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Crystallization kinetics of polypropylene: II. Effect of the addition of short glass fibres

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The effect of short glass fibres on the polypropylene (PP) crystallization kinetics and thermodynamics has been investigated. Although at high fibre percentages in the composite the spherulitic limits are not clearly defined, the presence of crystalline entities is evident. A marked decrease of the half time of PP crystallization, $\tau_{1/2}$, as well as a sensible increase of the overall crystallization rate, K_n, has been observed in the presence of fibres. However, at any crystallization temperature, a maximum of $\tau_{1/2}$ is reached at 20% glass fibre content in the composite followed by a continuous decrease as fibre percentage increases. A slight increase in the Avrami exponent as temperature increases is obtained although it is relatively independent of composite composition. In all cases an instantaneous nucleation takes place, a nucleant effect of fibres is evident, and no transcrystallinity has been observed with these short glass fibres. Fibres give rise to a marked increase in the crystallinity of the samples. The chain folding energy for PP crystallization (σ_e) decreases with fibre content, and a minimum is observed at 20% fibre content. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The ultimate properties of fibre-reinforced composites based on crystallizable thermoplastics are determined in part by the crystalline morphology of the polymer matrix[1,2] which in turn depends on the rates of nucleation and crystal growth that define the crystallization kinetics. However, reinforcing fibres have the potential to modify dramatically the crystallization characteristics of a given polymer matrix. In semicrystalline thermoplastic matrix composites, the nucleation and growth of a transcrystalline interface around the reinforcing fibre is thought to have a critical influence on the improvement of the stiffness and tensile strength. However, the mechanism by which transcrystallization occurs is not fully understood. Recently, efforts have been made to characterize the effect of fibre reinforcement on the crystallization of a variety of thermoplastic polymers[3–13]. Experimental evidence confirms that fibres can influence the crystallization kinetics and morphology of the matrix, however, conclusions from separate studies are often in disagreement.

Transcrystalline growth has been reported in PP crystallized in contact with carbon and aramid fibres[14,15] and some polymeric fibres[13,14,16–19]. In general, carbon and organic fibres readily nucleate transcrystallinity, while glass fibres give rise to it only occasionally. It has been suggested that in quiescent crystallization transcrystallinity does depend on fibre type and crystallization temperature. However, application of stress at the interface between a fibre and a supercooled polymer melt results in the growth of a transcrystallized interphase, independent of fibre type and crystallization temperature[20].

The fibre material, topology and surface coating, and the matrix type and thermal history, have all been reported to affect transcrystallization in these composites to some extent[21,22]. Some authors have observed in PP composites that if fillers and fibres act as nucleating agents the crystallinity of PP increases[23]. In the case of glass fibre/PP composites it has been deduced that an increase in the fibre percentage gives rise to a decrease in the spherulite size[24,25], and an increase in the crystallinity of the sample, spherulite growth rate and melt temperature of the composite[26]. The modification of crystalline morphology promoted by fibres is of great interest and it has been the central goal of many studies[2,27,28].

Based on the above discussion, and in order to investigate the matrix morphology of composites based on PP/low density polyethylene (LDPE) blend matrices and short glass fibres, the effect of small additions of LDPE on the crystallization kinetics of PP has previously been analysed[29]. The main goal of the present study is to evaluate the kinetic parameters and thermodynamic characteristics of PP in the presence of short glass fibres. Finally, in a future paper, the effect of both glass fibres and LDPE simultaneously on the morphology of PP will be analysed.

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EXPERIMENTAL

Isotactic PP (melt flow index 2.9, at 190°C and 5 kg, and density 0.905 g cm^{-3}) supplied by Repsol Química, S.A. Madrid (Spain) under the trade name Isplen PP-051 and 6 mm length chopped strands of E glass fibres, Grade E-11, supplied by Cristaleria Española S.A., Alcalá 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 15 min. Once the polymer was melted, the appropriate percentage of fibre was added. The compounds obtained were compression moulded at 200°C in a Collins press. The composition of the composites and the temperatures of crystallization that have been used in this study are shown in *Table 1*.

