Isothermal Crystallization of iPP in Model Glass-Fiber Composites

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ABSTRACT: Isothermal crystallization of iPP in model glass-fiber composites is studied by DSC, and the basic energetic parameters of crystallization are determined. Unsized untreated and thermally treated glass fibers are used in model composites to determine the role of the surface on nucleation and crystallization processes. Thermally treated glass fibers are found to exhibit a predominant nucleating effect as compared to unsized untreated ones, and the crystallization proceeds faster, resulting in lower values for the half-time of crystallization (10–120 s). The energy of formation of a nuclei of critical dimensions at a given T_c is also lower, and it decreases as the content of the fibers in the composite increases. The surface free energy of folding, $\sigma_e = 140 \times 10^{-3}$ J/m^2, was determined for iPP in the composite containing 50% glass fibers, while for pure iPP, $\sigma_e = 170 \times 10^{-3}$ J/m^2 was found. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 381–389, 1998

Key words: iPP; glass fibers; model composites; isothermal crystallization; DSC

INTRODUCTION

It is known that the presence of a solid surface (substrate) in contact with thermoplastic polymers during the crystallization from the melt generaly favors the heterogeneous nucleation[1,2] and often a growth of the transcrystalline zone.[3–5] The specific morphology of the polymer in the transcrystalline zone is expected to influence the adhesion at the interface, due to an increased nucleation density as well as the mechanical properties of the interphase due to a preferential orientation of the lamellae.[1]

Transcrystallization is possible when the energetic parameters for nucleation on the surface (substrate) are favorable as compared to the bulk of the polymer.[6,7] For iPP, transcrystallization has been observed in the presence of crystalline/semicrystalline substrates, such as carbon fibers and talc.[8,9–12] Numerous results are also reported on glass fiber/iPP composites concerning transcrystallization phenomena, many of them being conflicting. It was recently shown that the transcrystalline zone appeared only if the glass fiber is pulled out from the polymer melt or when shear stress is applied at given crystallization temperature.[8,12,13] On the other hand, although it has been found that the glass fiber increases the nucleation density,[9] the existence of a transcrystalline zone was not proved by microscopic investigations.[9,14]

This article is the second part of a study of model and bulk composites based on iPP and glass (or carbon) fibers, produced from knitted textile preforms of hybrid yarns.[15] In our previous article, the results on crystallization and fusion of textile-grade iPP, used for the processing of hybrid yarns and corresponding knitted fabrics, were reported.[16] The kinetics of crystallization of iPP in the dynamic and isothermal regime was followed by DSC, and the results were analyzed by Avrami, Ozawa, and Harnisch–Muschik methods. In this second part, the crystallization of iPP is analyzed by DSC in model

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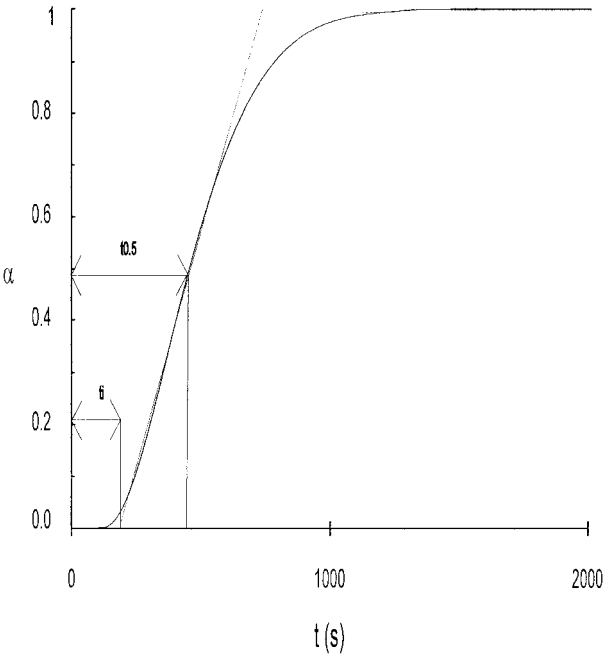

Figure 1 Schematic diagram of crystal conversion (a) versus time (t) with definition of induction time (t_i) and half-time of crystallization ($t_{0.5}$).

composites with glass fibers. When glass fibers are given thermal treatment, partial crystallization of the surface may be induced.[17] Mechanical properties of the fibers are decreased as a result of the creation of an uneven crystal structure on the surface of amorphous fibers. Energetic parameters of unsized untreated as well as thermally treated glass fibers were determined from the DSC data, in order to recognize the influence of surface treatment on the crystallization behavior and transcrystallization phenomena.

