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Crystallization kinetics of polypropylene: 1. Effect of small additions of low-density polyethylene

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In order to analyse the effect of small additions (up to 20 wt%) of low-density polyethylene (LDPE) on the crystallization kinetics and thermodynamics of an isotactic polypropylene (iPP), morphological studies of iPP/LDPE blends have been carried out. The results have shown that at LDPE percentages above 10% in the blend, the LDPE aggregates pass over the spherulitic limits and go into the intraspherulitic domains of the PP. The half-crystallization times ($\tau_{1/2}$) as well as the Avrami exponent (n) and the chain folding energy for PP crystallization (σ_e) increase markedly at LDPE percentages above 10% in the blend. The isothermal radial growth rate, G, of the PP in the blends is one-third of the plain polymer, although it remains constant at any blend composition. However, the overall kinetic rate constant seems to be influenced by the presence of the melt LDPE phase. In all cases, and according to the obtained results, an instantaneous nucleation takes place. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polypropylene/low-density polyethylene blends; morphology; crystallization)

INTRODUCTION

At present, polyolefins, such as polyethylene (PE) and polypropylene (PP), are the thermoplastics of higher consumption due to their special and varied physical and mechanical properties. However, in some cases, not all the characteristics of these materials are suitable; for instance, PE has a low modulus, and the relatively high glass transition temperature of PP renders it unsuitable for low-temperature applications. Thus, the study and development of their copolymers and physical blends arose. Among the few polymer mixtures that have found some application are blends of PP and low-density polyethylene (LDPE) and/or rubber copolymers due to their high impact strength over a wide range of temperature. In these blends, the polypropylene is the continuous phase and the softer component (LDPE, rubber) is the dispersed phase.

Polyolefin blends attract additional interest due to the possibility of recycling plastic wastes, mainly constituted by polyolefins[1,2], avoiding the complex and expensive processes of separation of the different components. On the other hand, the great advantage of reinforcing thermoplastic materials is the possibility of combining the tenacity of the thermoplastics with the strength and rigidity of the reinforcing agents[3,4]. With this aim, several investigations on the mechanical properties of short glass fibre reinforced PP/LDPE blends have been carried out in our laboratories[5,6] to analyse the effect of compounding method on the mechanical degradation of fibres[7] and mechanical properties of the composites[8], as well as on the morphology and fibre orientation[9], and the influence of glass fibre surface modification with a titanate coupling agent on the mechanical properties[10].

Physical properties of polymeric materials strongly depend on their microstructure and crystallinity, since it is at this microscopic level where failure of the materials takes place. To date, the most important aspects of polyolefin blends that have been investigated are related to the influence of their composition on the morphology, mechanical behaviour, melting temperature, crystallinity degree, and crystallization rate of the components on the melt state.

The crystallization kinetics of isotatic PP (iPP) has been widely studied by different methods[11–15], and, in general, has been well described by the Avrami equation[16,17]. However, although the typical value of the Avrami exponent, n, is about 3[13,14], some authors have reported values in the range of 2[18] and 4[19] that were attributed to different nucleation mechanisms. Big differences have also been observed in the reported data of the equilibrium melting temperature of the PP, ranging from 458[20] to 481 K[21], and even to 493 K[22], for fully oriented chains. It was previously observed that

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some mechanical properties of several physical blend compositions are above the theoretical values obtained from the rule of mixtures. These results have been attributed to interfacial effects and partial miscibility of the high-density polyethylene (HDPE) and PP chains in the melt[23]. However, at present, there is not much information on the compatibility of these polymers in the melt although the presence of individual melting points of both polymers in their physical blends indicates the incompatibility of these systems in the solid state. Initially, most of the studies were carried out on HDPE/LDPE[24] and PP/HDPE blends.

The PP/PE morphology has been recently discussed[25,26], and the effect of LDPE on crystallization kinetics of PP, in isothermal experiments, at temperatures above the melting temperature of the PE has been widely investigated[27–29]. Although it was previously reported that the PP spherulite growth rate, G, decreased in the presence of a second component[30,31], it has been shown that G is only temperature-dependent, and remains unaffected by the presence of another polymer[14,29].

The present study is the first part of a series of investigations carried out in our laboratories to analyse the effect of LDPE, fibre content and both components simultaneously on the iPP crystallization behaviour, by means of d.s.c., at temperatures above the LDPE melting temperature.

EXPERIMENTAL

LDPE (melt flow index 6.7 g min^{-1}, at 190°C and 2.16 kg, and density 0.916 g cm^{-3}) and iPP (melt flow index 2.9, at 190°C and 5 kg, and density 0.905 g cm^{-3}) supplied by Repsol Química, under the trade names Alkathene-017 and Isplen PP-051, respectively, were used in the present study.

Melt-blended specimens of these homopolymers with various compositions were prepared by two-rolls milling. The LDPE was added to the melt PP, and the blend homogenized for 15 min at 170°C. Then, the blends were compression moulded at 200°C in a Collin press. From the moulded plaques, samples were taken for the crystallization study. The composition of the blends and the temperatures of crystallization that have been used in this study are compiled in *Table 1*.

