Spherulite nucleation in polypropylene blends with low density polyethylene

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Primary nucleation of spherulites in blends of isotactic polypropylene (iPP) with low density polyethylene (LDPE) was investigated by means of differential scanning calorimetry and optical microscopy. The number of iPP spherulites in the blend decreases with increasing LDPE concentration to a much greater extent than follows from the decreasing amount of iPP. The shapes of spherulite size distributions indicate that athermal (heterogeneous) primary nucleation is inhibited. The density of primary nucleation in the blends decreases strongly with increasing mixing time. The same effect was observed in the blends with the nucleating agent which was added to iPP or LDPE. These experiments demonstrate that heterogeneous nuclei migrate across interphase boundaries from the iPP melt to the LDPE melt during the mixing process. It is suggested that the interfacial energy difference between the nuclei and the molten components of the blend is responsible for the migration of nuclei.

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

INTRODUCTION

The properties of blends of crystallizable polymers depend strongly on crystallinity, crystalline morphology and the degree of dispersion. The presence of dispersed particles might induce large changes in the overall crystallization kinetics, spherulite growth rate and the morphology of the polymer which is a continuous phase.

Among technologically very important blends, those containing isotactic polypropylene (iPP) and low or high density polyethylenes (LDPE, HDPE) behave as if the polyethylene inclusions were inert. The inclusions constitute geometrical obstacles to the iPP spherulite growth changing their morphology to any great extent but have little effect on the growth rate[1]. However, there are also some indications of interactions on the molecular scale[2]. There were also some indications reported of the inhibition of crystallization of iPP by the presence of dispersed polyethylenes following d.s.c. studies. The effect was initially attributed to the partial miscibility of iPP with polyethylene.

The changes in the crystallization kinetics are not caused by the change in the iPP spherulite growth rate since the rate does not change[1]. Therefore, it follows from the Avrami equation of the conversion of melt to spherulites that there must be a change in the spherulite nucleation either in induction time or in the number of spherulites.

This paper reports on a study of the crystallization behaviour and primary nucleation phenomena in iPP/LDPE blends crystallized from the melt.

EXPERIMENTAL

The materials employed were isotactic polypropylene (RAPRA, $\bar{M}_w = 307\,000$, $\bar{M}_n = 15\,600$, melt index 3.9, density 0.906 g cm^{-3}) and low density polyethylene (Montedison Fertene CF5, $\bar{M}_w = 135\,000$, $\bar{M}_n = 33\,750$, melt index 2.0, density 0.921 g cm^{-3}). Blends containing 0, 10, 20, 30, 40, 50, 60 wt% LDPE were prepared using a Rheocord–Haahe double-screw extruder at 190°C. Crystallization half-times at various temperatures were determined using a Perkin–Elmer DSC-2 calorimeter. Primary nucleation of spherulites was studied by means of a polarizing microscope equipped with a Mettler FP 5 hot stage.

The influence of time of mixing on primary nucleation was studied using blends prepared from iPP and polyethylene powders obtained by precipitation from xylene solution. Premixed powders were blended several times using a laboratory miniextruder (Custom Scientific Instruments Inc.). The blends obtained were crystallized isothermally on a Mettler hot stage in the form of 10–20 μm thick films and the number of spherulites in the blends per volume unit of iPP was then determined.

The spherulite size distributions were determined from thin sections (10 μm) of bulk, isothermally crystallized iPP and iPP/LDPE blends by means of polarizing microscopy. The fractions of sections of spherulites were recalculated to spherulite sizes using the transformation described in ref. 3.

In order to study the effect of the nucleating agent on the number of spherulites in the blends, 0.2 wt% of fine

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powder crystalline sodium benzoate was premixed with iPP and with polyethylene, and the following blends were prepared: (iPP + sodium benzoate) + LDPE and iPP + (LDPE + sodium benzoate). The change in the number of spherulites in isothermally crystallized films of those blends was studied as a function of the number of mixing passes in a screw extruder ($L/D = 25$) at 200°C.

RESULTS

Figure 1 shows the crystallization half-time of iPP as measured by d.s.c. in blends with various concentrations of LDPE as a function of crystallization temperature. It can be seen that the crystallization half-time increases as LDPE concentration increases. The plots of the enthalpy change vs. time of crystallization from d.s.c. do not show any marked change of induction time of iPP crystallization which could be attributed to the presence of polyethylene in the system. However, it is known[1] that the spherulite growth rate is little affected by the dispersed polyethylene particles in the blends. The main reason for the increase in the crystallization half-time seems to be the change of the primary nucleation density.