EXPERIMENTAL

Model composites were prepared by mixing chopped glass fibers (GF) with thin iPP film, previously prepared by melting the polymer at 473 K between two PTFE plates. For the preparation of the composites, untreated unsized (assignation: UGF), as well as thermally treated (assignation: TGF) glass fibers were used. Glass fibers (E-glass) (produced by OHIS, Skopje, Macedonia) with a nominal diameter of 13 μm were first treated 5 min at 573 K and then 30–120 min at 773 K. Consequently, the mechanical properties of the fibers are decreased, due to the crystallization at the surface.[17] Fiber-grade iPP with an MFI of 230°C 12–14 g/10 min (Daplen MT 55 Prespatex) was first melted to obtain a thin-film specimen and then placed into the DSC sample pan. Over the film, the chopped glass fibers are added, and the sample is rapidly heated to 478 K and the molten state held for 5 min to erase the thermal history of the polymer. Then, the sample is cooled

Table I Assignation of the Model Composites

	Content of GF (%)			
GF Assignation	0	20	30	50
TGF	iPP	CTGF2	CTGF3	CTGF5
UCF	iPP	CUGF2	CUGF3	CUGF5

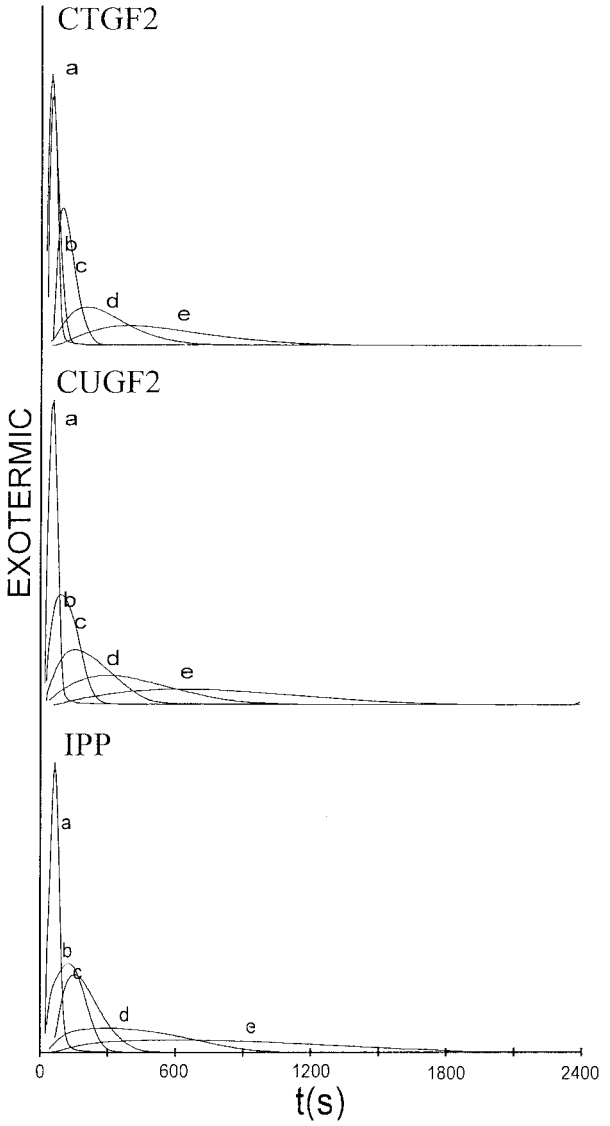

Figure 2 DSC traces of isothermal crystallization for pure iPP and model composites carried out at T_c: (a) 388 K; (b) 391 K; (c) 394 K; (d) 397 K; (e) 400 K.

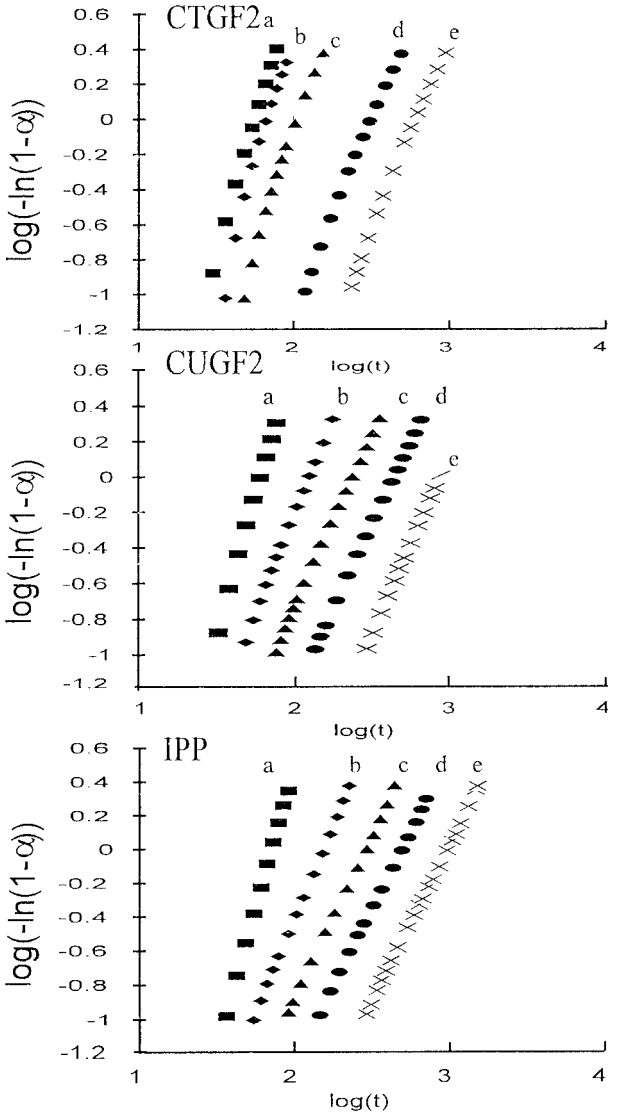

Figure 3 Avrami plots for the system shown in Figure 2.