There are a wide variety of techniques to investigate polymer microstructure and crystallinity. The first can be analysed by optical microscopy, scanning and transmission electron microscopy, and X-ray techniques, for example, and the latter is usually determined by measuring the density, specific volume and heat, electrical resistivity, and enthalpy of the materials. In general, d.s.c. is the most common technique used to study the crystallization kinetics of polymers.

The morphology and the radial growth rates of the PP spherulites were studied on thin films by using an optical polarizing microscope (Leika Metalographic Aristomet model), with a Mettler FP-90 automatic hot-stage thermal control. Blend samples were sandwiched between microscope cover slips, melted at 200°C for 10 min and then rapidly cooled to 130°C. The radius of the growing spherulites was measured as a function of time by taking photomicrographs at given intervals of time.

Table 1 Kinetic parameters of the studied blends

PP/LDPE (wt%)	T_c (K)	$-\log K_n$ (min)	n	$t_{1/2}$ (s)
100/0	398	1.09	2.60	137
	403	2.64	2.75	479
	405	3.27	2.70	856
	408	4.38	2.77	2001
95/5	398	1.11	2.76	133
	403	2.74	3.07	415
	405	3.16	3.01	594
	408	4.36	3.04	1441
90/10	398	1.66	2.70	217
	403	3.32	2.95	709
	405	4.01	3.03	1123
	408	6.24	3.86	2257
85/15	398	1.42	2.49	193
	403	2.82	2.75	559
	405	3.52	2.55	1254
	408	4.33	2.80	1849
80/20	398	1.41	2.08	241
	403	2.74	2.36	747
	405	3.11	2.26	1212
	408	4.32	2.52	2684

A Perkin-Elmer DSC-7 apparatus was used to analyse the thermal properties and the overall crystallization kinetics of the PP with the following standard procedure. The samples (about 10 mg) were melted at 200°C for 10 min in order to eliminate any thermal history of the material, then were rapidly cooled to the crystallization temperature, T_c, and maintained at that temperature during the time necessary for the complete crystallization of the PP homopolymer. The heat evolved during the isothermal crystallization (ΔH_c) was recorded as a function of time, at different crystallization temperatures.

The temperatures of crystallization were selected taking into account the melting temperature of the LDPE (377–379 K) in order to be sure that the PE is in the melt state during the isothermal crystallization of the PP. The experiments were carried out in a nitrogen atmosphere and the scans were obtained at 10°C min^{-1}. The isotherms were constructed by integrating the area under the exothermic peak according to equation (1) below. The crystallinity weight fraction was calculated through the total enthalpy method recommended by both Gray[32] and Richardson[33]. In all calculations, a crystal heat of fusion of 209 J g^{-1} has been used for PP[34].

The isothermal crystallization kinetics of a material were analysed by evaluating its degree of crystalline conversion (X_t) as a function of time, at a constant temperature. The variation of the crystallinity is related to the generated heat ratio at time t and at infinite time t_∞ according to the equation

$$X_t = Q_t/Q_\infty = \int_0^t (\mathrm{d}H/\mathrm{d}t)\,\mathrm{d}t \Big/ \int_0^\infty (\mathrm{d}H/\mathrm{d}t)\,\mathrm{d}t \qquad (1)$$

where $\mathrm{d}H/\mathrm{d}t$ is the rate of heat evolution.

On the other hand, parameters governing the crystallization of a polymer, such as the crystallization kinetic constant (K_n) and the Avrami exponent (n), can be calculated from the Avrami equation

$$\log[-\log(1 - X_t)] = n \log t + \log K_n/2.3 \qquad (2)$$

The n and K_n parameters can be used to interpret qualitatively the nucleation mechanism and morphology and overall crystallization rate of the polymer, respectively. From the graphic representation of log $[-\log(1-X_t)]$ *versus* log t, the Avrami coefficient n (slope of the straight line) and the crystallization kinetic constant K_n (intersection with the y axis) can be calculated. However, the value of K_n is very often obtained from the equation[35]

$$K_n = \ln 2/t_{1/2}^n \quad (3)$$

By means of the above equations, the crystallization kinetic constant (K_n), Avrami exponent, and others crystallization kinetic and thermodynamic parameters were calculated.

After crystallization the samples were heated to the melting point of the PP at a scanning rate of 10 K min^{-1}. The melting temperatures (T_m) were obtained from the maximum of the endothermic peaks.

The equilibrium melting temperature (T_m^o) is obtained from the intersection of two straight lines, the first one corresponding to the experimental melting temperature *versus* crystallization temperature and the second one to a straight line with slope equal to one, in a melting temperature *versus* crystallization temperature plot (Hoffman–Weeks plot).

