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Crystallization kinetics of polypropylene III. Ternary composites based on polypropylene/low density polyethylene blend matrices and short glass fibres

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The effect of, simultaneously, both short glass fibres (SGF) and low density polyethylene (LDPE), on PP crystallization kinetics and thermodynamics has been investigated. Glass fibres tend to initially compensate the delaying effect of LDPE on the PP crystallization as is shown by the values of the crystallization half time, $\tau_{1/2}$, as well as by the overall crystallization rate, K_n. However, at high glass fibre percentages in the composite (30–40%) a considerable increase of $\tau_{1/2}$ values is observed although they remain always below the corresponding values of the plain polymer. The isothermal radial growth rate of PP spherulites is hardly affected by both the fibres and the LDPE. According to the values of the Avrami exponents, it can be established that the spherulitic development arises from an athermal, instantaneous and heterogeneous nucleation with two-directional diffusion controlled growth. No transcrystallinity has been observed. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The microstructure of crystallizable polymer matrices plays a very important role in thermoplastic composite characteristics. The solidification of semicrystalline polymers, such as PP, from the melt takes place through nucleation and crystal growth, and when the process of solidification is completed, the entire volume of material is full of spherulites.

The spherulitic limits are microstructural discontinuities that can modify the properties of the material. So, comprehension of the crystallization kinetics is very important and useful to predict the most appropriate moulding conditions and to correlate the developed microstructure with the kinetics of transformation.

In composites, this situation is further complicated by the influence of the reinforcing fibres on the morphology of the matrix that arises from the nucleating effect of the fibres. When this nucleating effect on the fibre surface is very strong, the development of the spherulites is constrained to the normal direction of the fibre surface. This effect is known as transcrystallinity, and it was observed in polyetheretherketone/carbon fibre composites[1] that this phenomenon gives rise to a considerable increase of the normal tensile strength and toughness of these materials.

In order to analyze the crystalline morphology of the PP in short glass fibre reinforced composites based on PP/LDPE blends, previous studies were carried out to investigate the effect of LDPE[2] and glass fibres[3] on the crystallization kinetics of PP. In fact, due to the improvement of the impact behaviour through its blending with LDPE, and the increase of PP strength and stiffness by the incorporation of short glass fibres, many papers have been published on the crystalline morphology of the PP in their LDPE binary blends or glass fibre composites. However, there are not many studies devoted to investigate the microstructure and crystallinity of semicrystalline polymers in ternary compositions. The heterogeneous nucleation of various blend systems based on short glass fibre reinforced composites and poly(butylene terephthalate)/high density polyethylene/ionomer polymer blends has been analyzed by Joshi *et al*.[4] but only the glass fibre percentage was varied. Jancar and Dibenedetto[5] have investigated the effect of phase morphology on the tensile yield strength of PP/ethylene–propylene elastomer blends filled with inorganic filler, mainly focussing on the filler–PP and filler–elastomer adhesion.

The present study tries to analyze the combined effect of LDPE and glass fibres on the PP crystallization. LDPE percentages above 10% give rise to a marked increase of the half time of PP crystallization; however an opposite effect is produced by glass fibres, and high fibre contents (above 30%) in the composite cause a very noticeable decrease of the PP spherulite size. These effects have an influence on the composite behaviour and must be considered when the material is being processed.

EXPERIMENTAL

Isotactic polypropylene, iPP, (melt flow index 2.9 g min^{-1}, at 190°C and 5 kg, and density 0.905 g cm^{-3}) and low density polyethylene, LDPE, (melt flow index 6.7 g min^{-1},

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at 190°C and 2.16 kg, and density 0.916 g cm^{-3}), supplied by Repsol Química S. A. Madrid (Spain), under the trade names Isplen PP-051 and Alkathene-017, respectively, and 6 mm length chopped strands of E glass fibres (SGF), Grade E-11, supplied by Cristaleria Española S. A. Alcala de Henares, Madrid (Spain), were used in the present study.

The compounding was carried out in a hot-roll mill, at 180°C, and for a period of time of 15 min. Once the PP was melted, the appropriate percentages of LDPE and short glass fibres (SGF) were added. The obtained compounds were compression moulded at 200°C in a Collins press. From the moulded plaques, samples were taken for the crystallization study. The composition of the composites and the temperatures of crystallization that have been used in this study are shown in *Tables 1* and *2*.