to a given crystallization temperature (T_c) with cooling rate of 80 K/min. Isothermal crystallization is carried out at the T_c until crystallization was completed. The experiments were carried out with Perkin–Elmer DSC-7 analyzer under nitrogen, and the calibration was performed with indium and zinc. Based on the determined values for the enthalpy of crystallization, the extent of crystallization (crystal conversion), α, is calculated:

$$\alpha = \int_0^t (dH/dt)\, dt \Big/ \int_0^\infty (dH/dt)\, dt \qquad (1)$$

From the curves of α against time, the induction period (t_i)[18] as well as the half-time of crystalliza-

Table II Avrami Exponents and Overall Crystallization Rates for Pure iPP and Model Composites at Different T_c

T_c (K)	iPP		CTGF2		CTGF3		CTGF5		CUGF2		CUGF3		CUGF5	
	n	K	n	K	n	K	n	K	n	K	n	K	n	K
388	4.4	6.4×10^{-7}	3.0	4.84×10^{-6}	3.3	9.27×10^{-7}	3.1	1.73×10^{-6}	3.3	9.67×10^{-7}	3.2	1.75×10^{-6}	3.3	1.21×10^{-6}
391	2.2	1.5×10^{-5}	3.2	1.09×10^{-6}	2.4	1.25×10^{-6}	2.3	2.11×10^{-5}	2.3	1.28×10^{-5}	2.1	4.07×10^{-5}	2.4	1.43×10^{-5}
394	2.0	2.2×10^{-5}	2.6	4.92×10^{-5}	2.2	9.80×10^{-6}	2.2	1.06×10^{-5}	2.0	1.44×10^{-5}	2.0	2.79×10^{-5}	2.1	1.47×10^{-5}
397	2.0	1.3×10^{-5}	2.1	4.45×10^{-6}	2.2	2.20×10^{-6}	2.1	5.33×10^{-6}	2.0	5.55×10^{-6}	1.8	1.84×10^{-5}	2.0	2.32×10^{-6}
400	1.9	3.2×10^{-6}	2.1	1.10×10^{-6}	2.1	1.25×10^{-6}	2.1	1.43×10^{-6}	2.8	7.56×10^{-9}	2.1	1.84×10^{-5}	2.0	1.85×10^{-6}

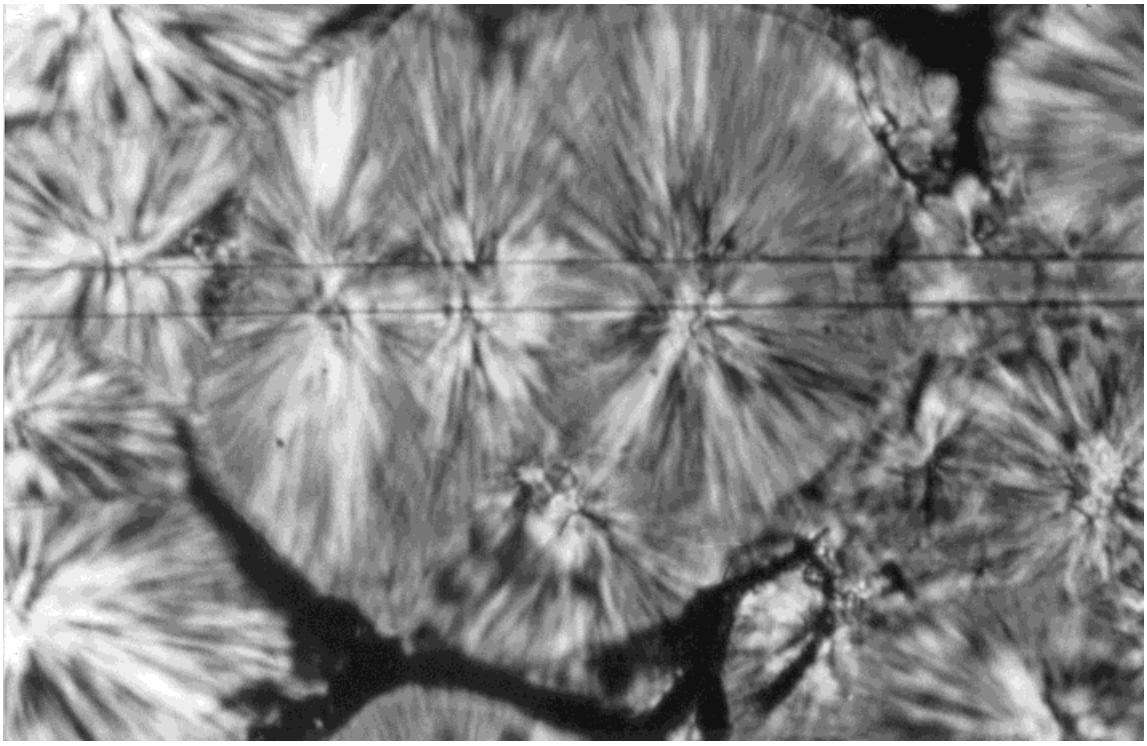

Figure 4 Polarizing optical micrograph of iPP crystallized in the presence of TGF.

tion ($t_{0.5}$) are determined as shown in Figure 1. Model iPP/glass-fiber composites were prepared with 20, 30, and 50 mass % of untreated unsized and thermally treated glass fibers, assigned as CGU and CGT, respectively, as presented in Table I.