The morphology of the PP matrix was studied on thin films by using an optical polarizing microscope Leika Metalographic Aristomet model, with a Mettler FP-90 automatic hot-stage thermal control. Composite samples were sandwiched between microscope cover glass, melted at 200°C for 10 min and then rapidly cooled to 130°C. The PP spherulitic growth was observed by taking photomicrographs at due intervals of time.

The crystallization kinetics and thermal characteristics of PP were determined in a DSC-7 Perkin–Elmer d.s.c. with the following standard procedure: The samples (about 10 mg of 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 time for complete crystallization of the matrix. The heat evolved during the isothermal crystallization (ΔH_c) was recorded as a function of time, at different crystallization temperatures. The experiments were carried out in 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 both Gray[30] and Richardson[31]. In all calculations a crystal heat of fusion of 209 J g^{-1} has been taken for PP[32].

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) and the crystallinity of the composites were obtained from the maximum and the area of the endothermic peaks, respectively. The equilibrium melting temperatures of the PP in the studied materials (T_m^0) were obtained from the melting temperature vs. crystallization temperature plots (Hoffman–Weeks plots).

Parameters governing the crystallization of a polymer, such as the Avrami exponent (n) and the crystallization kinetic constant (K_n), can be calculated from the Avrami equation[33,34].These parameters can be used to interpret qualitatively the nucleation mechanism and morphology and overall crystallization rate of the polymer, respectively.

Finally, the crystallization thermodynamic and kinetic of the samples have been analysed on the basis of the secondary nucleation theory of Hoffman and Lauritzen[35] which is expressed by

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

where $\Delta T = T_m^0 - T_c$, 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

Table 1 Kinetic parameters of the studied composites

PP/SGF (wt%)	T_c (K)	$-\log K_n$ (min)$^{-n}$	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
90/10	398	0.16	2.77	60
	403	1.57	3.08	172
	405	2.22	3.02	288
	408	3.41	3.29	585
80/20	398	0.69	2.67	95
	403	2.32	3.06	306
	405	2.74	3.02	430
	408	4.12	3.25	996
70/30	398	0.38	2.52	73
	403	1.76	2.56	254
	405	2.23	2.58	380
	408	3.32	2.76	842
60/40	398	0.25	2.65	65
	403	1.94	3.17	219
	405	2.36	2.98	330
	408	3.70	3.27	726

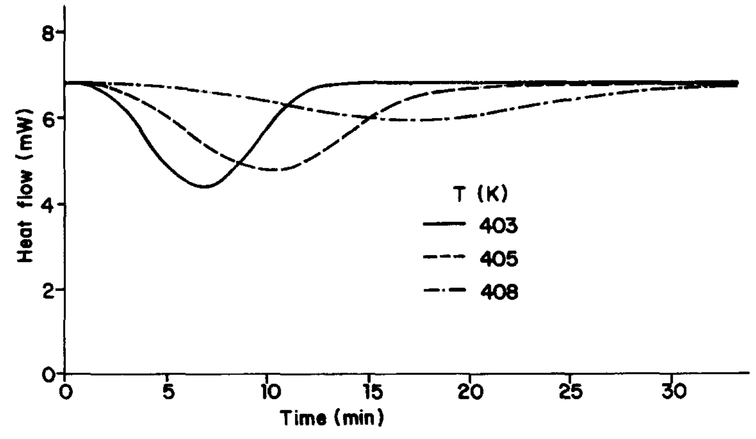

Figure 1 Effect of temperature on crystallization isotherms of a 80/20 PP/GF composite

calculated with a high precision from the Williams–Landel–Ferry equation[36], given by

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

where C_1 and C_2 are constants whose values are assumed to be 4.12 kcal mol^{-1} (17.24 kJ mol^{-1}) and 51.6 K, respectively (the T_g of pure PP has been taken as 260 K). When plotting $(1/n)\log K_n + \Delta F/2.3RT_c$ vs. $T_m/T_c\Delta T$, the value of $4b_0\sigma\sigma_e/k_B\Delta H_f$ can be calculated from the slope of the straight lines, and bearing 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^{-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 isotactic PP lamellar crystals, σ_e, as a function of composite composition.

