Crystallization Behavior of PP/PP-g-MAH/GFR PA66 Blends: Establishment of their Continuous-Cooling-Transformation of Relative Crystallinity Diagrams

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ABSTRACT: Polypropylene/polypropylene-grafted-maleic anhydride/glass fiber reinforced polyamide 66 (PP/PP-g-MAH/GFR PA 66) blends-composites with and without the addition of polypropylene-grafted-maleic anhydride (PP-g-MAH) were prepared in a twin screw extruder. The effect of the compatibilizer on the thermal properties and crystallization behavior was determined using differential scanning calorimetry analysis. The hold time was set to be equal to 5 min at 290°C. These conditions are necessary to eliminate the thermomechanical history in the molten state. The crystallization under nonisothermal conditions and the plot of Continuous-Cooling-Transformation of relative crystallinity diagrams of both PP and PA 66 components proves that PP is significantly affected by the presence of PP-g-MAH. From the results it is found that an abrupt change is observed at 2.5 wt % of PP-g-MAH as a compatibilizer and then levels off. In these blends, concurrent crystallization behavior was not observed for GFR PA66. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1620–1626, 2007

Key words: polypropylene/polyamide blends; glass fibers; PP-g-MAH compatibilizer; crystallization kinetics; differential scanning calorimeter; CCT diagrams

INTRODUCTION

Polypropylene–polyamide (PP/PA) blends have received a great attention during the last decade.[1–15] In fact, on one hand, their formulation results in a combination of thermomechanical properties (impact resistance, heat resistance) of polyamides, and on the other hand, their inertness to humidity and ease of processing because of the presence of polypropylene.

But because of their incompatible character, several attempts have been undertaken to compatibilize these blends using polypropylene grafted acrylic acid or maleic anhydride, ionomers, and finally bloc copolymers of functionalized styrene.[9,10]

The effect of compatibilization on crystallization is an important aspect because crystallinity has a profound effect on major properties such as impact resistance as well as other mechanical and physical–chemical properties. The way that crystallinity and crystalline structures are induced in the blend components are also important aspects to be considered.[9,10]

Since the properties of such polymers depend on microstructure, many studies dealing with crystallization of PP/PA blends have been reported. Then, the crystallization behavior under isothermal and nonisothermal conditions and the resulting microstructure have been extensively studied using various methods such as differential scanning calorimetry (DSC), IR spectroscopy, optical microscopy, wide angle X-ray scattering, small angle X-ray, and electron microscopy.[1–13,16–19]

The conventional ways to express the effect of some additives on crystallization is by measuring the relative crystallinity from DSC's exotherm peak as a function of time or temperature. This approach has been used for both neat polymers as well as for polymer blends.[14–19] Few works exist in the literature regarding the influence of the concentration of the compatibilizer on the coincident crystallization behavior in compatibilized blends, especially for the component of higher crystallization temperature as the matrix phase.[14,15,20]

Recently, new approaches based on a concept developed in physical metallurgy to follow the crystallization behavior of neat polymers have been introduced by Alberolla,[16,21] Bas,[17,18] and Vandramini,[19] termed the Continuous-Cooling-Transformation of

TABLE I
Raw and Formulated Materials

Materials	ρ (g/cm^3)	T_m (°C)	MFI/MVI (g/10 min/cm^3/10 min)	M_n (g/mole)	M_w/M_n	AEG (amine end Group) (µeq/g)	Nom. code	Supplier
PP homopolymer	0.905	Range 140–170	230°C/2.16 Kg (MFI) 10.6	40,000	5.9	–	Sabic® PP 575 P	SABIC
PP-*g*-MAH	–	162	190°C/2.16 Kg (MVI) 120	–	–	–	Fusabond® P M613-05 -MAC (Medium Anhydride Compatibilizer)	DuPont
PA66	1.14	260*	275°C/5 Kg (MVI) 150	18,000	–	42	Ultramid® A3W	BASF
GFR (30 wt %) PA 66	1.36	260*	–		–	–	Ultramid® A3WG6	BASF
PP/GFRPA66	–	–	–					–
PP/PP-g-MAH/ GFRPA66	–	–	–		–	–		–
Stabilizer	1.15	Range of 110–125	–		–	–	IRGANOX®1010	Ciba

relative crystallinity (CCT) diagrams. They evidence the changes in the crystallized fraction versus cooling rate. These latter diagrams also illustrate the evolution of the relative (or absolute) crystallinity index versus time and temperature.