THEORETICAL BACKGROUND

From the DSC scans (isothermal crystallization at given T_c and then melting of the crystallized sample), the equilibrium melting temperature (T_m^0) was determined by the Hoffman–Weeks method[19]:

$$T'_m = T_m^0(\gamma - 1)/\gamma + T_c/\gamma \qquad (2)$$

where γ is a constant which represents the ratio between the final thickness of the crystalline lamellae and the initial critical thickness, and T'_m is the observed melting temperature of the sample isothermally crystallized at T_c.

According to the kinetic theory of polymer crystallization,[20] assuming that the lamellar growth controlled by a process of coherent two-dimensional surface (secondary) nucleation, the temperature dependence of k is given by the relation

$$\log(k)/n = A_0 - \Delta F^*/2.3RT_c - \Delta\Phi^*/2.3KT_c \qquad (3)$$

where A_0 is a constant (with the assumption that primary nucleation density at each T_c examined does not vary with time); ΔF^*, the activation energy for the transport of crystallizing units across the liquid/solid interface; and $\Delta\Phi^*$, the energy of formation of a nucleus with critical dimensions, expressed as[20]:

$$\Delta\Phi^* = 4b_0\sigma\sigma_e T_m/\Delta H_f \Delta T \qquad (4)$$

In this equation, b_0 is the molecular thickness; σ and σ_e, the crystal growth lateral surface energy and the crystal fold surface energy, respectively; ΔH_f, the enthalpy of fusion; and $\Delta T = T_m^0 - T_c$, supercooling. ΔF^* is usually expressed as the activation energy of the viscous flow given by the Williams–Landell–Ferry relation[21]:

$$\Delta F^* = C_1 T_c/(C_2 + T_c - T_g) \qquad (5)$$

where C_1 and C_2 are constants (C_1 = 17.2 kJ/mol; C_2 = 51.5 K) and T_g is the glass transition temperature. In further calculations, the literature value of T_g = 260 K (ref. 22) was used for all model composites.

The plot $[\log(k)/n + \Delta F^*/2.3RT_c]$ versus

$T'_m/T_c\Delta T$ yields a straight line with the slope proportional to

$$4b_0\sigma\sigma_e/2.3K\Delta H_f \quad (6)$$

from which $\Delta\Phi^*$ and σ_e are obtained assuming that $b_0 = 0.525$ nm,[22] $\Delta H_f = 209$ kJ/kg,[23] and $\sigma = 0.1b_0H_f$.

The $T^0_m = f(T'_m)$ relation is given by the Gibbs–Thompson equation[24,25]:

$$T'_m = T^0_m[1 - (2\sigma_e/\Delta H_u l)] \quad (7)$$

where l represents the lamellar thickness and ΔH_u is the heat of fusion per unit volume of the polymer with 100% crystallinity ($\Delta H_u = 1.99 \times 10^8$ J/m^3).

The thickness of the critical crystal's coherent two-dimensional nucleus is given as[24]

$$l^* = 2\sigma_e/\Delta G_u \quad (8)$$

where ΔG_u is the difference between free energy for the polymer melt and crystal and can be approximated by $\Delta H_u\Delta T/T_m$.

RESULTS AND DISCUSSION

Based on DSC scans of isothermal crystallization (Fig. 2), crystal conversions were determined, and as evidenced from Figure 3, the plot $\log[-\ln(1-\alpha)]$ versus $\log(t)$ yields a straight line, indicating that the kinetics of crystallization follows the Avrami equation[26]:

$$\log[-\ln(1-\alpha)] = \log(k) + n\log(t) \quad (9)$$

The rate constant k and the Avrami exponent n were determined and the values are reported in Table II. A tendency of decreasing values of n with increasing T_c is found in the investigated interval of T_c. Also, at a constant but higher supercooling ($T_c = 388$ K and $T_c = 391$ K), the n value decreases with increasing glass fiber content. Transcrystallization was not observed in the vicinity of the fiber surface during the crystallization of iPP from the melt (Fig. 4).

DSC melting curves of the isothermally crystallized samples are shown in Figure 5. The equilibrium melting temperature of iPP in the composites is determined by the Hoffman–Weeks method, using the values of the maxima of low-temperature melting peaks. The value of $T^0_m = 457$ K is obtained and is close to the values presented for iPP in the literature.[27] It can be noticed from Table III that T^0_m decreases and the γ constant increases as the content of glass fibers in the model composites increase.