RESULTS AND DISCUSSION

From *Figure 1*, where the crystallization isotherms of the 20% glass filled PP composite at the different temperatures used in this study are graphically represented, it can be deduced that the crystallization of PP is strongly affected by temperature. An increase of 10° in the crystallization temperature involves an increase of more than 10 times the half time of crystallization. Although less noticeable than the effect of temperature, the composite composition affects the PP crystallization as shown in *Figure 2*, where the crystallization isotherms, at 403 K, of the PP filled with different glass fibre percentages are compiled. From this figure it is deduced that the primary crystallization of PP in the composites is almost completed before the crystallization of the plain polymer has reached 50–75% of crystallization conversion. Consequently, it can be suggested that the fibres act as heterogeneous nucleation agents for PP.

Figure 3 shows the morphology of two polypropylene/glass fibre composites with different polymer/fibre ratio (A: 80/20 and B: 70/30), crystallized at the same temperature (403 K) and time (5 min). As can be deduced, the crystallization rate of the PP increases as fibre content does, which confirms that a nucleating effect of the glass fibres on the PP crystallization is evident. It could also be suggested that at fibre percentages above 20% in the composite, the PP spherulites are not well defined and their size decreases which could be attributed to restrictions created by the glass fibres on the development of a spherulitic structure.

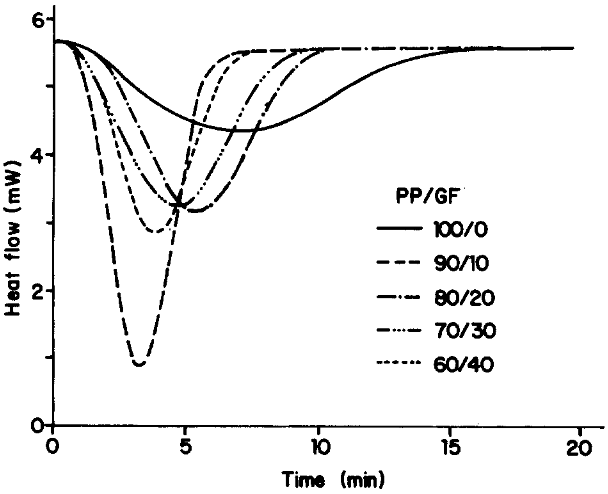

Figure 2 Effect of GF on PP crystallization isotherms, at 403 K

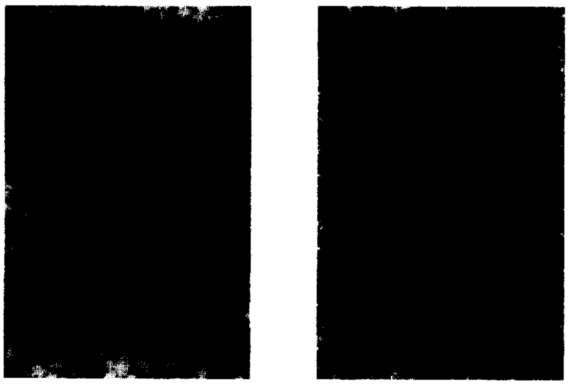

Figure 3 Morphology of PP/GF composites crystallizing at 403 K. (A) 80/20; (B) 70/30 (50×)

