DSC Analysis of Crystallization and Melting Behavior of Polypropylene in Model Composites with Glass and Poly(ethylene terephthalate) Fibers

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ABSTRACT: Isothermal and nonisothermal crystallization of maleic anhydride grafted polypropylene (PP), which is used for the production of split warp knit composite preforms,[1] are analyzed in model composites to determine the influence of reinforcement glass fibers (GF) and poly(ethylene terephthalate) (PET) binding yarns on the crystallization kinetics. Basic energetic parameters of crystallization are determined, and the melting behavior of PP in model composites is analyzed. The crystallization of PP carried out in nonisothermal and isothermal regimes is facilitated in the presence of GF, and the additional effects of PET fibers are also shown. Better conditions for nucleation, resulting in lower energy for formation of a stable nucleus and lower critical dimensions, are proposed as a reason for this. The crystal structure of PP in model composites exhibits lower lamellae thickness and is less disposed to recrystallization. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 239–246, 1999

Key words: DSC; crystallization; melting; polypropylene; glass fibers; poly(ethylene terephthalate)

INTRODUCTION

In recent years thermoplastic composites produced from different textile preforms in which continuous reinforcement fibers are combined with thermoplastic polymers in the form of fibers or powder have been getting much attention.[1,2] It was previously shown that some disadvantages of woven structures widely used presently can be overcome in warp knitted or directly oriented structures produced from hybrid yarns.[3] The hybrid yarns are composed of glass fibers (GF) and polypropylene (PP) split films with a fiber volume fraction of 50%, and a small amount of poly(ethylene terephthalate) (PET) yarns (2% volume fraction) is used as binding material to fix the straight inserted hybrid yarns into textile preforms.[4] The experimental results obtained on PP/GF composites demonstrated the importance of this third auxiliary component for the overall properties of the material. For the production of these composites modified low viscous PP was used for split film production and a special fiber sizing was developed for GF in order to enable good impregnation and thus fast processing (Table I).

It is well known that the properties of semicrystalline polymers used in composite materials are related to the morphology developed during processing cycle heating (melting) and cooling

Table I   Description of Samples and Their Codes

Sample	Code	Polymer	Glas Fiber (vol %)
Pure polymer	PP	i-PP	/
Composite	CPPG	i-PP	0.43
Composite	CPPGPT	i-PP+PET	0.43+0.11

(crystallization). Our previous investigations carried out by polarizing optical microscopy showed that the presence of maleic anhydride grafted PP (PPgMAH) used as a modifier for PP split films leads to alteration of the crystallization kinetics, although a spherulitic morphology similar to neat PP was developed.[5] The nucleation activity of GF and PET yarns used to produce the composite preforms was also analyzed, and the results are presented elsewhere.[5] It was also shown that differently treated and sized glass fibers might exhibit different nucleating ability toward isotactic PP (i-PP).[6,7] To study the influence of GF alone and in combination with PET yarns on the crystallization of PP, model composites are analyzed. In this article the results of a DSC analysis on isothermal and nonisothermal crystallization of PP in model composites are presented.

EXPERIMENTAL

Isothermal and nonisothermal crystallization of PPgMAH, which is used for the production of split warp knit composite preforms, consisting of continuous GFs, polymer split film, and fixed PET yarns,[1] were analyzed by DSC. For this purpose model composites were prepared with the same polymer/glass fibers/PET yarns ratio as in real warp knit material (46 : 43 : 11 vol %). PPgMAH (MFI = 36 g/10 min) was produced from commercial homopolypropylene (weight average molecular weight, M_w, of 158,500 determined by GPC, and polydispersity index, Mw/Mn, of 6.36) and commercial grade modifier (Polybond 3150) with a M_w of 90,000 and a grafting degree of 1.5% MAH.

The experiments were carried out with a Perkin–Elmer DSC-7 analyzer under nitrogen, and the calibration was performed with indium and zinc.