Finally, the crystallization thermodynamic and kinetic of the samples have been analysed on the basis of the secondary nucleation theory of Hoffman and Lauritzen[36] that is expressed by the equation

$$(1/n)\log K_n + \Delta F/2.3RT_c = A_0 - (4b_0\sigma\sigma_e T_m)/(2.3k_B\,\Delta H_f\,T_c\,\Delta T) \quad (4)$$

where $\Delta T = T_m^0 - T_c$, and σ and σ_e are the free energies per unit area of the surfaces of the lamellae parallel and perpendicular to the chain direction, respectively. ΔH_f is the enthalpy of fusion and b_0 is the distance between two adjacent fold planes. If it is assumed that the spherulite nucleus density is independent of time, Δt, blend composition and T_m, then A_0 may be considered constant. ΔF is the activation energy for the transport process at the liquid–solid interface, and can be calculated from the Williams–Landel–Ferry equation[37], given by the expression

$$\Delta F = \Delta F_{WLF} = (C_1 T_c)/(C_2 + T_c - T_g) \quad (5)$$

where C_1 and C_2 are constants whose values are assumed to be 4.12 kcal mol^{-1} (17.24 kJ mol^{-1}) and 51.6 K, respectively (T_g is the glass transition temperature of the pure polypropylene). When plotting $1/n\,(\log K_n) + \Delta F/2.3RT_c$ *versus* $T_m/T_c\,\Delta T$, the value of $4b_0\sigma\sigma_e/k_B\,\Delta H_f$ can be calculated from the slope of the straight lines, and having in mind that b_0, σ, ΔH_f, and the Boltzman constant k_B have the following values given in the literature: 5.24 Å, 11 mJ m^{-2}, 50 cal g^{-1} (209 J g^{-1}) and 1.35×10^{-16} erg mol^{-1} K^{-1}, respectively, it is possible to calculate the value of the free energy of folding of iPP lamellar crystals, σ_e, as a function of blend composition.

RESULTS AND DISCUSSION

In order to analyse the effect of temperature on PP crystallization, the crystallization isotherms of the PP in the PP/LDPE blend with 20% of LDPE, at the different crystallization temperatures used in this study, are graphically represented in *Figure 1*. As can be seen, the time to reach the maximum degree of PP crystalline order increases as the crystallization temperature increases.

In the same manner, and to analyse the effect of the blend composition on the PP crystallization, the crystallization isotherms of all the samples, obtained at 403 K, are represented in *Figure 2*. From this figure, it can be deduced that at very low LDPE percentages in the polymer blend, the crystallization time of the PP slightly increases. However, at LDPE contents above 10% in the blend, a marked increase of the PP crystallization time is observed, which is attributed to a hindrance effect of the melt LDPE for the arrangement of the crystallizable chains of the PP. In fact, and as can be observed in the microphotographs obtained in a polarizing microscope (*Figure 3*), when the crystallization of the PP is complete, LDPE separated domains were observed for all LDPE concentrations studied. At LDPE concentrations below 10% in the blend, these domains remain out of the PP spherulitic limits and were in the interspherulitic contact regions (*Figure 3a*), but at higher percentages the LDPE domains were in both inter- and intraspherulitic regions of the PP (*Figures 3b*, *3c* and *3d*). That is, during the crystallization process of the PP the LDPE particles are first ejected by the crystal front and then occluded in intraspherulitic regions. From these results it can be deduced that the overall rate of crystallization of the PP is strongly depressed by the addition of LDPE. The radial growth rate of PP spherulites also decreases in the presence of LDPE particles, as can be deduced from

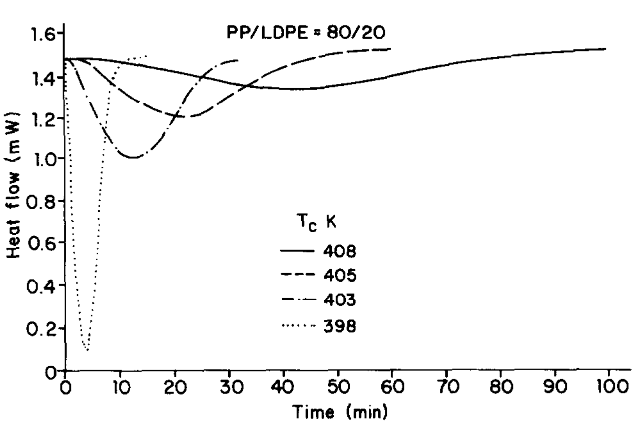

Figure 1 Effect of temperature on crystallization isotherms of an 80/20 PP/LDPE blend

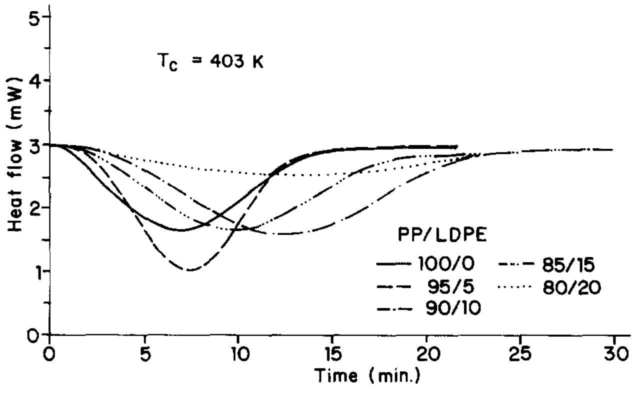

Figure 2 Effect of LDPE content on the polypropylene crystallization isotherms, at 403 K