In *Figure 2* the change in the number of primary nuclei calculated from Avrami plots is plotted as a function of LDPE concentration for two different temperatures. The curves with circles are plotted for the number of spherulites recalculated to the volume fraction of iPP in the blends. The drastic drop in the number of spherulites in the iPP fraction is due to the presence of LDPE droplets in the blends.

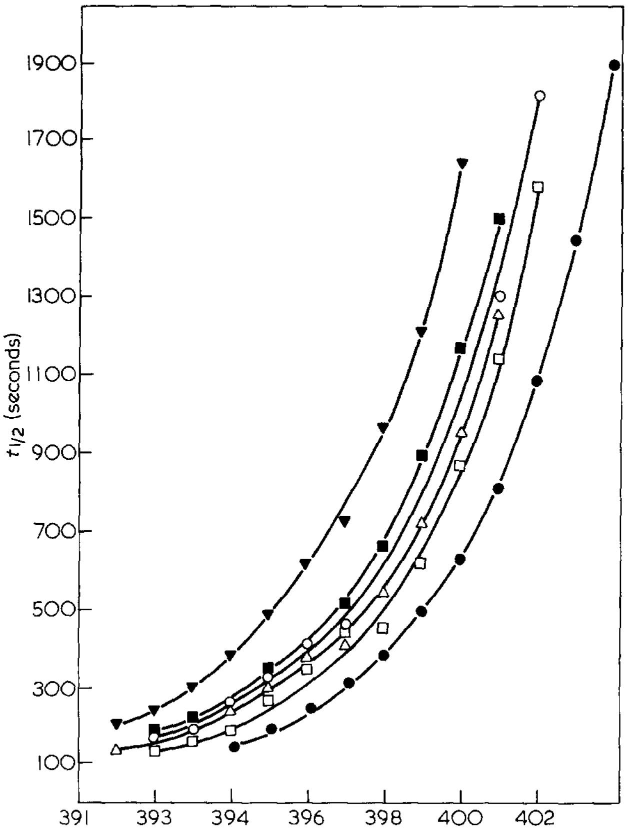

Figure 1 Crystallization half-time of various iPP/LDPE blends plotted vs. crystallization temperature: (●), iPP/LDPE 100/0; (□), iPP/LDPE 90/10; (△), iPP/LDPE 80/20; (○), iPP/LDPE 60/40; (■), iPP/LDPE 50/50; (▲), iPP/LDPE 40/60

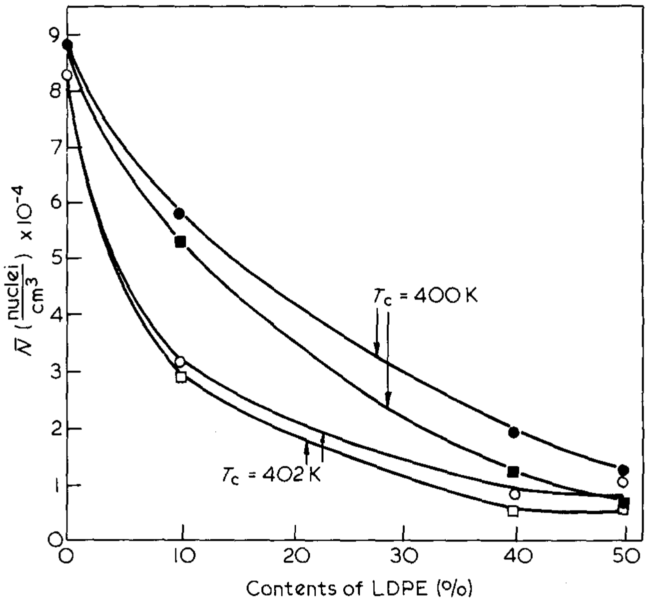

Figure 2 Number of primary nuclei calculated from Avrami plots for iPP/LDPE blends as a function of LDPE concentration (□, ■ – calculated per volume of the blend; ○, ● – calculated per volume fraction of iPP in the blend)