In the isothermal regime the samples were rapidly heated to 478 K and the molten state was held 5 min to erase the thermal history of the polymer. Then the samples were cooled to a given crystallization temperature (T_c) with a cooling rate of 80 K/min. Isothermal crystallization was carried out at T_c with a cooling rate of 80 K/min. Isothermal crystallization was carried out at T_c until crystallization was completed.

Figure 1   Conversion curves of pure PP and PP in composites.
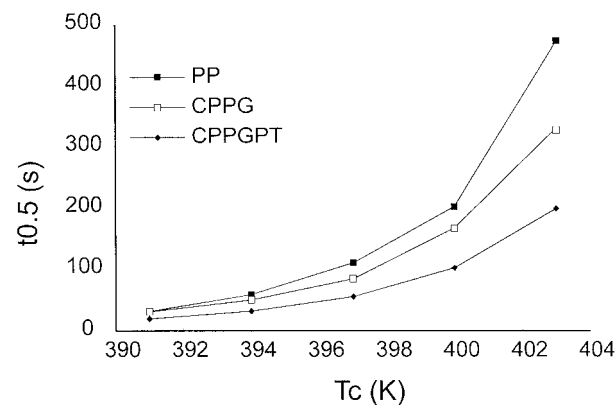
Figure 2   Dependence of $t_{0.5}$ for polymer and composite samples on T_c.
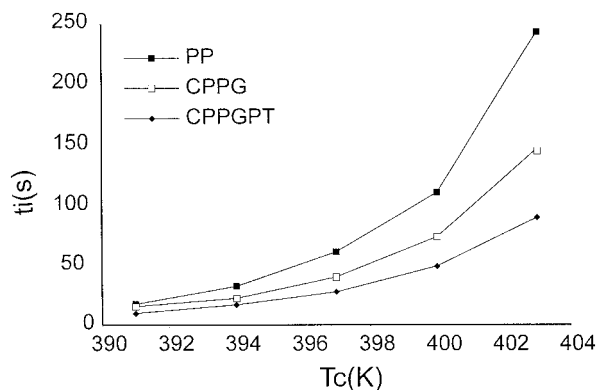
**Figure 3** Dependence of induction time of PP and composites on T_c.

The samples were cooled at different cooling rates (β = 1, 3, 5, 10, 15, and 20 K/min) to analyze the effect of cooling rate on the crystallization kinetics.

Theoretical background for calculations of parameters of crystallizations are given in our previous articles.[6,7] Based on the experimental DSC data, induction time (t_i) and half-time of crystallization ($t_{0.5}$) were determined.[7]

RESULTS AND DISCUSSION

Isothermal Crystallization

From the curves of crystal conversion (Fig. 1) it is obvious that at given T_c crystallization proceeds faster in model composites containing GF, and crystal conversion reaches its highest values for composites containing GF and PET yarns. The effect of fibers on the crystallization of polymer is also shown in Figure 2, where the half-time of crystallization is presented versus T_c. The $t_{0.5}$ is lowest for the composite containing both glass and PET fibers.
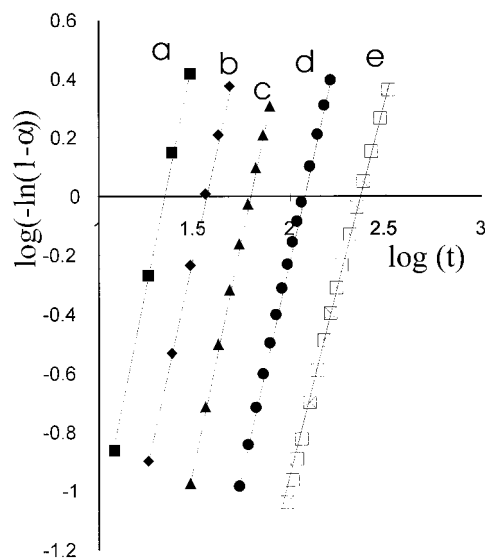

Figure 4 Avrami plots of CPPGPT at different T_c (K): (a) 391, (b) 394, (c) 397, (d) 400, (e) 403.