The morphology of the PP matrix was studied on thin films by using an optical polarizing microscope—a Leika Metalographic Aristomet model, with a Mettler FP-90 automatic hot-stage thermal control. Composite samples were sandwiched between microscope cover glasses, melted at 200°C for 10 min and then rapidly cooled to the crystallization temperature. The PP spherulitic growth was observed by taking photomicrographs at appropriate intervals of time.

Table 1 Kinetic parameters of the studied composites

PP/LDPE/SGF (wt %)	T_c (K)	$-\log K_n$ (min)	n	$\tau_{1/2}$ (s)
95/5/0	398	1.11	2.76	133
	403	2.74	3.07	415
	405	3.16	3.01	594
	408	4.36	3.04	1441
95/5/10	398	0.48	2.31	82
	403	1.88	2.90	236
	405	3.20	3.10	578
	408	3.70	3.17	790
95/5/20	398	0.69	2.44	99
	403	2.17	2.88	301
	405	3.45	3.05	720
	408	3.96	3.10	1015
95/5/30	398	0.73	2.79	96
	403	2.32	2.95	327
	405	3.60	2.99	853
	408	4.19	3.11	1189
95/5/40	398	1.01	2.44	134
	403	2.60	2.72	473
	405	3.98	2.96	1171
	408	4.31	2.83	1759

Table 2 Kinetic parameters of the studied composites

PP/LDPE/SGF (wt %)	T_c (K)	$-\log K_n$ (min)	n	$\tau_{1/2}$ (s)
90/10/0	398	1.66	2.70	217
	403	3.32	2.95	709
	405	4.01	3.03	1123
	408	6.24	3.86	2257
90/10/10	398	1.06	2.73	128
	403	2.62	3.02	392
	405	3.54	3.09	746
	408	4.37	3.11	1358
90/10/20	398	1.07	2.75	128
	403	2.64	3.04	392
	405	3.88	3.13	924
	408	4.43	3.17	1334
90/10/30	398	1.47	2.79	176
	403	3.15	2.96	614
	405	4.03	3.18	991
	408	4.68	2.95	2042
90/10/40	398	1.46	2.88	170
	403	3.04	2.97	560
	405	3.91	2.78	1344
	408	4.65	2.97	1952

The crystallization kinetics and thermal characteristics of the PP were determined in a DSC-7 Perkin–Elmer differential scanning calorimeter with the following standard procedure: the samples (about 10 mg in weight) 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 necessary time for the complete crystallization of the matrix. The heat evolved during the isothermal crystallization (H_c) was recorded as a function of time, at different crystallization temperatures. The experiments were carried out in a nitrogen atmosphere and the scans were obtained at 10 K min^{-1}. The isotherms were constructed by integrating the area under the exothermic peak. The crystallinity weight fraction was calculated through the total enthalpy method recommended by Gray[6] and Richardson[7]. In all calculations a crystal heat of fusion of 209 J/g has been taken for the polypropylene[8].

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) of the composites were obtained from the maximum of the endothermic peaks. The equilibrium melting temperatures (T_m^0) were obtained from the melting temperature *versus* crystallization temperature plots (Hoffman–Weeks plots).

The crystallization parameters of the PP, such as the crystallization kinetic constant (K_n) and the Avrami exponent (n), have been calculated from the Avrami equation[9,10]. These parameters can be used to interpret qualitatively the nucleation mechanism and morphology and overall crystallization rate of the polymer, respectively.

Finally, the crystallization thermodynamics and kinetics of the samples have been analyzed on the basis of the secondary nucleation theory of Hoffmann[11] that is expressed by the following equation:

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

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 interphase and can be calculated with high precision from the Williams–Landel–Ferry equation[12], given by the following expression:

$$\Delta F = \Delta F_{WLF} = (C_1 T_c)/(C_2 + T_c - T_g) \qquad (2)$$

where C_1 and C_2 are constants whose values are assumed to be 4.12 kCal/mol (17.24 KJ/mol) and 51.6 K, respectively. The glass transition temperature (T_g) of pure PP has been taken as 260 K. 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 Boltzmann constant, k_B, have the following values given by the literature: 5.24 Å, 11 mJ/m^2, 209 J/g, and 1.35×10^{-16} erg/mol K, respectively, it is possible to calculate the value of the free energy of folding of