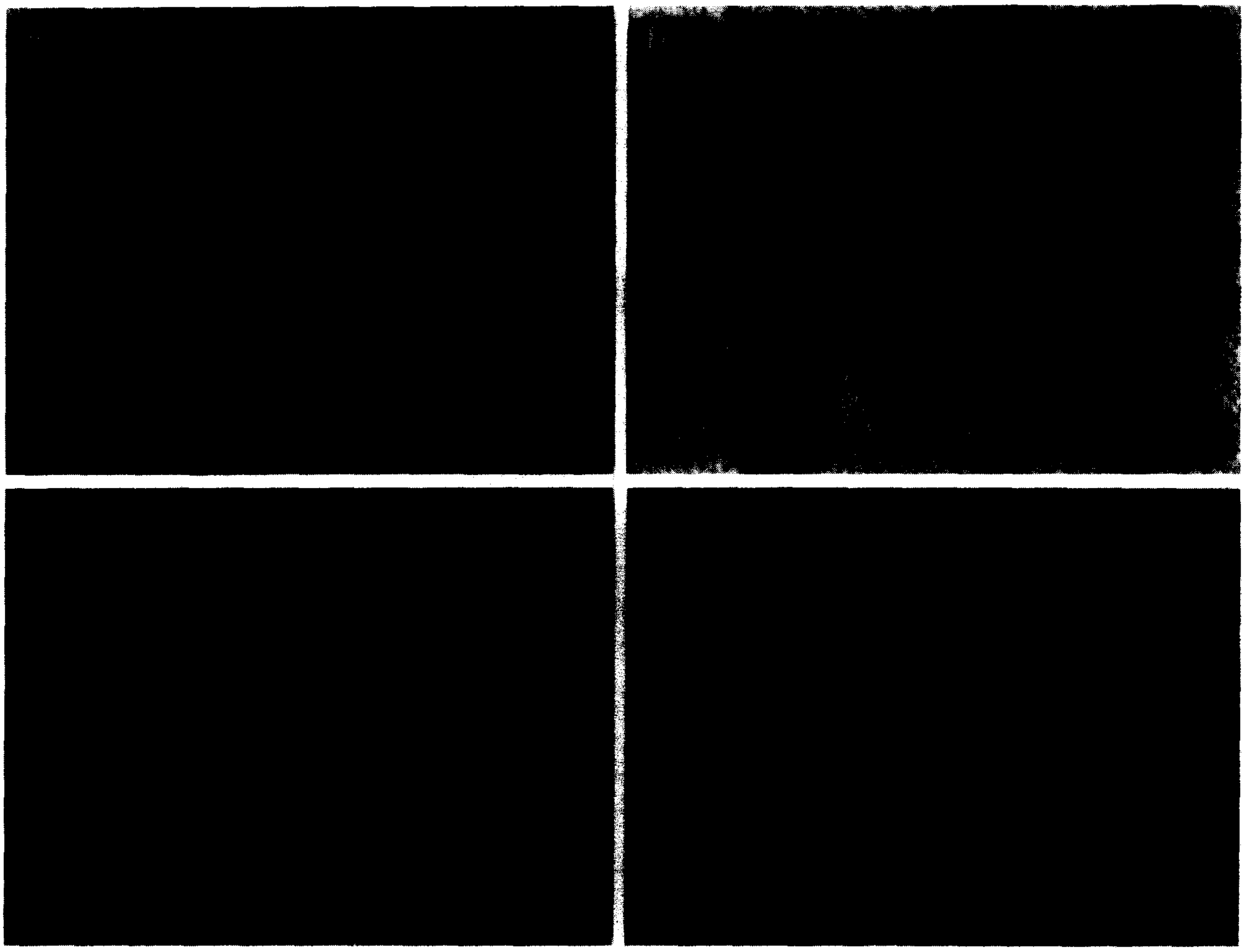

Figure 3 Morphology of crystallized PP/LDPE blends: (a) 95/5, (b) 90/10, (c) 85/15 and (d) 80/20. (125×)

Figure 4. However, no differences between the radial growth rate of PP spherulites in the plain polymer and in their blends with LDPE were observed by other authors[14,29], although in the presence of other polymers it decreased as the percentage of the LDPE in the blend increased[31]. The isothermal radial growth rate, G, was measured at 403 K (*Figure 5*).