Compared to PP the t_i for composites are decreased and the influence of PET yarn is especially pronounced, although its content in model composites is far lower compared to GF (Fig. 3). This is obviously due to enhanced nucleation ability and the possibility of heterogeneous nucleation in the presence of PET. The results obtained by polarizing optical microscopy showed the existence of a transcrystalline zone on the surface of PET fibers.[8] PET fibers are known to be able to cause transcrystallization. The Avrami plots for this particular model composite are linear (for all investigated T_c), enabling determination of rate constants (k) and Avrami exponents (n) (Fig. 4). The values of the Avrami exponents are given in Table II. The highest values for n are determined for the pure PP while similar n are found for both model composites, pointing out a similar mechanism of crystallization. Overall crystallization

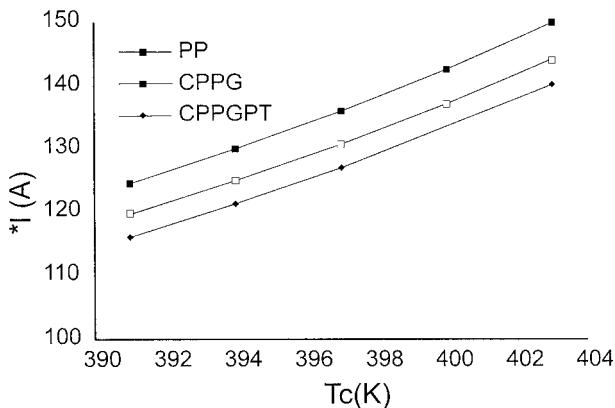**Table II   Avrami Index n and Overall Kinetic Constant k at Different T_c**

T_c (K)	PP		CPPG		CPPGPT	
	n	k	n	k	n	k
391	3.6	$2.4 10^{-6}$	3.3	$8.0 10^{-6}$	3.2	$4.4 10^{-5}$
394	3.4	$7.3 10^{-7}$	2.7	$1.8 10^{-5}$	3.0	$2.1 10^{-5}$
397	3.3	$1.2 10^{-7}$	2.6	$6.0 10^{-6}$	3.0	$3.3 10^{-6}$
400	3.0	$7.0 10^{-8}$	2.5	$1.9 10^{-6}$	2.9	$1.1 10^{-6}$
403	3.0	$7.5 10^{-9}$	2.4	$7.3 10^{-7}$	2.4	$1.9 10^{-6}$
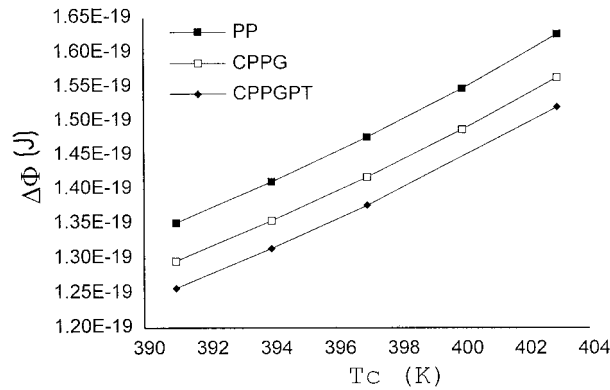
Figure 5 Energy of formation of nucleus of critical dimensions determined for pure polymer and PP in composites versus T_c.

constants, k, are higher for the composite containing GFs and PET yarns; because k is related to the nucleation process, the differences are probably the result of the differences in this stage of crystallization. The lamellae's growing rate at given temperature is controlled by secondary nucleation on the existing crystallites. According to the kinetic theory of crystallization of polymers,[9] the energy for creation of a nucleus of critical dimensions and the critical dimensions of the growing nucleus are determined (see Figs. 5, 6). Nucleation is obviously favored in composites, because lower values for energy and critical dimensions are determined as compared to PP; thus, the rate of crystallization is increased. Surface folding free energy is also lowest for the composite with GFs and PET yarn.