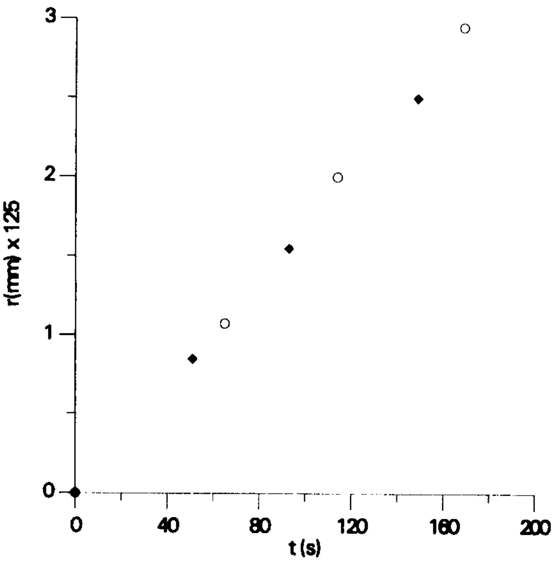

Figure 4 Spherulitic growth rate of PP at 403 K in the plain polymer (■) and in the presence of fibres (○)

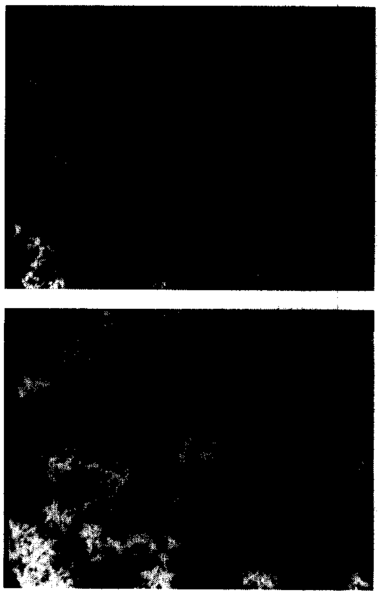

Figure 5 Micrographs of PP crystallization in the presence of 10% GF at 403 K. (A) 2 min; (B) 3.5 min (125×)