The half-times of PP crystallization ($t_{1/2}$) in the studied blends are compiled in *Table 1*. As can be seen, at LDPE contents of about 10% a marked increase of $\tau_{1/2}$ is observed, which could indicate that at about this percentage the LDPE particles start to exceed the spherulitic limits of the PP crystalline structures, finally to be located in the PP spherulites, obstructing the crystalline development of the PP. Normally, $\tau_{1/2}$ increases as the LDPE content in the blend and crystallization temperature increase, at least in the blend composition ranges that have been investigated. The presence of a melt LDPE phase seems to influence the rate of crystallization of PP, as has also been observed by other authors[38]. As can be deduced from *Figure 6*, the half-time of PP crystallization is more affected by the crystallization temperature than by the blend composition, and, in all cases, the curves follow the same tendency, with a noticeable increase of the slope above 403 K.

Kinetic data for pure PP and PP/LDPE blends are shown in *Figures 7* and *8*, and are represented in the form of Avrami plots. These plots have been obtained from equation (2), and from them, the Avrami exponent (n) has been calculated for all the samples. The values of the kinetic constant of crystallization, K_n, Avrami constant, n, and half-time of crystallization, $\tau_{1/2}$, as calculated

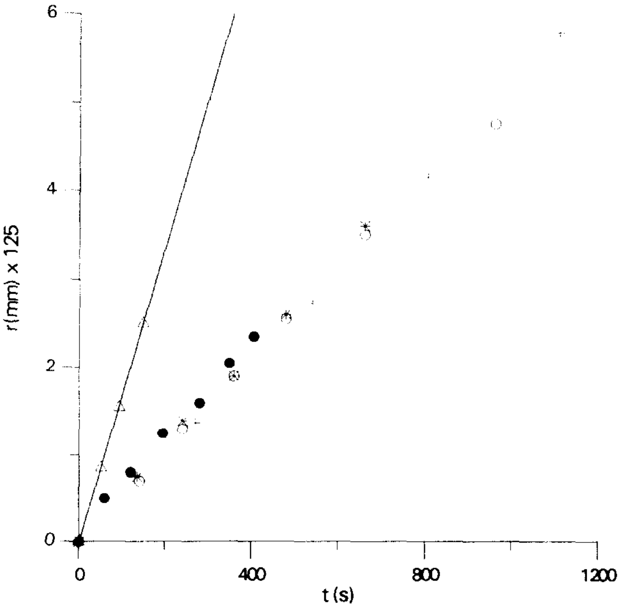

Figure 4 Spherulitic growth rate of polypropylene at 403 K in the plain polymer (△) and in the PP/LDPE blends: +, 95/5; ○, 90/10; *, 85/15; ●, 80/20