The Hoffman–Weeks method was used to determine the equilibrium melting temperature the and γ constant, and the results are presented in Table III.

Table III   Surface Energy σ_e, Equilibrium Melting Temperature T_m, and γ Constant Determined from Isothermal DSC Data

|	σ_e ($\mathrm{Jm^{-2}}*10^3$)	T_m^o (K)	γ
PP	187	461.82	2.49
CPPG	178	461.19	2.49
CPPGPT	171	460.381	2.57

Nonisothermal Crystallization

The conclusions derived for isothermal crystallization were confirmed by the results obtained on nonisothermal crystallization. Nonisothermal crystallization started at higher temperatures in composites compared to PP (Fig. 7) as a result of the nucleation ability of the fibers, and the overall crystallization process was shifted toward a higher temperature range (see Figs. 8, 9).

During crystallization from the melt carried out with different cooling rates, evidence on transcrystallization might be obtained, especially at lower cooling rates, consisting of a double (or shoulder) exothermal peak. However, this was not the case in our investigated composites (Fig. 10).

Ozawa plots for PP and composites with GFs give straight lines; but for a sample containing PET the plot is no longer linear, which implies that the influence of these yarns has become predominant. Therefore, it is difficult to interpret the kinetics of crystallization by the Ozawa theory (see Fig. 11).[10] Obviously, even at low concentration, PET play a major nucleating role for PP.

To calculate the nucleation activity (θ) of foreign additives and substrates during the crystal-