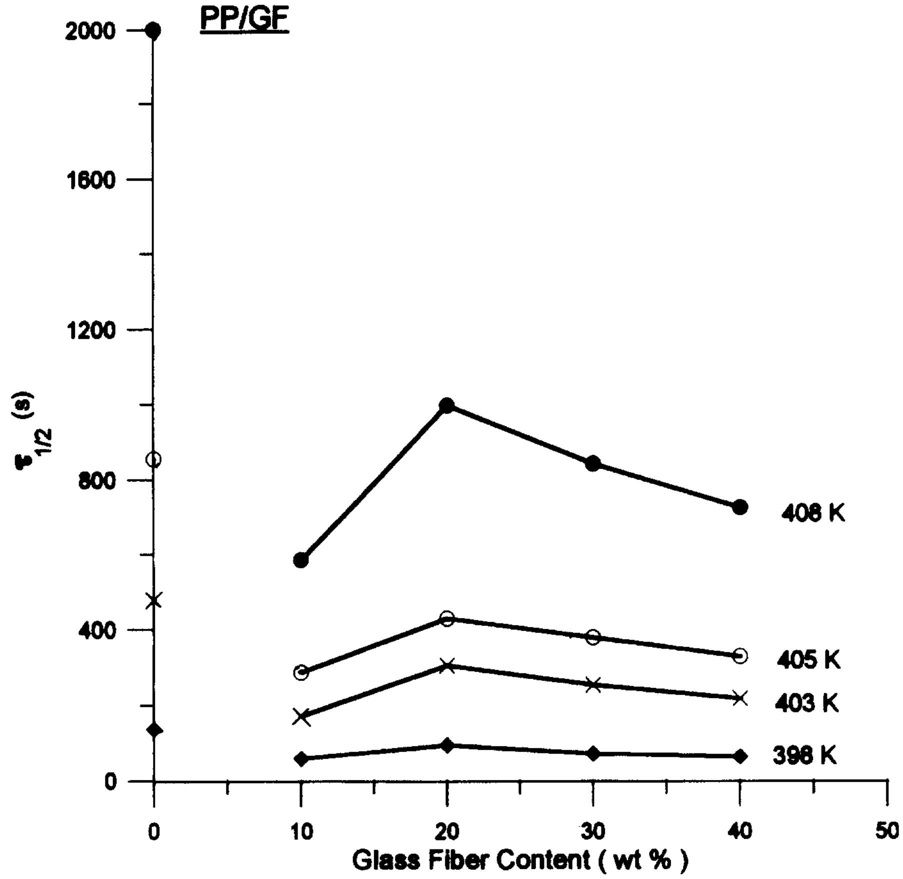

Figure 6 Effect of glass fibre content on the half time of PP crystallization ($\tau_{1/2}$) at different crystallization temperatures

In fact, these characteristics were previously stated by the authors[24]. From *Figure 4* it is deduced that the radial growth rate of the PP spherulites in the presence of glass fibres is the same as that in the plain polymer. The isothermal radial growth rate, G, was measured at 403 K and calculated by the expression $G = \mathrm{d}R/\mathrm{d}t$. In our case, no transcrystalline growth of PP crystals has been observed on the glass fibres as can be deduced from *Figure 5*.

The half times of PP crystallization ($\tau_{1/2}$) in the studied

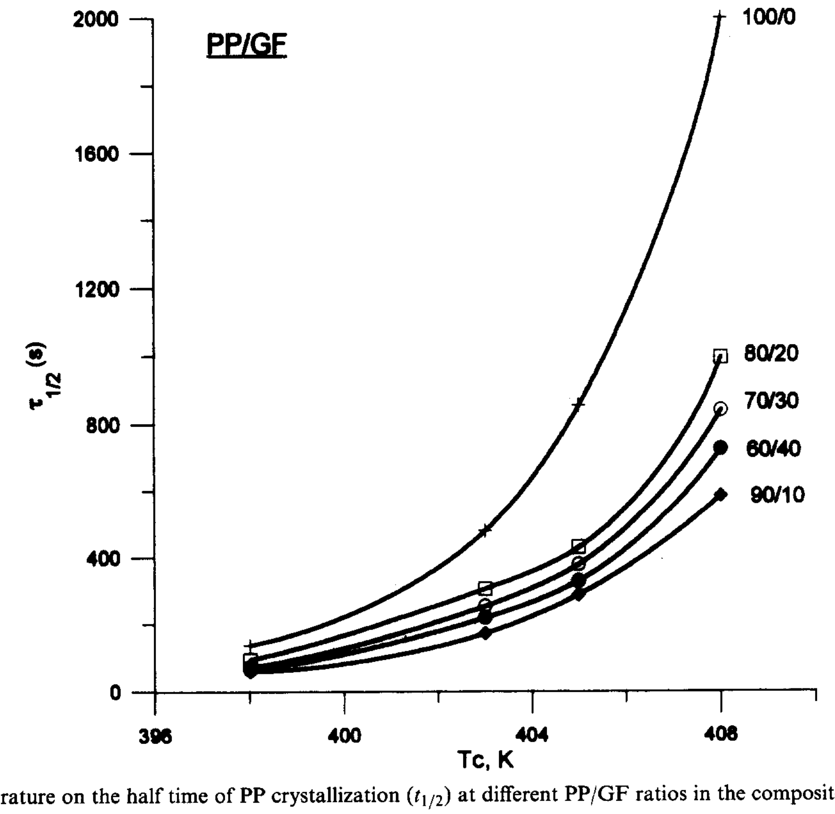

Figure 7 Effect of temperature on the half time of PP crystallization ($t_{1/2}$) at different PP/GF ratios in the composite