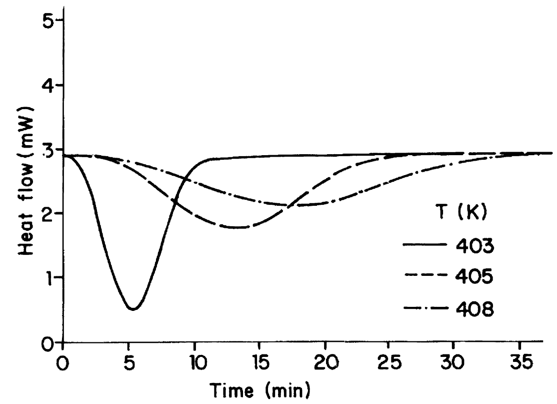

Figure 1 Effect of temperature on crystallization isotherms of a composite based on 95/5 PP/LDPE blend and 20% SGF

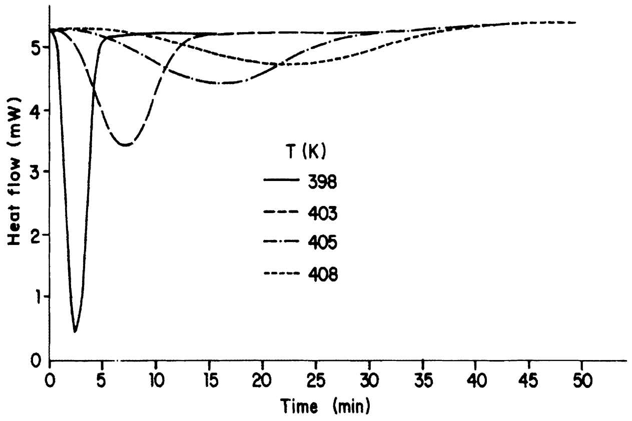

Figure 2 Effect of temperature on crystallization isotherms of a composite based on 90/10 PP/LDPE blend and 20% SGF

isotactic polypropylene lamellar crystals, σ_e, as a function of composite composition.

RESULTS AND DISCUSSION

From *Figures 1* and *2*, where the crystallization isotherms of the 20% short glass fibre filled composites based on PP/LDPE blend matrices with 5 and 10% LDPE content, respectively, at the different temperatures used in this study, are graphically represented, it is deduced that the crystallization of the PP in the composite is strongly affected by temperature. As shown in *Tables 1* and *2*, an increase of ten degrees in the crystallization temperature involves an increase of more than 10 times the half time ($\tau_{1/2}$) of PP crystallization. In all cases, $\tau_{1/2}$ increases more than 30% as the LDPE percentage in the polymer matrix increases from 5 to 10%. In fact, the delaying effect of LDPE on the PP crystallization was previously observed by the authors in PP/LDPE blends[2]. However, in that case this effect was more sensible (increments of about 60–90% in $\tau_{1/2}$) than in the presence of fibres (15–60% only) which indicates that the delaying effect of LDPE on the PP crystallization kinetics is partially compensated by the nucleating effect of glass fibres. In general, and at low percentages, the glass fibres act as a nucleating agent. However, at high fibre percentages, the half time of PP crystallization increases, this effect being more noticeable at lower undercooling temperatures. The combined effect of both high LDPE and glass fibres contents is very noticeable on the crystallization delay of PP although it is always below the $\tau_{1/2}$ value of PP in the plain polymer. It looks like the nucleating effect of glass fibres is partially compensated, at very high fibre percentages, by a restriction of the folding of the polypropylene chains.

The composite composition affects the PP crystallization as shown in *Figures 3* and *4*, where the crystallization isotherms of the composites based on 95/5 and 90/10 PP/LDPE blend matrices, respectively, with different fibre contents, are represented at 403 K. From these figures it is deduced that, in general, the primary crystallization of PP in the composites is almost completed before the crystallization of the plain polymer had reached 50–70% of crystallization conversion. An exception to this behaviour is observed in composites with very high glass fibre content (30 and 40%).