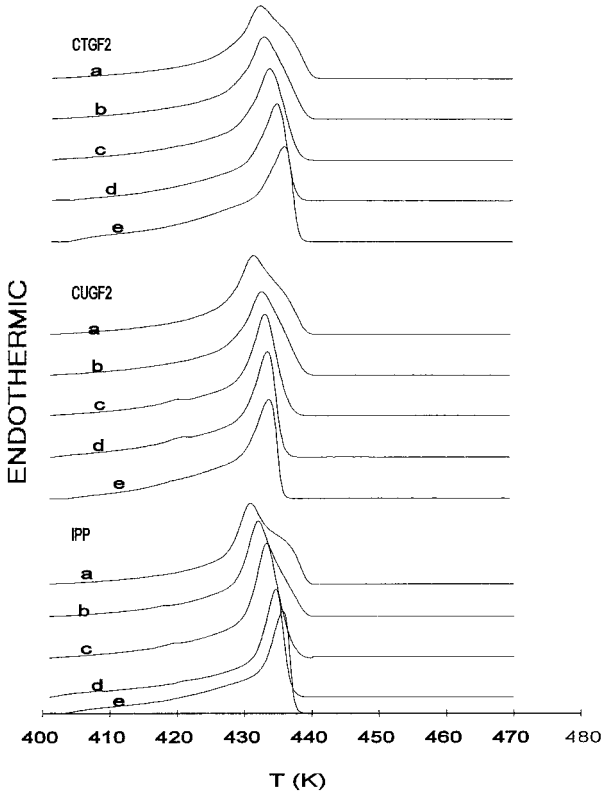

Figure 5 DSC melting curves (heating rate: 10 K/min) of pure iPP and iPP in model composites after isothermal crystallization carried out at different temperatures—T_c: (a) 388 K; (b) 391 K; (c) 394 K; (d) 397 K; (e) 400 K.

Different values for σ_e are determined for model composites containing 20–0.50% mass glass fibers, ranging from 140 to 173 $\times 10^{-3}$ J/m^2, lower than $\sigma_e = 178 \times 10^{-3}$ J/m^2 determined for pure iPP. Data for σ_e of iPP reported in the literature range from 40×10^{-3} J/m^2 (ref. 28) to 230×10^{-3} J/m^2,[29] and the differences are usually related to different values of the constants used, including T^0_m.

Figures 6 and 7 show the induction time, which at a given T_c is defined as time for the formation of the equilibrium nucleus with critical dimensions[18] against the glass fiber content. t_i decreases as the fiber content increases, and this tendency also appears to be dependent on the thermal treatment of the fibers. At constant T_c, t_i is lower for the composites containing treated as compared to unsized untreated glass fibers.

Table III Equilibrium Melting Temperature, Surface Free Energy of Folding, and γ Constants for Pure i-PP and Model Composites

	CTGF				CUGF			
GF (%)	T_m (K)	$\sigma_e \times 10^3$ (J/m^2)	γ	*γ	T_m (K)	$\sigma_e \times 10^3$ (J/m^2)	γ	*γ
0	457.13	178	2.67	2.70	457.13	178	2.67	2.70
20	451.60	147	3.24	3.30	453.77	157	2.94	2.98
30	454.30	158	3.06	3.10	456.87	172	2.70	2.73
50	451.24	140	3.36	3.42	453.42	151	3.26	3.29

* γ = l/*l.

The crystallization rate constant depends on the half-time of crystallization and the overall crystallinity[30]:

$$k = \ln 2/t_{0.5}n \quad (10)$$

and is also related to the nucleation density (N) and spherulite growth rate[19]:

$$k = 4\pi\rho_c G^3 N/3\rho_a(1 - \alpha_\infty) \quad (11)$$

$$N = N_0 \exp(-\Delta\Phi/2.3KT + \Delta F/2.3RT) \quad (12)$$

In our previous examinations based on polarizing optical microscopy[31] it was shown that the spherulitic growth rate is practically unchanged and similar for iPP and the model composites. In the temperature range investigated (T_c = 389–409 K), the values of 0.5–4.7 μm/min for G were determined and are constant at a given T_c. The half-time of crystallization $t_{0.5}$ for iPP and the model composites as a function of T_c and the glass fiber content is shown in Figures 8 and 9, respectively. The values of $t_{0.5}$ for composites containing treated glass fibers are lower than for pure iPP and the composites with untreated glass fibers for