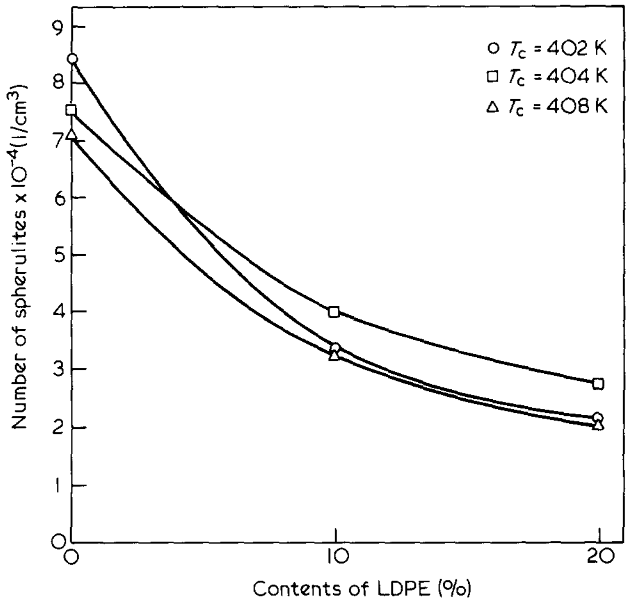

Figure 3 Number of spherulite centres measured from thin sections of bulk isothermally crystallized iPP/LDPE blends as a function of LDPE concentration: (○) T_c=402 K; (□) T_c=404 K; (△) T_c=408 K

The numbers of spherulites per unit volume measured from thin sections of isothermally crystallized blends in the bulk are presented in *Figure 3* for increasing contents of LDPE in the blends. Similarly as for thin films, the number of spherulites in the bulk decreases rapidly as the LDPE concentration increases. These observations suggest very distant interactions (as much as 10 μm and more) of the iPP matrix with LDPE droplets which, from the physical point of view, is impossible.

The studies of the changes in spherulite size distribution (polarizing microscopy of thin sections) due to the addition of LDPE particles (see *Figures 4a* and *4b*) indicate that the heterogeneous nuclei disappear from the iPP matrix in the blends. This conclusion follows from computer simulation data for three modes of primary

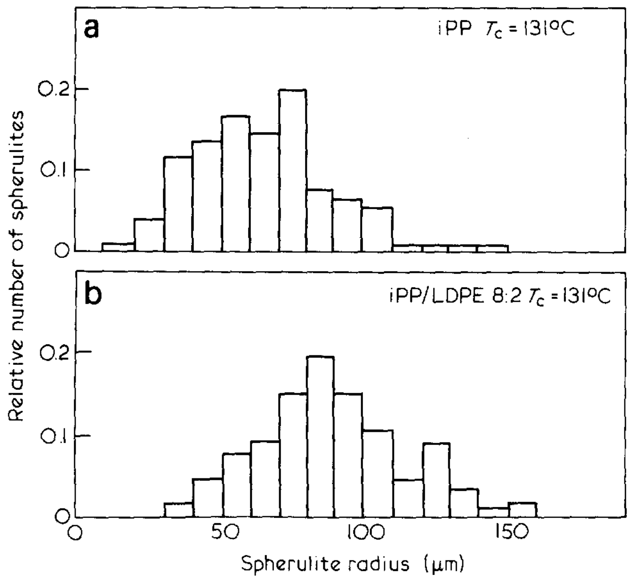

Figure 4 (a) and (b): Spherulite size distributions as measured from thin sections of bulk isothermally crystallized iPP and iPP/LDPE 8:2 blend

Table 1 Density of iPP spherulite nuclei in iPP and in 70:30 iPP/LDPE blends (number of spherulites x 10^4 per 1 cm^3 of iPP)

Composition	Crystallization temperature 125°C	127°C	Ratio N_{127}/N_{125}
iPP powder	11.4	9.0	0.78
iPP/LDPE powders	10.9	7.7	0.70
iPP/LDPE 1x mixed	7.8	4.9	0.64
iPP/LDPE 2x mixed	6.5	3.9	0.60
iPP/LDPE 3x mixed	5.8	3.3	0.56

nucleation[4,5]. Our hypothesis was that the disappearance of heterogeneous nuclei from the iPP matrix in blends was related to their migration from iPP to polyethylene during the mixing process. In order to test that hypothesis we carried out two sets of experiments:

(i) Powders of iPP and LDPE were prepared from xylene solutions by rapid precipitation with methanol, thoroughly rinsed with methanol and then dried to constant weight at 70°C in a vacuum. The iPP and LDPE powders were premixed at appropriate concentrations and mixed several times in a miniextruder. After each pass a small specimen was separated for spherulite nucleation studies. All samples were melted at 230°C and kept for 5 min at that temperature in order to destroy all self-seeded nuclei.

Isothermal crystallization of samples in the form of 10 μm thin films was carried out at 125°C and 127°C. The results of determination of the number of spherulites per volume of iPP for the blends containing 30 wt% of LDPE are presented in *Table 1*.