Figure 6 Thickness of the critical nucleus versus T_c.
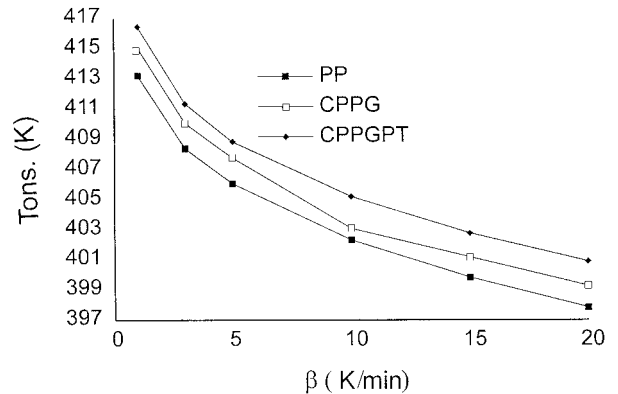
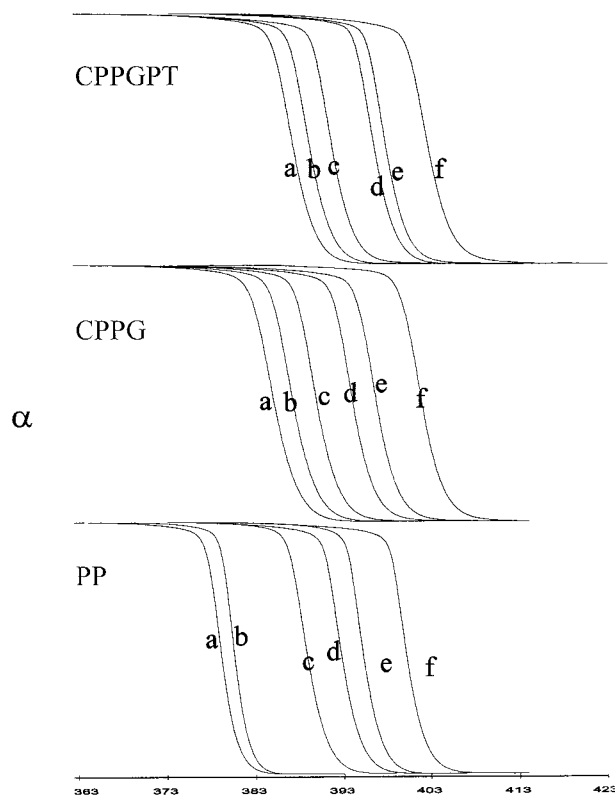**Figure 7** Crystallization onset temperature versus cooling rate.
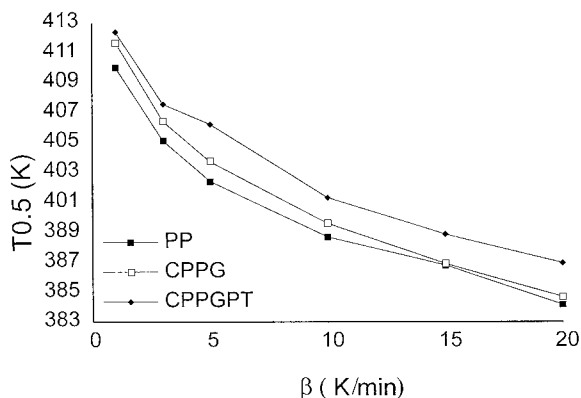
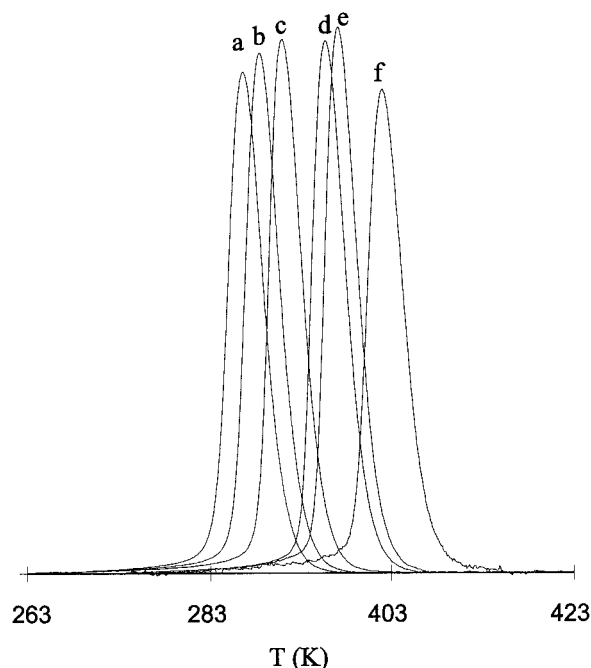**Figure 8** Dependence of temperature at half-conversion for PP and PP in composites on cooling rate.

lization of the polymer melt, a method was proposed by Dobreva et al.[11] for analyzing DSC data. θ is defined as

$$\theta = A_{k3}^*/A_{k3}^o,$$

where

Figure 9 Conversion curves of PP and PP in composites at different cooling rates (β, K/min): (a) 20, (b) 15, (c) 10, (d) 5, (e) 3, (f) 1.

Figure 10 DSC thermograms of CPPGPT at different cooling rates (β, K/min): (a) 20, (b) 15, (c) 10, (d) 5, (e) 3, (f) 1.

$$A_{k3}^o = 16\pi\sigma V_m^2/3\Delta S_m^2 \Delta T_p^2$$

is the work of homogeneous nucleation, and A_{k3}^* is the work of heterogeneous nucleation. $\Delta T_p = T_m^o - T_{c\max}$ (where $T_{c\max}$ corresponds to the crystallization peak temperature in the nonisothermal regime). Clearly, θ is unity for absolutely inert substrates and is practically zero for very active substrates. Following the formalism presented in Dobreva et al.,[11] the Avrami equation for nonisothermal conditions can be transformed into[12,13]

$$\log(\beta) = \text{const} - B^o/2.3\Delta T_p^2$$

$$B^o = 16\pi\sigma V_m^2/3T_m^o\Delta S_m^2$$

where β is the cooling rate.