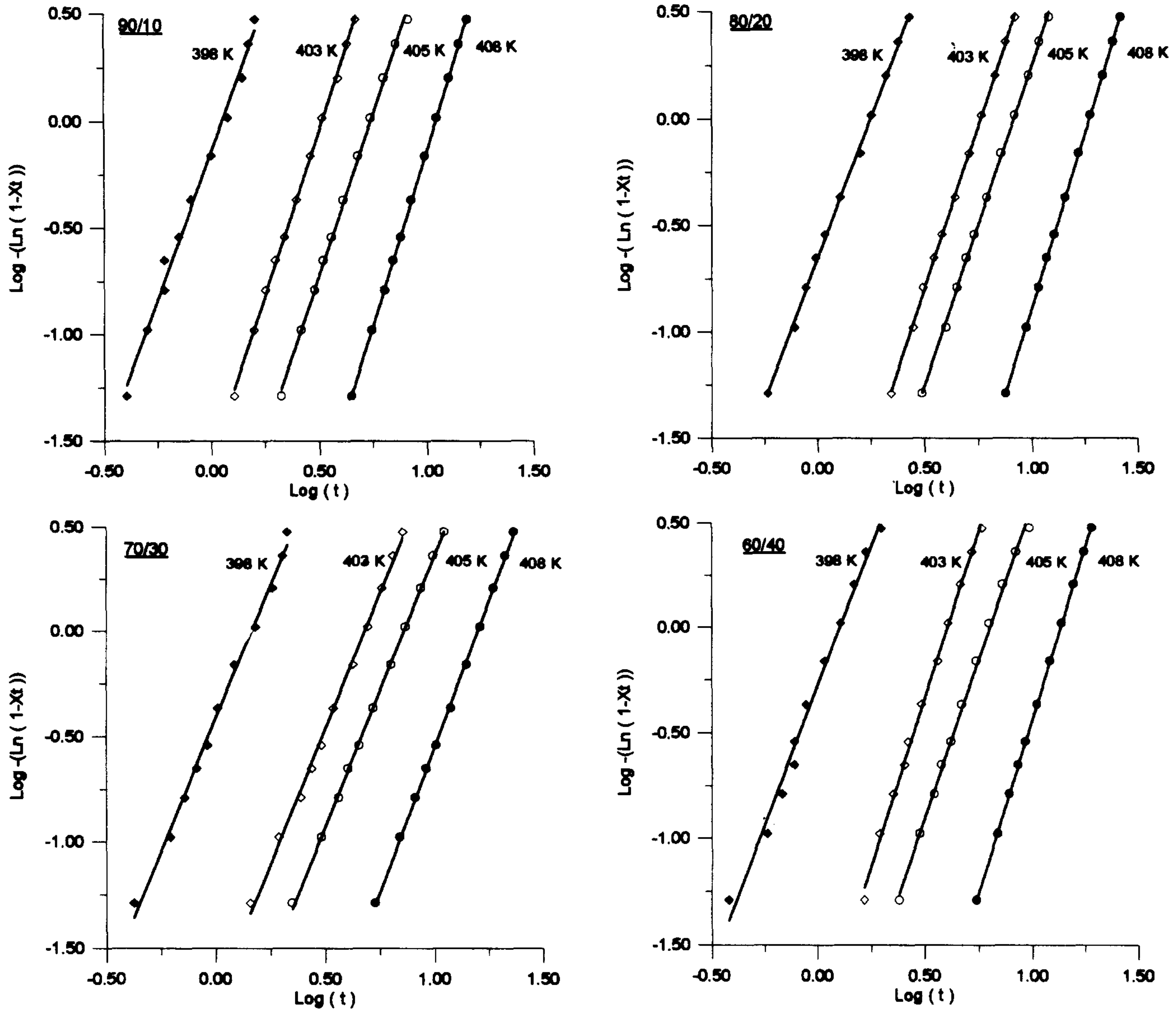

Figure 8 Avrami plots of PP/GF composites at different crystallization temperatures