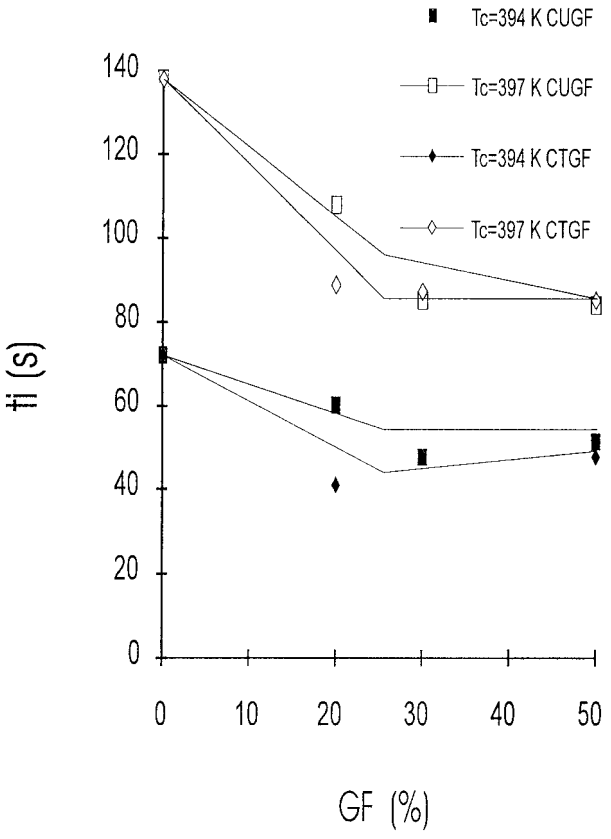

Figure 6 Induction time versus glass-fiber content.

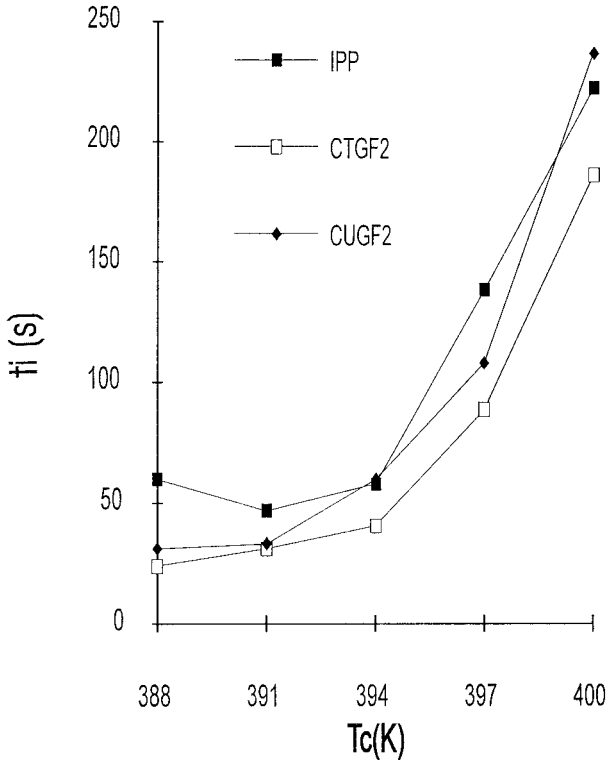

Figure 7 Induction time of crystallization versus T_c.

a given T_c. Also, $t_{0.5}$ for a given T_c decreases with an increase of the glass fiber content, which is in agreement with eqs. (10) and (11): $t_{0.5}$ decreases (k increase) as the nucleation density increases if G is approximately constant.[9] The observed differences between the composites containing untreated and treated glass fibers might be attributed obviously to the predominant nucleating effect of treated fibers. A similar trend is found for t_i, thus pointing out that the overall kinetic rate constant k depends on the rate of nucleation.

The energy of formation of a nucleus of critical dimension at given T_c is lower for the composites compared to pure iPP and decreases as the content of glass fibers in the model composites increases (Figs. 10 and 11). The effect of the fiber's thermal treatment is again evident, since in the case of treated fibers, the lowest values of $\Delta\Phi^*$ are obtained at each T_c and each W_{gf}.

The values for critical thickness l^* against T_c are shown in Figure 12. Based on these results, a conclusion can be derived that better thermodynamic conditions are reached when treated fibers

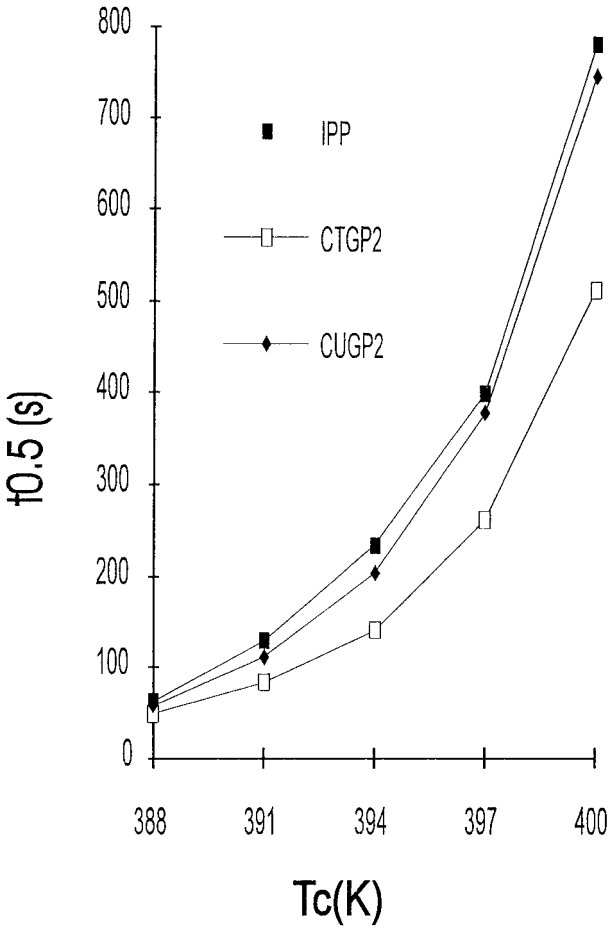

Figure 8 Half-time of crystallization versus T_c.