Other authors have used these concepts for polymers under high cooling rates but rarely for polymer blends.[14,15] CCT diagrams can be useful tools to give evidence for the microstructure gradients developed in injection molded items.[17] Unfortunately, these concepts have not been used for reinforced polymer blends.

Therefore, in the present work, the effect of the concentration of the compatibilizer [polypropylene-grafted-maleic anhydride (PP-*g*-MAH)] on the global crystallization process of both PP and GFR PA 66 when blended at 30/70 wt %, respectively, is investigated. Their CCT diagrams are established.

EXPERIMENTAL

Materials and blends preparation

The materials used in this study and formulations are shown in Tables I and II. Glass Fiber Reinforced Polyamide 66 (GFRPA66) (Ultramid® A3WG6 from BASF, Germany) was dried under vacuum for 72 h at 110°C before blending. Polypropylene (PP) (Stamylan® P become Sabic® PP 575 P, from SABIC, Saudi Arabia) had a Melt Flow Index of 10.6 g/10 min, and was also dried in oven at 80°C during 48 h. PP-*g*-MAH (Fusabond® P M613-05-MAC) (Medium Anhydride Compatibilizer) was supplied by DuPont (France).

The blends were prepared in a corotating twin screw extruder ($L/D = 40$). The barrel temperature profile ranges from 265 to 280°C. The screws speed

was set to 200 rpm. The TSE used was a ZSE 18 HP 40D from Leistritz Extrusionstechnik GmbH. The blends considered are PP (30 wt %) in GFRPA66 (70 wt %). The amount of PP-*g*-MAH used was 2.5, 5, 7.5, and 10 wt %.

Testing

To perform the crystallization tests, both DSC 821^e Mettler Toledo STAR^e system and DSC 7 Perkin-Elmer were used under nitrogen flux to avoid thermal oxidation. The sample mass is about 8 mg and the instruments were calibrated using Indium ($T_m = 156.60$°C, $\Delta H_f = 28.5$ J/g) and Zinc ($T_m = 419.47$°C, $\Delta H_f = 108.37$ J/g), respectively.

In any study concerning the crystallization of polymers, it is necessary to eliminate the thermomechanical history of the material, i.e., to destroy any preexisting crystalline germs capable of acting as nucleating agents for subsequent crystallization. To carry out this part of study, all materials were heated at 50°C/min to a temperature above their melting temperature, starting at 270°C till 350°C, with an increment of 10°C. Then, they were kept at each holding temperature for 5 min. Samples were then cooled at

TABLE II
Blends Formulation

N°/wt %	F1	F2	F3	F4	F5
PP homopolymer	30	27.5	25	22.5	20
PA 66 (GFR 30 wt %)	70	70	70	70	70
PP-g-MAH	0	2.5	5	7.5	10
MAH Grafting degree	1	1	1	1	1
Stabilizer Irganox® 1010; In PP part	2	2	2	2	2