The activity of the substrate θ, is then given by the ratio of the two slopes B^* and B^o (Fig. 12). For the composites without PET the θ is 0.84; for the composites containing GF and PET the θ is 0.81.

Melting Behavior

The melting behavior of PP was investigated to determine the stability of the formed crystalline structure upon crystallization.
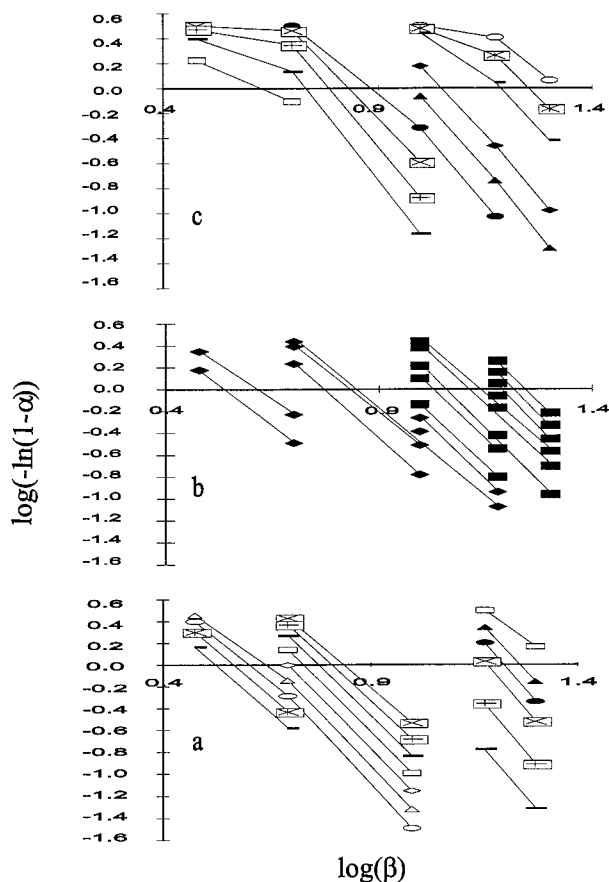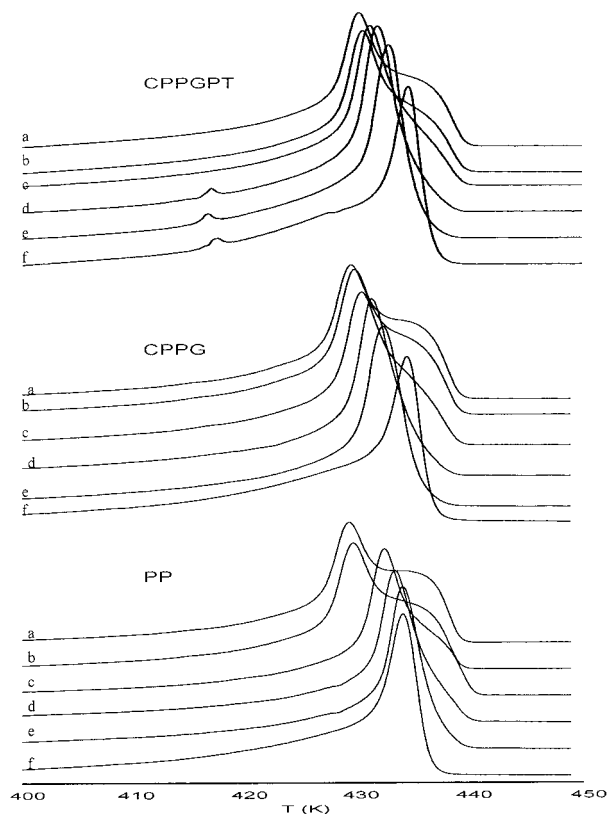
Figure 11   Ozawa plots for (a) PP, (b) CPPG, and (c) CPPGPT.