composites are compiled in *Table 1*. In all cases, the composites show a very noticeable decrease in $\tau_{1/2}$ as compared with the plain polymer which is attributed to a nucleant effect of glass fibres on PP crystallization. When plotting the half time of PP crystallization vs. the glass fibre content (*Figure 6*), a maximum is observed at 20% glass fibre content in the composite which could be due to restrictions caused by the fibres on the mobility of PP segments. At higher fibre percentages (above 20%) this effect is overcome by the nucleant capability of the fibres. Finally, both effects compensate each other and small variations of the half time of PP crystallization are observed. $\tau_{1/2}$ is more affected by the crystallization temperature than by fibre content, as can be seen in *Figure 7*, and, in all cases, the curves follow the same tendency, with a noticeable increase of the slope at above 403 K.

A semiquantitative analysis of the time dependence of the isothermal crystallization process can be obtained by using the Avrami equation in its logarithmic form. From these plots (*Figure 8*) the Avrami parameter, n, and the kinetic constant, K_n, have been calculated. These values are compiled in *Table 1*. In all cases fractional values of n were obtained. For the simplified Avrami theory, integral values of n are required. However, fractional values of n have been theoretically accounted in the general statistical Avrami theory of crystallization, assuming a partial time of overlapping of primary nucleation and crystal growth[37]. Fractional values of n may be expected if certain constraints are imposed such as diffusion controlled growth.

As can be deduced from *Table 1*, the Avrami exponent normally increases as crystallization temperature increases and shows a slight increase in the composites as compared with bulk PP. However, it remains almost constant and hardly varies as fibre content increases. According to the obtained values of n (about three), it can be established that the spherulitic development is coming from an athermal and instantaneous nucleation, although the growth is not constant as deduced from the fractional values of n. These values ($2 < n < 3$) suggest an heterogeneous nucleation with two-directional diffusion controlled growth.

A noticeable increase in the kinetic constant K_n of PP crystallization is obtained when a 10% short glass fibre is added to PP. In all cases the kinetic constant is higher in the composites which suggest that a nucleant effect of the fibre is evident. It is expected that increased growth,

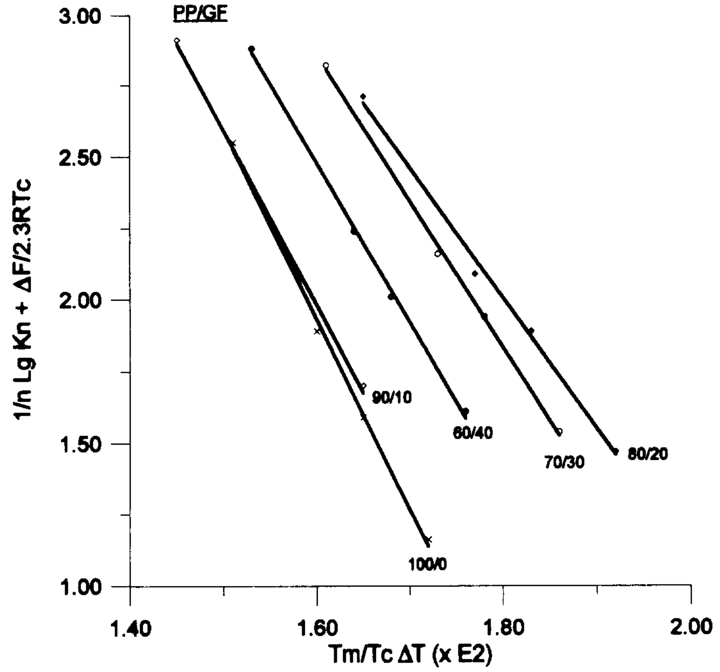

Figure 9 Plots of equation (3) for pure PP and for PP crystallized from glass fibre composites of different composition