Blends (PP 30 wt %/GFR PA 66 70 wt %).
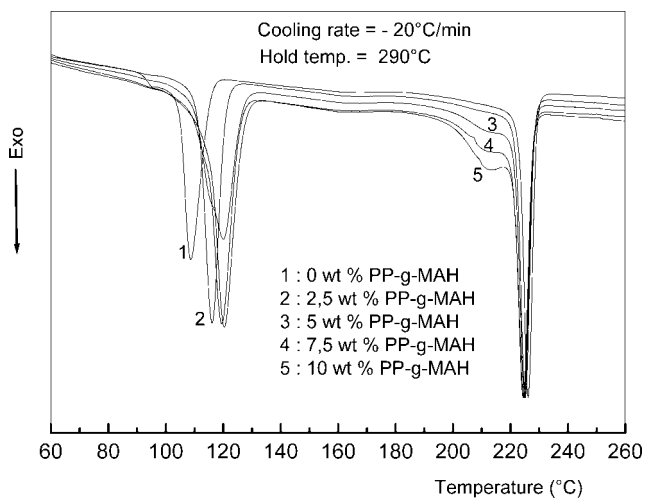
Figure 1 Exotherms of PP and GFR PA 66 components in blends-cooled from T hold = 290°C.
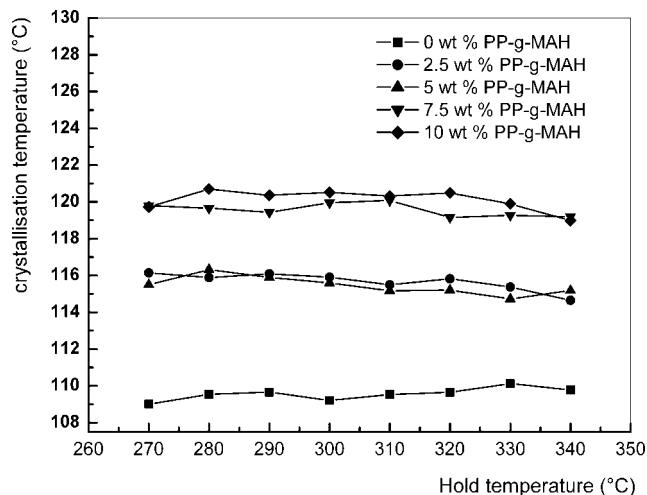

Figure 2 Crystallization behavior of PP in blend-composites for 0 wt % to 10 wt % of PP-g-MAH, cooled from the molten state, maintained during 5 min.

−20°C/min. Nonisothermal crystallization kinetics are recorded during this decrease in temperature. The typical DSC thermograms are shown as exotherms in Figure 1.

As far as the nonisothermal crystallization of the different materials is concerned, this test was performed using a program called "multitasking." The samples were heated at 50°C/min from ambient temperature till a hold temperature (chosen T hold). They were held at this temperature for 5 min and then cooled at various cooling rates till ambient temperature. The crystallization temperatures (T_c) are then recorded from the exothermic crystallization peak.

RESULTS AND DISCUSSION

Study of the aptitude of materials to crystallization

It is known that the thermal history in the melt could affect the crystallization behavior of polymers. Thus, no molten crystalline seeds or local chain organization could remain at temperatures above the melting point.[17–19] Thus, the presence of such primary nuclei decreases the crystallization free energy barrier and thus increases the crystallization rate. Such a phenomenon is also defined as self-nucleation.[18] To determine the optimal conditions of the molten state leading to a decrease in this "memory" effect, two parameters (i.e., hold time and hold temperature) were chosen.

The hold time has been set to 5 min. In fact, it has been reported in the literature[17,18] that the hold time at the hold temperatures being considered has a negligible effect on the crystallization temperature. For the determination of a unique hold temperature (T_{hold}), it is necessary to plot T_c versus T_{hold}. From the obtained thermograms (Fig. 1) the T_c of each

component in the blends was taken at the maximum of the peak and recorded versus hold temperatures. The results for PP and GFRPA66 component are shown in Figures 2 and 3, respectively. The effect of various amounts of PP-g-MAH is also illustrated in the same figures. The existence of an interval comprised between 290 and 310°C, where the crystallization temperature (T_c) of PP and GFRPA66 does not change as a function of the hold temperature (T_{hold}), is obtained.