From these results it can be seen there is a large decrease in the number of spherulites for the longer mixed samples. This result indicates that the time intervals during which the two molten polymers are in contact and by the surface area of their contact are important. This, in turn, suggests migration of heterogeneous nuclei from the iPP melt to polyethylene in the course of mixing. The driving force of the migration, i.e., crossing the interface, can only be the interfacial energy difference between the nuclei in molten iPP and the nuclei in molten polyethylene. That difference would force the nuclei to migrate to LDPE. Some support for that hypothesis comes from the change of ratio of the number of nuclei active at 127°C to the number of nuclei active at 125°C (see *Table 1*). It can be seen the more active nuclei, capable of giving rise to spherulites at higher temperatures, migrate faster. Therefore they exhibit a more negative interfacial energy difference with respect to the polyethylene melts.

(ii) In the second set of experiments we intended to observe the migration of heterogeneous nuclei. Sodium benzoate was chosen as a very effective nucleating agent[6,7].

Sodium benzoate (fine powder) was mixed in the extruder with iPP granules and separately with LDPE granules (concentration of 0.2 wt% of iPP in the blend). The following blends were prepared: iPP with nucleating agent/LDPE (iPP*/LDPE), iPP/LDPE with nucleating agent (iPP/LDPE*), and for comparison iPP/LDPE, all blends containing 20 wt% LDPE. The blends were additionally mixed several times in a single-screw extruder. After each mixing pass a small sample was taken for isothermal crystallization study at 132°C. The numbers of spherulites per unit volume of samples were determined after completion of crystallization. The data are plotted in *Figure 5*. It can be seen that the number of spherulites decreases in all samples as the number of mixing passes increases.

The numbers of spherulites per volume unit converge to the same value independently of the initial location of the nucleating agent in the sample. Sodium benzoate particles do not migrate from LDPE in the blend iPP/LDPE* although its concentration is much higher in LDPE than in iPP while almost all the nucleating agent from iPP is transferred to LDPE in the iPP*/LDPE blend after a sufficiently high number of mixing passes.

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

(1) The migration of heterogeneous nuclei for iPP

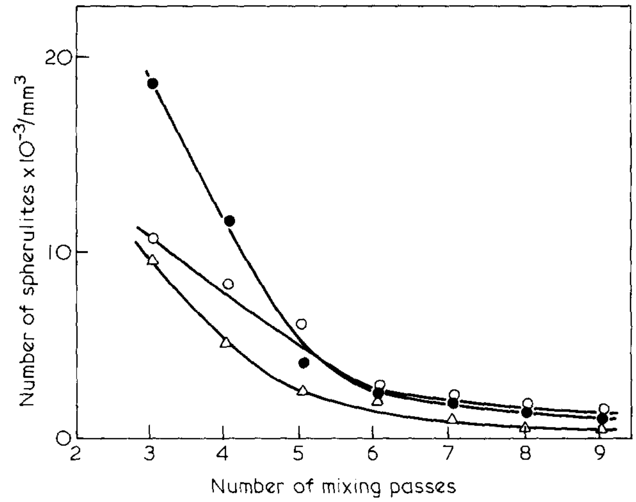

Figure 5 Numbers of spherulite centres per volume unit in iPP/LDPE 8:2 blends with nucleating agent (sodium benzoate) as a function of number of mixing passes. Asterisks denotes the polymer to which initially the nucleating agent was introduced. (●) PP*/LDPE; (○) PP/LDPE*; (△) PP/LDPE. T_c=132°C

spherulites is observed during preparation and mixing of iPP blends with polyethylene.

(2) The driving force for the transfer of heterogeneous nuclei across the interface between the components of the blend is the interfacial energy difference of those nuclei when they are surrounded by the iPP melt and when they are surrounded by the polyethylene melt. Since the crystals of iPP should have similar values of interfacial energy as heterogeneous nuclei for iPP, the contact with the LDPE melt is preferred by the crystalline phase of iPP. This last result gives rise to the previously described phenomena[1] that the spherulites growing from the iPP melt do not reject LDPE inclusions.

REFERENCES

1 Gałeski, A. Pracella, M. and Martuscelli, E. *J. Polym. Sci. Polym. Phys. Edn.* in press

2 Martuscelli, E., Silvestre, C. and Abate, G. *Polymer* 1982, **23**, 229

3 Gałeski, A. *Int. Polym. Sci. Technol.* 1980, **7**, T/28

4 Gałeski, A. *J. Polym. Sci. Polym. Phys. Edn.* 1981, **19**, 721

5 Gałeski, A. and Piórkowska, E. *J. Polym. Sci. Polym. Phys. Edn.* 1981, **19**, 731

6 Binsbergen, F. L. *Polymer* 1970, **11**, 253

7 Beck, H. N. *J. Appl. Polym. Sci.* 1967, **11**, 673