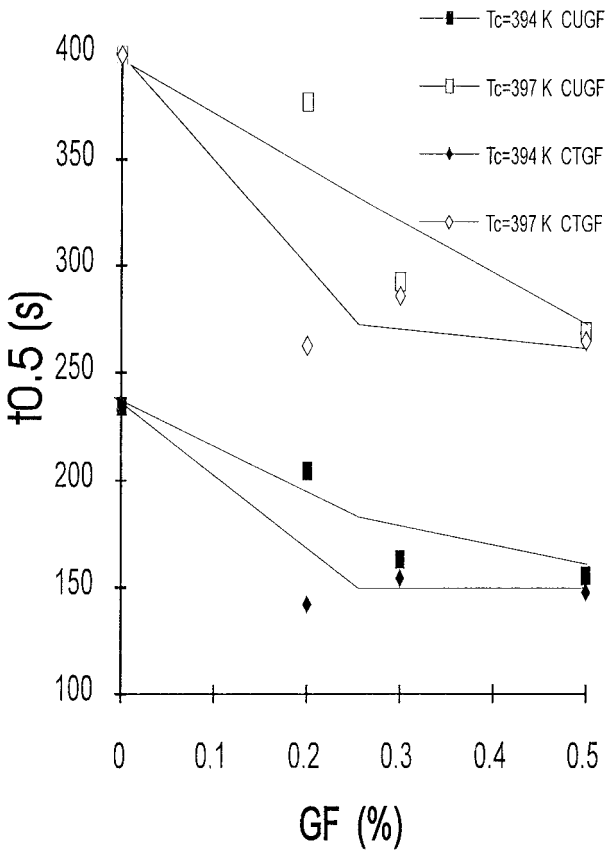

Figure 9 Half-time of crystallization versus glass-fiber content.

are used for the preparation of model composites. The results for γ determined by the Hoffman–Weeks method and from eqs. (7) and (8) (γ^*) are summarized in Table III. The differences between γ and γ^* are within 10^{-2}, pointing out the significance of the equations used for calculating l^*.

CONCLUSION

A quantitative approach based on the theory of the crystallization of polymers, enabling the determination of the basic energetic parameters of iPP/glass-fiber model composites is presented. It was shown that in the presence of glass fibers isothermal crystallization of iPP occurred faster, and the values of t_i and $t_{0.5}$ were lowest for composites containing treated fibers. During the isothermal crystallization of iPP in the presence of fibers, the crystalline lamellar thickness increased as the fiber content increased. Thermally treated glass fibers are found to exhibit a predominant nucleating effect as compared to untreated

unsized fibers. The energy of formation of a nucleus of critical dimensions at given T_c is also lower in the presence of fibers, and it decreases as the content of fibers in the composite increases. For the composites containing 50% TGF glass fibers, the value of $\sigma_e = 140 \times 10^{-3}$ J/m^2 was determined, while for the pure iPP matrix, σ_e is 178 $\times 10^{-3}$ J/m^2.

NOMENCLATURE LIST OF SYMBOLS

T_m^0	equilibrium melting temperature
T'_m	observed melting temperature of the sample
T_g	the glass transition temperature
ΔT	supercooling
t_i	incubation time
$t_{0.5}$	half time of crystallization
γ	constant which represents the ratio between the final thickness of the crystalline lamellae and the initial critical thickness

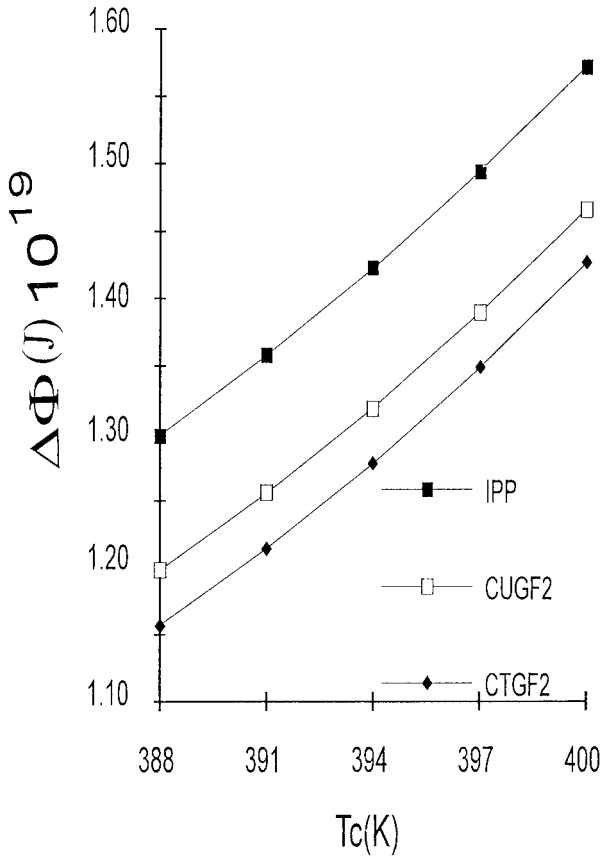

Figure 10 Energy of formation of nucleus of critical dimensions versus T_c.