This interval permits to detect a unique hold temperature in the molten state for all considered polymeric systems and equals 290°C, as shown in Figures 2 and 3. Taking into account such variations of the crystallization temperature versus the molten state temperature, the chosen holding conditions in
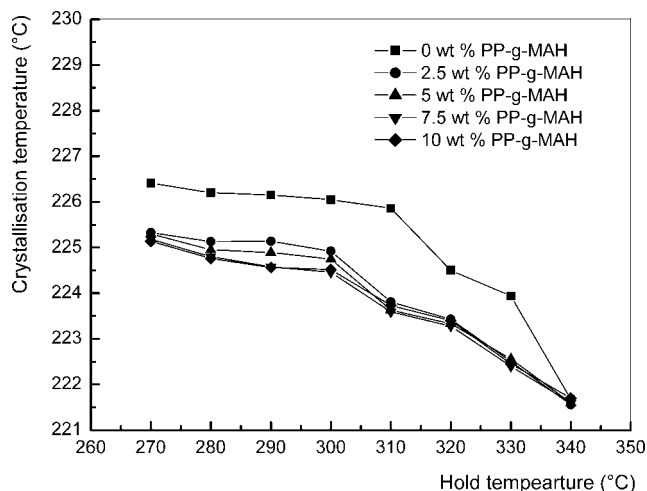

Figure 3 Crystallization behavior of GFR PA 66 part in blend-composites for 0 wt % to 10 wt % of PP-g-MAH, cooled from the molten state, maintained during 5 min.
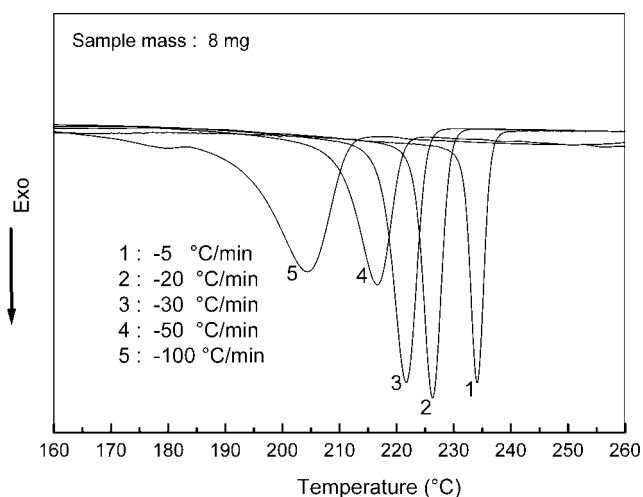
Figure 4 Exothermic thermograms at various cooling rates of GFRPA66 in PP/2.5 wt % PP-g-MAH/GFRPA66 blends.

the melt state are 290°C for 5 min, which could be considered as a good compromise between the self-nucleation and the degradation process. These conditions are in agreement with those defined by many authors.[18,22] Yet, the selected holding temperature corresponds to the processing temperature of GFRPA66, which is the matrix in these reinforced blends and is equal to 290°C as reported in its data sheet,[23] while the processing temperature of PP must not exceed 310°C to avoid thermal degradation.

It can be noticed that the compatibilizer can act as nucleating agent. In fact, the discussion related to the crystallization of neat polymers directly applies to compatibilized polymer blends, in which crystallization occurs within nearly pure resin. The presence of the compatibilizer may strongly affect the overall crystallization growth rates. Figure 2 evidences the effect of PP-g-MAH on the crystallization temperature of PP in the reinforced blends. Adding various amounts of PP-g-MAH as a compatibilizer increases crystallization temperature of PP to 120°C, while the T_c of PP component in uncompatibilized blend was 111°C. PP-g-MAH can provide a nuclei center for PP to enhance the crystallization growth. However, the presence of PP-g-MAH seems to cause a slight decrease of the T_c of GFRPA66 in these reinforced blends (Fig. 3).

