Vougdava, B., Simonov-Emelyanov, I. D., Kuleznev, N. V. and Zubov, P. I. *Plast. Massy.* 1982, **11**, 24
6 Teh, J. W. *J. Appl. Polym. Sci.* 1983, **28**, 605
7 Karger-Kocsis, J., Kalló, A. and Kuleznev, V. N. *Polymer* 1984, **25**, 279
8 Martuscelli, E., Silvestre, C. and Bianchi, L. *Polymer* 1983, **24**, 1458
9 Gałęski, A., Pracella, M. and Martuscelli, E. *J. Polym Sci., Polym. Phys. Edn.* 1984, **22**, 739
10 Gałęski, A., Bartczak, Z. and Pracella, M. *Polymer* 1984, **25**, 1323
11 Bartczak, Z., Gałęski, A. and Martuscelli, E. *Polym. Eng. Sci.* 1984, **24**, 1155
12 Omenyi, S. N. and Neumann, A. W. *J. Appl. Phys.* 1976, **47**, 3956
13 Omenyi, S. N., Neumann, A. W., Martin, W. W., Lespinard, G. M. and Smith, R. P. *J. Appl. Phys.* 1981, **52**, 796
14 Bartczak, Z. and Gałęski, A. (in preparation)
15 Gałęski, A. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 721
16 Gałęski, A. and Piorkowska, E. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 731
17 Wunderlich, B. 'Macromolecular Physics', Academic Press, New York, 1976, Vol. 2, p. 51
18 Olley, R. H., Hodge, M. A. and Basset, D. C. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 627
19 Last, A. G. M. *J. Polym. Sci.* 1959, **39**, 543
20 Beck, H. N. *J. Appl. Polym. Sci.* 1965, **9**, 2131
21 Binsbergen, F. L. *Kolloid. Z.Z. Polym.* 1970, **238**, 389
22 Avrami, M. *J. Chem. Phys.* 1941, **9**, 177
23 Mandelkern, L. 'Crystallization of Polymers', McGraw-Hill, New York, 1964
24 Grenier, D. and Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 1655
25 Kowalewski, T. and Gałęski, A. (in preparation)