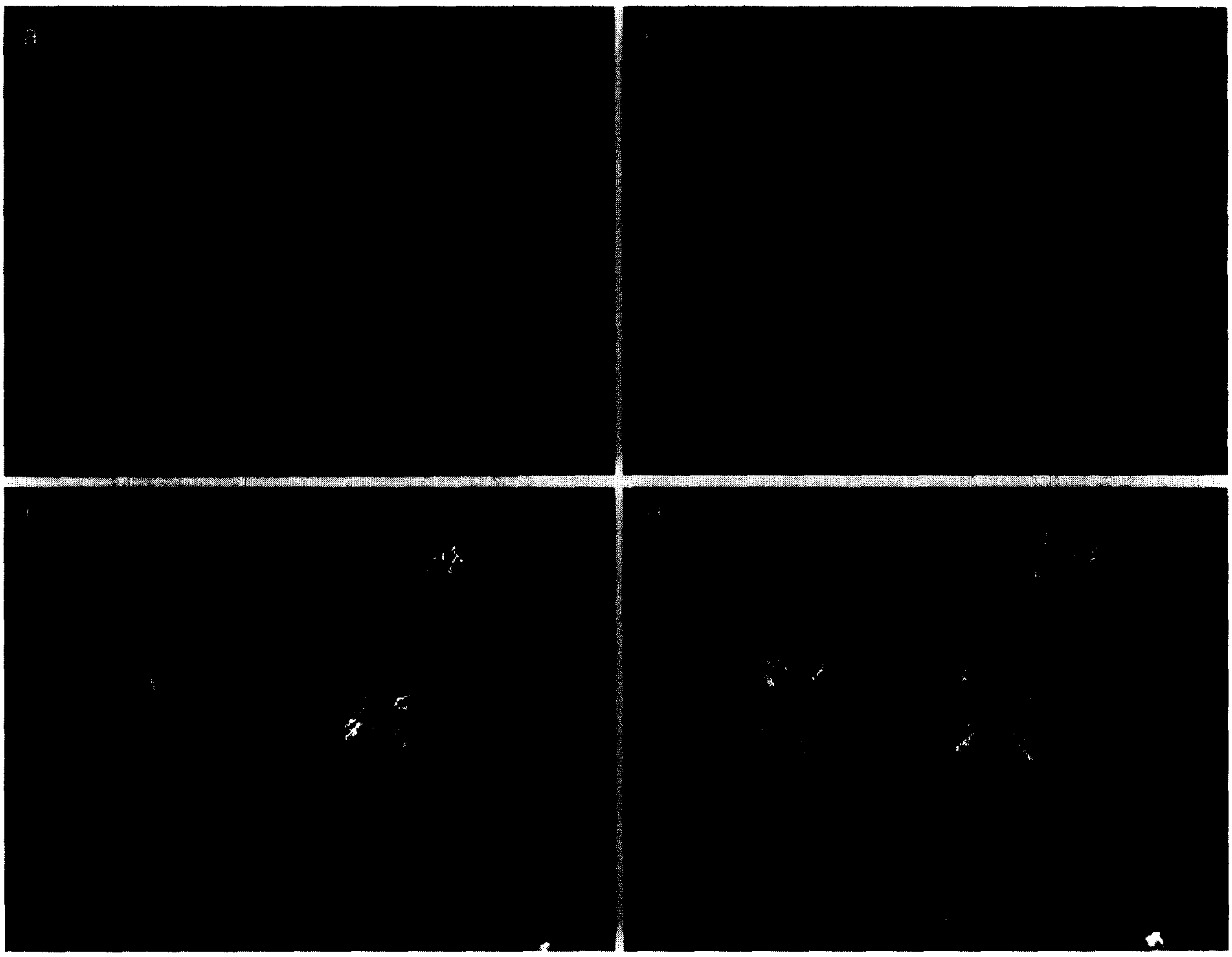

Figure 5 Micrographs of PP crystallization in a 95/5 PP/LDPE blend, at 403 K. (a) 5 min, (b) 9 min, (c) 19 min and (d) 25 min

from equation (3), are compiled in *Table 1*. With increasing isothermal crystallization temperature, the Avrami exponent slightly increases while the intercept log *K* decreases.

The Avrami exponents are between 2 and 3 over the crystallization temperature range studied. According to the values of the Avrami exponents, it can be established that the spherulitic development arises from an athermal

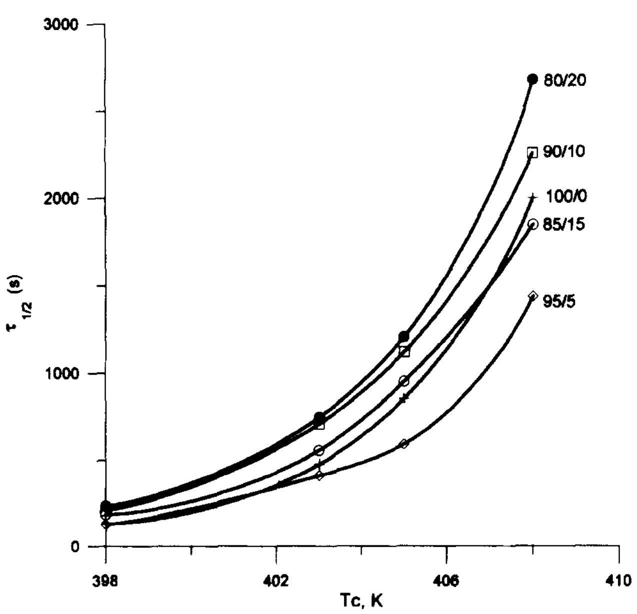

Figure 6 Half-time of PP crystallization ($\tau_{1/2}$) versus crystallization temperature (T_c), in PP/LDPE blends