As can be deduced from *Tables 1* and *2*, in the unreinforced matrices, the half time of PP crystallization increases as the LDPE percentage in the matrix increases from 5 to 10%. When glass fibres are added to the polymer blend, a decrease of $\tau_{1/2}$ is observed at first. However, in all cases, $\tau_{1/2}$ tends to increase at fibre glass percentages above 20% in the composites. The half time of PP crystallization

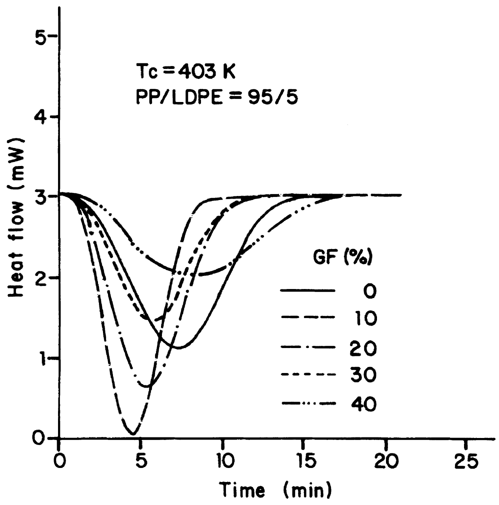

Figure 3 Effect of glass fibre percentage on the PP crystallization isotherms at 403 K, in a polymer matrix based on a 95/5 PP/LDPE blend

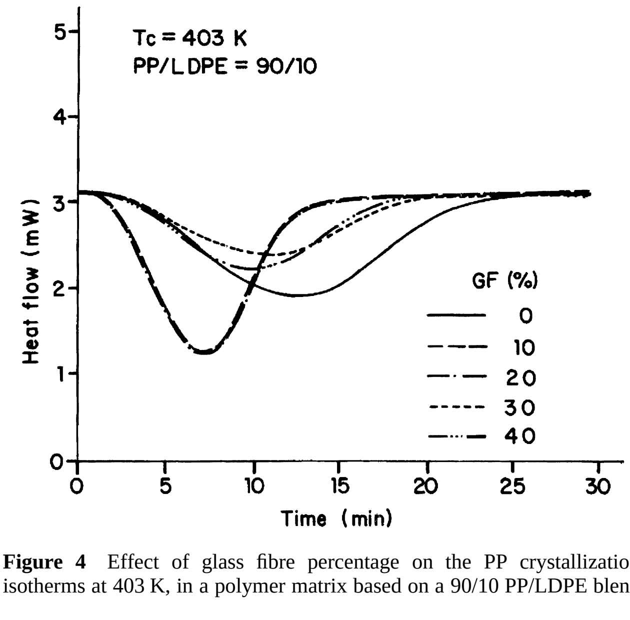

Figure 4 Effect of glass fibre percentage on the PP crystallization isotherms at 403 K, in a polymer matrix based on a 90/10 PP/LDPE blend