Nonisothermal crystallization study

For engineering purposes, nonisothermal crystallization of polymers is of great interest because injection molding, for example, is a nonisothermal semibatch processing technique. On the basis of the crystallization thermograms obtained under nonisothermal conditions, and using some metallurgical concepts,

the CCT diagrams are established. This relatively new approach in semicrystalline polymers allows showing the evolution of the relative crystallinity index as a function of time and temperatures under continuous cooling conditions. The realization of the thermal cycle using the "multitasking" program in DSC 7 PE apparatus leads to exothermic thermograms, as shown in Figure 4. The cooling from the molten state was achieved at a rate ranging from −5°C/min till −100°C/min. The integration of the surface area under the exothermic peak by the use of "partial area" software gives the evolution of the relative crystallinity index as a function of temperature at different cooling rates. Typical curves for PP and GFRPA66 with 2.5 wt % PP-g-MAH compatibilizer are shown in Figures 6 and 7, respectively. All nonisotherms have a sigmoïdal shape, typical of polymer crystallization behavior. This results from a double mechanism, i.e., nucleation and growth phenomena. In fact, because the nucleation and growth rates simultaneously vary with temperature, the non-isothermal crystallization rate evolves globally.[14–19]

From Figure 6, it is clearly seen that the cooling rate affects greatly the crystallization of each part in the blends. In fact, the higher the cooling rate, the lower the crystallization temperature (the peak shifts to lower temperatures). This makes the crystallization more difficult. This phenomenon has been reported earlier by several researchers.[14,15,17,18]

The effect of the compatibilizer content is evidenced in Figures 2 and 5. The presence of PP-g-MAH as compatibilizing agent increases the crystallization temperature (T_c) of dispersed phase (PP). In fact, the T_c of PP shift from 110°C to 117°C when 5 wt % of PP-g-MAH was added. These results can be ascribed to the nucleating effect of the compatibilizer
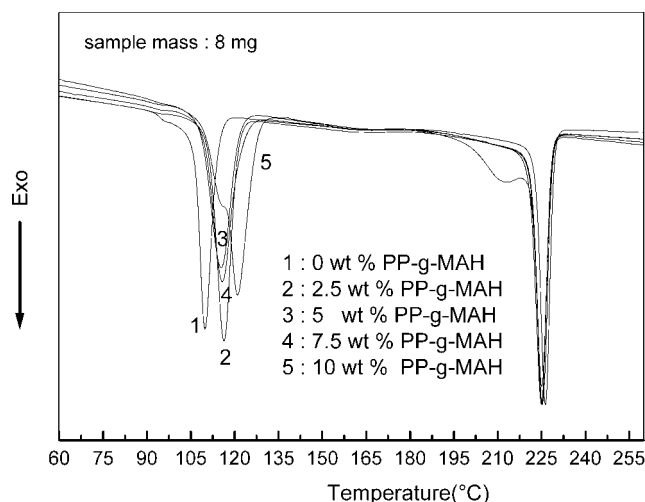

Figure 5 Effect of the compatibilizer content on crystallization of GFRPA66 and PP in blends-composites under fixed cooling rate (−20°C/min.).
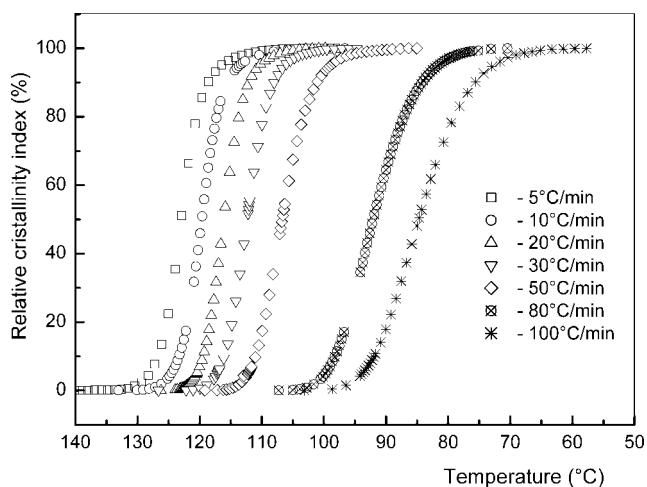
Figure 6 Evolution of the relative crystallinity index as a function of temperature for PP component in the blends at 2.5 wt % of PP-*g*-MAH and under various cooling rates.

on the crystallization of the PP component. However, the effect of the compatibilizer on the crystallization behavior of the matrix (GFRPA66) is negligible (See Fig. 5). Similar observations have been reported in the literature.[20,24]

In addition to these observations it can be noticed the presence of bend in the crystallization peak of PP and GFRPA66, in the blends when the amount of compatibilizer was high (10 wt %). This might be attributed to the formation of PP-*g*-MAH-*co*-PA66 block copolymer. Similar finding have been reported elsewhere.[20,24–27] The bend corresponds to each part of the block copolymer. The delay in crystallization might be hindered by this link between the different components of the blends.