Upon isothermal crystallization carried out in the temperature range investigated, no recrystallization was observed during melting, which enables the correct determination of the equilibrium melting temperature.
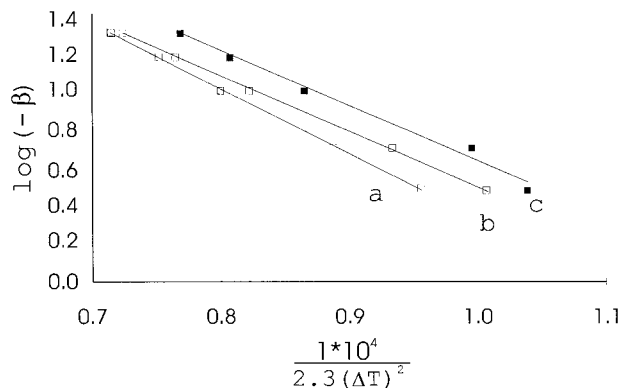

Figure 12 $\text{Log}(-\beta)$ versus $1/(2.3\Delta T_p^2)$ for (a) PP, (b) CPPG, and (c) CPPGPT.

Figure 13   Heating thermograms ($\beta = 10$ K/min) of PP and composites crystallized at different cooling rates ($-\beta$ K/min): (a) 20, (b) 15, (c) 10, (d) 5, (e) 3, (f) 1.

Recrystallization of PP was observed after nonisothermal crystallization, when the formed crystal structure was less stable and perfect. DSC melting traces of nonisothermally crystallized samples are shown in Figure 13. Two melting peaks appeared as a result of the recrystallization process; obviously, the higher the difference between them the more significant recrystallization becomes. To evaluate the influence of GFs in this process, the PC program GRAMS and an approximation with asymmetric log-normal functions were used in curve fitting and low and high peak temperature were determined as a function of cooling rate (Fig. 14).

The presence of fibers in model composites obviously influences the shape and the disappearance of two melting peaks, and it could be concluded that a more stable crystal structure is formed compared to PP. This is caused by shifting the crystallization toward a higher temperature range in the presence of fibers and thus by the formation of a more stable structure that is less susceptible to recrystallization. On the other
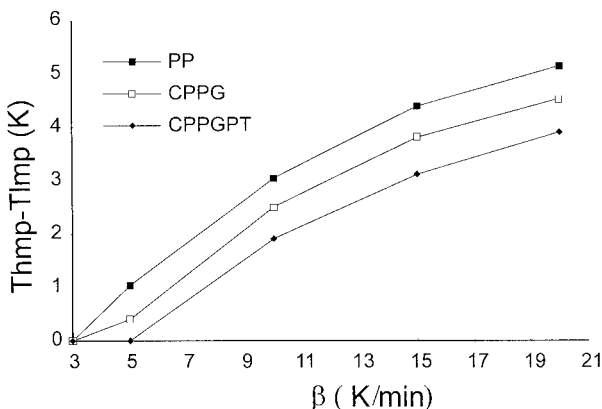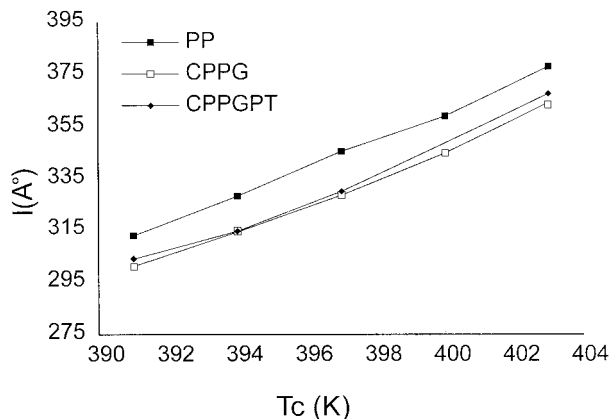
Figure 14 Difference between the temperatures of high (T_{hmp}) and low melting (T_{lmp}) peaks versus cooling rate.