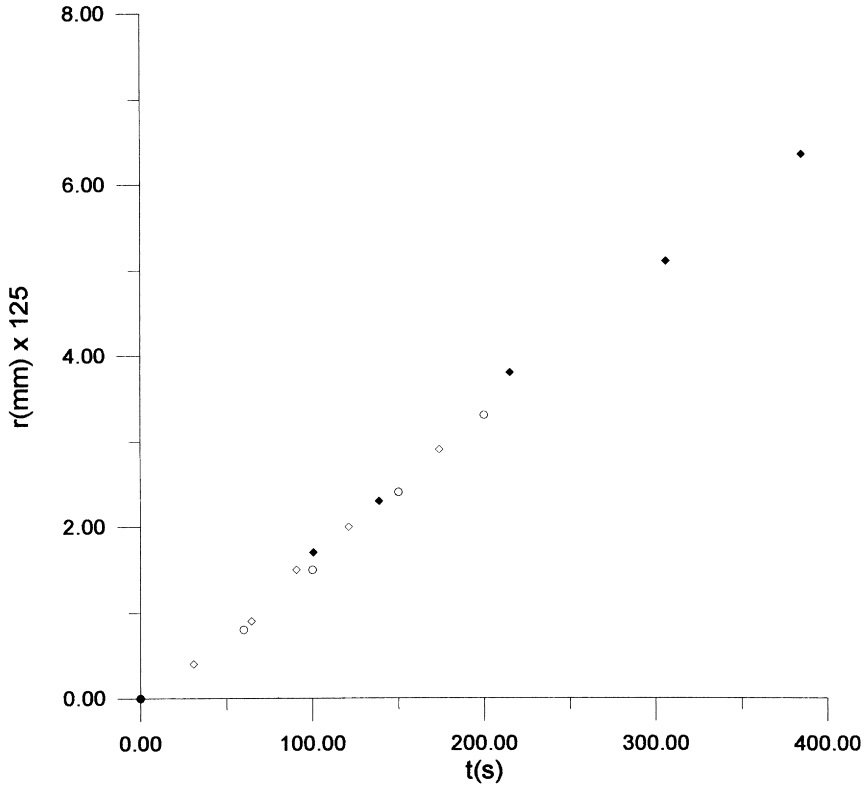

Figure 5 Spherulitic growth rate of polypropylene at 403 K in the plain polymer (○) and in a polymer matrix based on 95/5 PP/LDPE blend (□) and 90/10 (■) in the presence of fibres (×125)

is, in general, more affected by the crystallization temperature than by either the blend matrix composition or glass fibre content in the composite, with a noticeable increase at T_c above 403 K.

Kinetic data for the PP/LDPE/glass fibre composites were obtained from the Avrami plots. The values of the kinetic constant of crystallization, K_n, the Avrami exponent, n, and the half-time of crystallization, $\tau_{1/2}$, as calculated from the Avrami plots are compiled in *Tables 1* and *2*. With increasing isothermal crystallization temperature, the Avrami exponent slightly increases while the intercept log K_n decreases and consequently $\tau_{1/2}$ increases.

The Avrami exponents are between 2 and 3 over the crystallization temperature range studied. According to these values, it can be established that the spherulitic development arises from an athermal, instantaneous and heterogeneous nucleation with two-directional diffusion controlled growth as deduced from the fractional values of n. At the same T_c the Avrami exponent hardly varies with both glass fibre content in the composite and blend matrix composition, at least in the range of blend ratios investigated.

At any crystallization temperature, the kinetic constant of the PP shows a sharp increment when 10% of glass fibres is added to the blend matrix. However, above this percentage the value of K_n tends to decrease as fibre content in the composite increases, although in all cases the kinetic constant is higher in the composites than in the plain polymer. It looks like the nucleating effect of the fibres is partially compensated, at fibre contents above 20% in the composite, by the restrictions they create on the mobility of PP segments. In the absence of LDPE a minimum in the K_n value was obtained at 20% glass fibre content in the composite, so it can be suggested that low percentages of LDPE (5%) contribute (with an additive effect) to the decrease of the PP crystallization rate. The same results are obtained with 10% LDPE content in the blend matrix.

The isothermal radial growth rate of PP spherulites, at 403 K, is hardly affected by both the fibres and the LDPE, as can be deduced from *Figure 5* where the PP spherulitic radius *versus* time is graphically represented. The radial growth rates of PP spherulites were 7.8, 7.5, 7.9 μm/min (less than 2% of error) for the plain polymer, and ternary composites with 5 and 10% LDPE, respectively. When the crystallization of the PP is completed, separated domains of LDPE were observed at both LDPE concentrations studied as shown in *Figures 6* and *7*. However, at LDPE concentrations below 10% in the blend, these domains mainly remain out of the PP spherulitic limits and were in the interspherulitic contact regions (*Figure 6c*), but at 10% LDPE content in the blend matrix the LDPE domains were in both inter and intraspherulitic regions of the PP (*Figure 7c*). This effect gives rise to a decrease of the PP overall rate of crystallization, as is confirmed by the increase of the half times of PP crystallization ($\tau_{1/2}$) in all the composites when the LDPE percentage in the matrix composition goes from 5 to 10%.