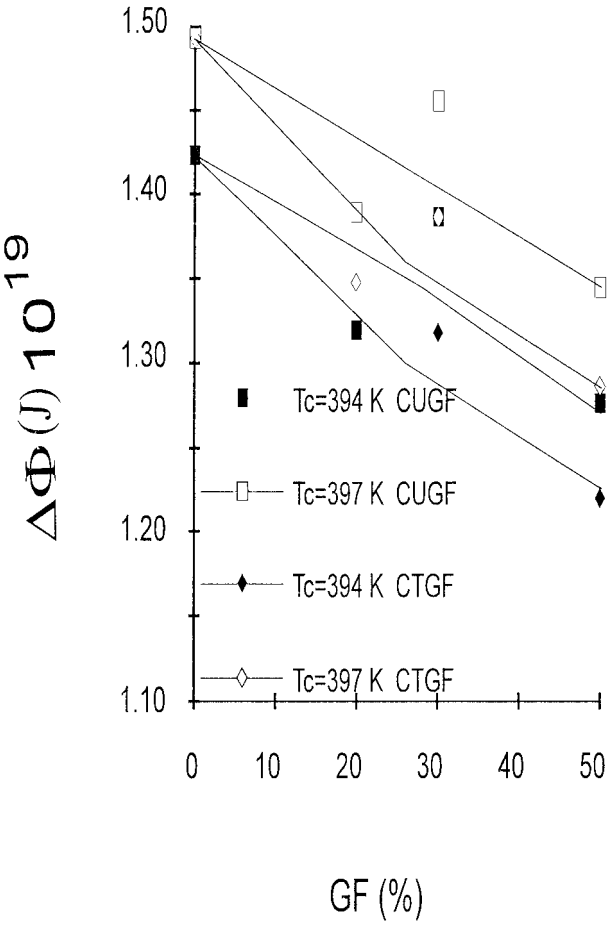

Figure 11 Energy of formation of nucleus of critical dimensions versus glass fiber content.

A_0	constant
ΔF^*	activation energy for the transport of crystallizing units across the liquid/solid interface
$\Delta\Phi^*$	energy of formation of a nucleus with critical dimensions
σ	crystal growth lateral surface energy
σ_e	crystal fold surface energy
ΔH_f	enthalpy of fusion
k	rate constant
n	Avrami coefficient
R	universal gas constant
K	Boltzman constant constant
b_0	molecular thickness
C_1 and C_2	constants
l	lamellae thickness
l^*	critical thickness of the crystal' coherent two-dimensional nucleus
ΔH_u	the heat of fusion per unit volume
ΔH_f	heat of fusion

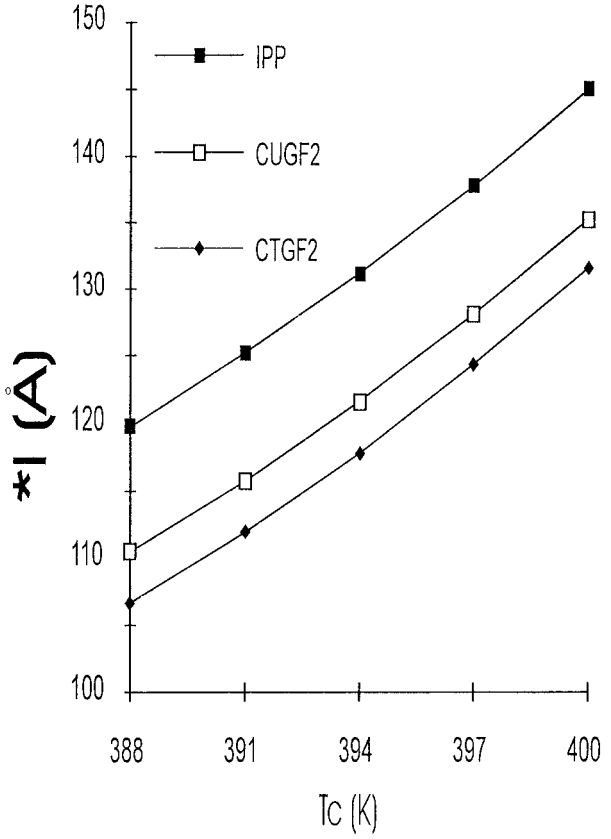

Figure 12 Thickness of the critical nucleus versus T_c.

ΔG_u	is the difference between free energy for polymer melt and crystal
N	nucleation density
G	spherylite growth rate
ρ_c	crystal density
ρ_a	amorphous density
α	crystal conversion

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