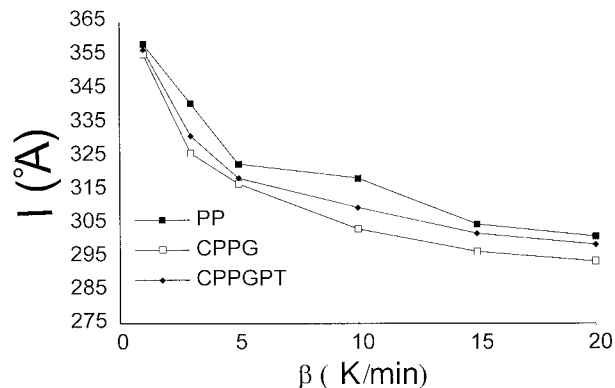**Figure 16** Dependence of lamellar thickness on cooling rate.

hand, the lamellae thickness determined for PP is higher for pure polymer for all the investigated cooling rates and at each T_c (Figs. 15, 16).

It is obvious that the equilibrium melting temperature decreases with increasing nucleating efficiency of the fibers as was previously shown.[6,14]

The appearance of double melting peaks during DSC scans of polymers is usually attributed to the existence of crystallites with different sizes,[15] and different crystal structure,[16–19] and processes of recrystallization taking place during heating.[20] Recently, the concept of recrystallization during the heating run is favored.[21] The endothermic melting process might be accompanied by the exothermic process of crystallization, resulting in splitting of the melting peak. It was also found that recrystallization of i-PP during the DSC experiments can be caused by transformation of the less stable α1 phase into the more

stable α2 phase, which is possible at temperatures above 420 K.[22–24] Clearly, the tendency for recrystallization is more pronounced when the existing crystal structure is less stable and is formed either at lower T_c (isothermal crystallization) or on cooling at higher cooling rates (nonisothermal crystallization),[25–28] as well as when the heating run is performed at lower heating rates.

In our experiments the heating was performed under a constant rate to analyze the influence of GFs and PET on the structure formed. As can be seen from Figures 13 and 14, two melting peaks are finally becoming one as a result of the originated stable structure,[21] when the crystallization is performed nonisothermally, by cooling with β = 3 K/min for the polymer and composite without PET, and by cooling with β = 5 K/min for the composite with PET.

CONCLUSION

Based on the determined energetic parameters of crystallization, some conclusions could be derived. The crystallization of PP carried out in nonisothermal and isothermal regimes is facilitated in model composites (i.e., in the presence of GFs). Additional effects of PET fibers were also found. Better conditions for nucleation, resulting in lower energy for formation of a stable nucleus and its lower critical dimensions, were proposed as a reason for this. The resulting crystal structure of PP in model composites exhibits lower lamellae thickness but is less disposed to recrystallize and is more stable.

NOMENCLATURE

t_i induction time
$t_{0.5}$ half-time of crystallization

Figure 15 Dependence of lamellar thickness on T_c.

k	rate constant
n	Avrami coefficient
T_c	crystallization temperature
T_m^o	equilibrium melting temperature
T_m	observed melting temperature
l	lamellar thickness
l^*	critical thickness of crystal nucleus
T_g	glass transition temperature
ΔT	supercooling
ΔT_p	undercooling at which the $d\alpha/dT$ reaches the its peak values
A_{k3}^o	work of homogeneous nucleation
A_{k3}^*	work of heterogeneous nucleation
V_m	molar volume
ΔS_m	molar entropy of melting

Greek Letters

α	crystal conversion
β	cooling rate
γ	constant representing the ratio between the final thickness of crystalline lamellae and initial critical thickness
σ_e	crystal fold surface energy
σ	crystal growth lateral surface energy
θ	parameter for nucleation activity

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