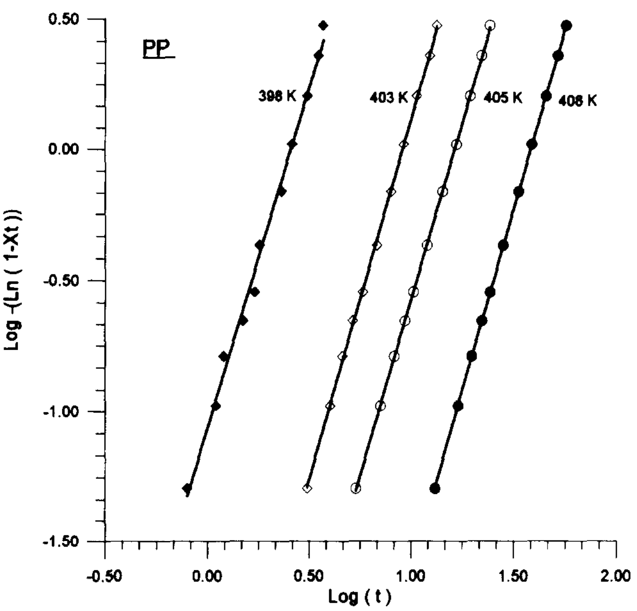

Figure 7 Avrami plots of polypropylene at different crystallization temperatures

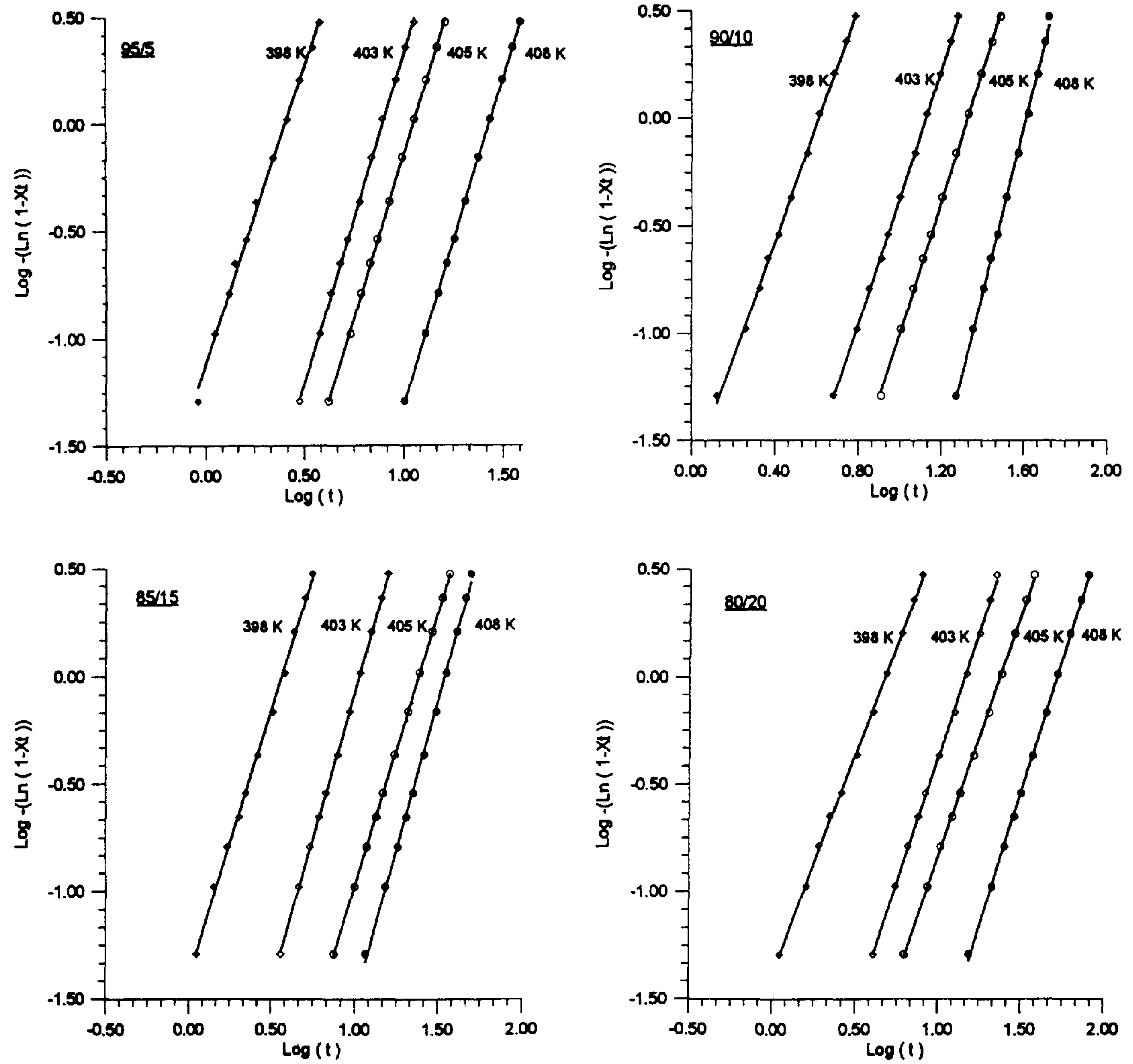

Figure 8 Avrami plots of PP/LDPE blends at different crystallization temperatures

and instantaneous nucleation, although the growth is not constant as deduced from the fractional values of n. At the same T_c, the Avrami exponent increases with the addition of 5% LDPE to the PP, and then decreases as the LDPE percentage in the blend increases, following a similar tendency at all the crystallization temperatures investigated. An increase in the Avrami exponent is usually attributed in the

Table 2 Values of T_m, T_m^0 and σ_e of the PP in the blends

		PP/LDPE ratio				
	T^a (K)	100/0	95/5	90/10	85/15	80/20
T_m (K)	398	438	437.31	437.64	437.80	437.70
	403	440	439.22	439.43	439.91	439.64
	405	441.2	440.56	440.82	440.96	440.71
	408	442.5	441.88	441.40	442.30	442.34
T_m^0 (K)		471.1	470.86	463.28	470.50	475.38
σ_e (mJ m^{-2})		186	169	132	167	170