The melting temperatures of PP in the isothermally crystallized composites were determined from the maxima of the fusion peaks obtained by heating the samples directly from T_c, at a heating rate of 10 K min^{-1}. The melting temperatures are compiled in *Tables 3* and *4*. From these Tables it is deduced that the melting temperature of the PP increases as the undercooling decreases or crystallization temperature increases which is directly related with the size of the PP crystals. At low fibre percentages (10%) an increase of T_m is observed which can be related with an increase of the crystallinity and the formation of more perfect crystals. At high fibre percentages the overall crystallization process is delayed and the crystals are

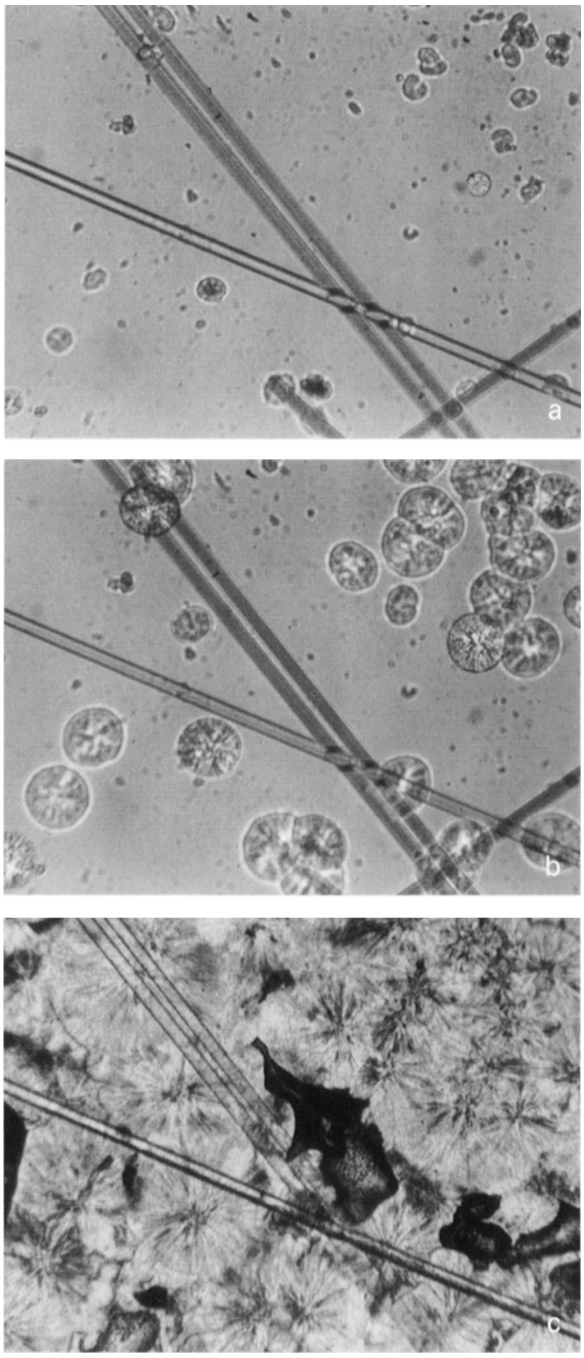

Figure 6 Micrographs of polypropylene crystallization in the presence of SGF, in a matrix based on 95/5 PP/LDPE blend, at 403 K (×125)