Table 2 Thermal and thermodynamic characteristics of the composites

	T(K)	100/0	90/10	80/20	70/30	60/40
T_m(K)	398	438	437.5	438.1	437.6	436.4
	403	440	439.9	439.5	439.2	438.5
	405	441.2	440.3	441.1	440.3	439.7
	408	442.5	442.4	441.9	441.8	441
T_m^0(K)		471.1	473.9	464.5	466.1	469.4
% Crystall.	398	34.6	41.5	39.9	41.7	40.3
	403	36.7	42.9	41.8	46.3	43.9
	405	37.5	50.7	44.3	55.5	49.3
	408	—	46.6	45.7	48	46.3
σ_e (erg cm^{-2})		186	171.6	128	143.8	156.2

nucleated to start at time zero, would speed up the kinetics. However, a minimum is observed at 20% fibre content in the composite. Above this percentage the value of K_n slightly increases and remains almost constant at fibre percentages above 30%. In fact the behaviour of the kinetic constant is similar to that of the half time of PP crystallization in the composites confirming that a compromise between the nucleating effect of glass fibres and the restrictions caused by its own fibres on the mobility of PP segments is evident.

The melting temperatures and enthalpies of fusion of 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 heating rate of 10 K min^{-1}. The melting temperatures and crystallinity of the samples are compiled in *Table 2.*

The melt temperature of the PP increases as the supercooling decreases or crystallization temperature increases which is directly related with the size of the PP crystals. On the other hand, the size of the PP crystals decreases as fibre content in the composite increases, as is evident from the melting temperature of the composites which normally decreases with increasing fibre percentage in the material. This effect is very noticeable at fibre contents above 30% in the composite as previously shown in *Figure 3*.

Generally, the crystallinity of PP is higher in the composites than in the plain polymer, and it increases as crystallization temperature increases. The higher crystallinity of the composites can be attributed to the nucleating effect of the fibres. This effect has also been observed with several mineral fillers in PP composites[23,38].

The equilibrium PP melt temperatures T_m^0 were calculated from the Hoffman–Weeks plots. The obtained values are compiled in *Table 2*. The equilibrium PP melt temperature increases at 10% fibre content and above this fibre percentage is lower than the plain polymer although a tendency to increase as fibre content increases is observed. These values must be taken in mind with some restrictions since no ideal conditions are present in two-phase composite materials. If a comparison among the T_m^0 of the composites is made, a minimum can be observed at 20% fibre content.

The crystallization thermodynamics of PP in the melt, in the presence of fibres, have been calculated through the secondary nucleation theory [equations (1) and (2)]. The obtained values of σ_e are compiled in *Table 2*. As can be observed, the chain folding energy of PP decreases with the addition of glass fibre but it tends to increase again at about 30% fibre content in the composite, and above this fibre percentage remains almost constant. Anyway there is no explanation for the low value of σ_e in the composite with 20% glass fibre.

CONCLUSIONS

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

(a) Glass fibres affect markedly the crystallization of PP. A noticeable decrease in the half time of PP crystallization is observed by the addition of glass fibres to PP. Glass fibres have an accelerating influence on PP crystallization which leads to a

25–50% reduction in the crystallization time due to their strong nucleating effect.

(b) The isothermal radial growth rate of PP spherulites remains unchanged in the presence of glass fibres. However, the PP spherulite size shows a very noticeable decrease at fibre percentages above 30% in the composite as shown by optical microscope and deduced from the decrease of T_m as fibre percentage increases. The degree of crystallinity of the composites increases as fibre content increases which is indicating that the glass fibres act as nucleant agents.

(c) No transcrystallinity growth of PP has been observed on the glass fibre surface.

(d) The Avrami exponents are between 2.5 and 3.2 over the crystallization temperature range investigated. According to these values it can be established that spherulite development is coming from an athermal and instantaneous nucleation, although the growth is not constant as deduced from the fractional values of *n*.

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

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