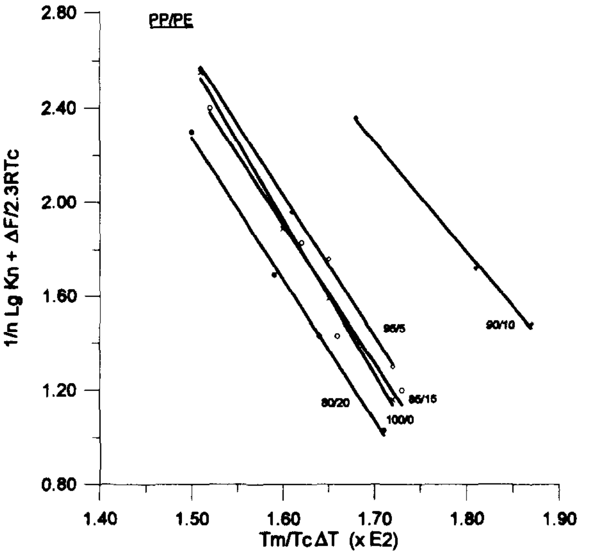

Figure 9 Plots of equation (4) for pure PP and for PP crystallized from blends of different composition

literature to a change from instantaneous to sporadic nucleation.

From the values of the kinetic constant of crystallization, compiled in *Table 1*, it can be deduced that the crystallization behaviour of the PP is more dependent on the temperature than on the blend composition. This effect is also observed by comparing the PP half-times of crystallization as a function of LDPE percentage in the blend and crystallization temperature.

The melting temperatures and enthalpies of fusion of the PP in the isothermally crystallized samples were determined from the maxima and the area, respectively, of the fusion peaks obtained by heating the samples directly from T_c, at a rate of $10\,\mathrm{K\,min^{-1}}$. The melting temperatures of the samples are compiled in *Table 2*.

The melt temperature of the PP increases as the crystallization temperature increases, which is directly related to the size of the PP crystals. From the PP melt temperature in the studied blends, after isothermal crystallization, it was possible to calculate the equilibrium PP melt temperature (T_m^0) in each case, by plotting T_c *versus* T_m and observing the intersection of this line with that having a slope equal to 1 and passing through zero. The corresponding values of T_m^0 for the PP in the studied blends are compiled in *Table 2*. As can be seen, these estimated temperatures vary slightly with the LDPE content in the blend.

The values of the kinetic parameters can be used to calculate the crystallization thermodynamics of the PP in the melt in the presence of LDPE. To do this, the secondary nucleation theory given by equations (4) and (5) can be used. Firstly, the activation energy for the transport process at the liquid–solid interface, ΔF, is calculated from equation (5). This energy corresponds to the reptation energy of a molecular chain from a supposed solid state, where it is unordered, to an ordered solid state. This transport energy depends on the polymer glass transition temperature, T_g, and on the crystallization temperature, T_c, at which the transport phenomenon takes place. Once these values were calculated, it was possible to plot equation (4), which gave a straight line with a negative slope. The values of $1/n \log K_n + \Delta F/2.3RT_c$ *versus* $T_m/T_c\,\Delta T$ are graphically represented in *Figure 9*. The slope of these lines will be equal to $4b_0\sigma\sigma_o/k_B\,\Delta H_f$. If it is considered that the free energy per unit of lamellar surface (σ_e) in the molecular chain direction, the distance between two adjacent folded parallel planes (b_0), and the melting enthalpy of the PP (ΔH_f) are independent of blend composition, the free energy of chain folding of PP crystals to form a lamellae can be calculated. The obtained values of σ_e are given in *Table 2*.

As can be seen, the chain folding energy of the PP decreases in the presence of small quantities of LDPE (5–10%) while at higher LDPE percentages it tends to increase again. This suggests that, at low percentages LDPE can contribute to the folding of the PP chains. However, at higher percentages, the molecular ordering of the PP chains is obstructed by the greater number of LDPE droplets in the melted blend. In fact, as previously mentioned, the spherulitic boundaries of the PP are exceeded by the small aggregates of LDPE at LDPE contents above 10%.

CONCLUSIONS

From the above results, the following conclusions may be deduced:

- the isothermal radial growth rate of the PP spherulites in the PP/LDPE blends decreases to about one-third of the plain polymer, and does not depend on blend composition.
- The presence of liquid LDPE in the melt blends influences the crystallization of iPP. The half crystallization time of the PP is only slightly affected by small additions of LDPE. However, at LDPE percentages above 10% this time is markedly increased. The increase in $\tau_{1/2}$ may be interpreted only by assuming that both polymers are entirely or partially compatible in the melt in the range of the studied crystallization temperatures.
- The half crystallization time of the PP strongly depends on crystallization temperatures.
- The chain folding of the PP chains is only affected by the LDPE aggregates at LDPE percentages above 10%.
- The Avrami exponent for the PP crystallization depends more on the LDPE concentration in the blend than on the crystallization temperature. In all cases, and according to these values, an instantaneous nucleation is suggested.
- According to the thermodynamics of the studied systems, the chain folding energy for the PP crystallization decreases at low LDPE percentages in the blend. However, the energy requirements for the PP chain folding increases at LDPE percentages above 10% due to the obstruction created by the LDPE aggregates that are present in the blend.

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