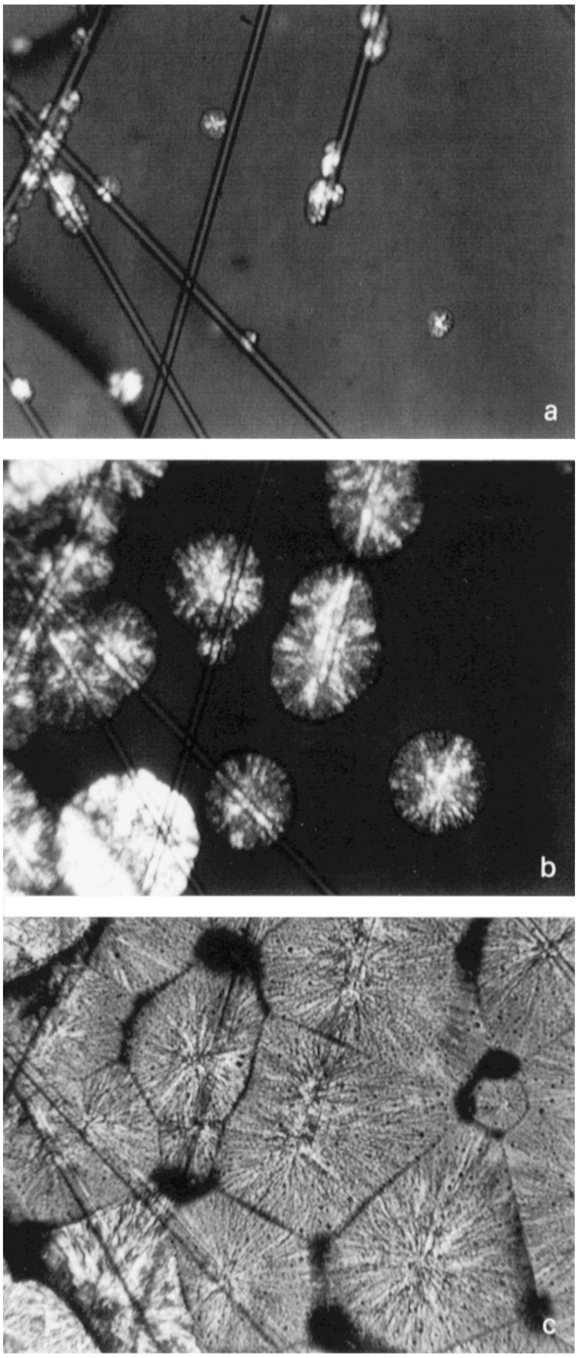

Figure 7 Micrographs of polypropylene crystallization in the presence of SGF, in a matrix based on 90/10 PP/LDPE blend, at 403 K

smaller and less perfect, which is confirmed by the decrease of T_m—this effect being more noticeable as fibre percentage in the composite increases. The differences among the T_m values are less noticeable in the presence of 10% LDPE in the composite, which is attributed to a diluent effect of LDPE neutralizing the effect of fibres.

The crystallization thermodynamics of PP in the melt have been calculated through the secondary nucleation theory and the obtained values of the chain folding energy (σ_c) compiled in *Tables 3* and *4*. As can be seen, at low LDPE percentages (5%) in the matrix, the PP chain folding energy decreases as fibre content in the composite increases. However, in the presence of 10% LDPE, a maximum in σ_c is obtained at 20% fibre content in the composite and it then tends to decrease as fibre percentage increases, which can be due to a diluent effect of the LDPE.

CONCLUSIONS

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

Small additions of short glass fibres to the PP/LDPE blends investigated, partially compensate the delaying effect of LDPE on the PP crystallization due to the nucleating effect of glass fibres. However, high fibre percentages (above 20%) contribute to the delaying effect of LDPE on PP crystallization.

The isothermal radial growth rate of PP spherulites is hardly affected by both the glass fibres and the LDPE. However, and as can be deduced from the decrease of T_m, the PP spherulite size decreases at high fibre percentages (above 30%) in the composite.

Table 3 Thermal and thermodynamic characteristics of the composites (PP/LDPE/SGF)

	T(K)	95/5/0	95/5/10	95/5/20	95/5/30	95/5/40
T_m(K)	398	437.3	439.0	438.4	436.1	435.6
	403	439.2	441.6	440.8	438.3	437.7
	405	440.6	—	—	—	—
	408	441.9	443.3	442.3	440.8	439.8
T_m^0(K)		470.9	469.8	463.9	469.4	462.7
σ_e(erg/cm^2)		169	152	128	161	134

Table 4 Thermal and thermodynamic characteristics of the composites (PP/LDPE/SGF)

	T(K)	90/10/0	90/10/10	90/10/20	90/10/30	90/10/40
T_m(K)	398	437.6	437.1	437.2	436.2	436.3
	403	439.4	438.9	439.0	438.2	438.2
	405	440.8	—	—	439.0	438.4
	408	441.4	441.4	441.3	440.4	440.4
T_m^0(K)		463.3	466.5	465.0	462.7	460.8
σ_e(erg/cm^2)		127	142	145	130	125

No transcrystallinity growth of PP has been observed on the glass.

The Avrami exponents are between 2 and 3 over the crystallization temperature range investigated, which suggests that spherulitic development is coming from an athermal, instantaneous, and heterogeneous nucleation, with two-directional diffusion controlled growth although this growth is not constant as deduced from the fractional values of n.

At glass fibre percentages below 30% in the composite a decrease in the chain folding energy of the PP chains is observed. However, above this fibre percentage it remains almost constant as fibre content in the composite increases.

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