GFRPA66 in the considered blends exhibits the fastest rate of primary crystallization compared with PP (Figs. 6 and 7). The curves shown in Figure 7 illustrate the abrupt and drastic decrease in the crystallization rate caused by the impingement of crystal entities occurring at above 70% relative crystallinity. This phenomenon was observed by Chuah et al.,[24] and attributed to the branching mechanisms that lead to solid sheaves.

CCT diagrams

From the curves given in Figures 6 and 7 and following the methodology of plotting CCT diagrams as reported in the literature,[17] the methodology to plot the CCT is detailed (Fig. 8).

The sample is subjected at a given cooling rate at which the exothermic peak of crystallization is recorded [Fig. 8(a)].

From the exothermic peak recording for each cooling rate, the relative crystallinity ratio X_c (T) can be determined using the following relationship:

$$X_c(T) = \frac{\Delta H_c(T)}{\Delta H_c(\infty)}$$

where $\Delta H_c(\infty)$ is the total area under the crystallization exotherm for a given cooling rate and ΔH_c (T) is the partial area for a chosen crystallization temperature T_c and for the same cooling rate. The variations of the relative crystallinity index $[X_c(T)]$ versus temperature are shown in Figure 8(b).

From the *S*-shaped curves, and for each cooling rate i.e., (−20°C/min), the X_c (i.e., 95%) and its corresponding temperature is extracted from Figure 8(b), and put into Figure 8(c) on the line corresponding to the cooling rate used. As far as the straight lines were drawn previously by two points, the first one, $t = 0$ for start temperature, i.e., 290°C, and the second one $t = t_{required}$ at the final temperature, i.e., 30°C, in most cases and for each cooling rate as shown in Figure 8(c). The CCT diagram can be drawn for the analyzed cooling rates range by plotting the graphs representing equal transformation [Fig. 8(c)]. The continuous line gives the time corresponding to 95% relative crystallinity index. The straight lines express the cooling laws for seven cooling rates (5, 10, 20, 30, 50, 80, and 100°C/min).

The CCT diagrams drawn with relative crystallinity indexes are established for both PP and GFRPA66 components in blends by plotting the crystallization temperature for 95% crystallized fraction versus time for different cooling rates and are shown in Figures 9 and 10, respectively.

The half "C" shape of the CCT diagrams shows that the crystallization domain of PP and PA is narrow 40°C. The half "C" shape of the CCT diagram gives evidence of the competition between nucleation and growth phenomena. At high temperature,
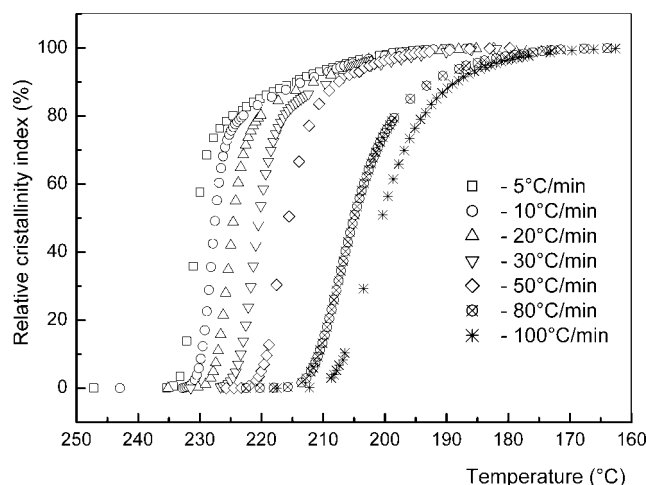

Figure 7 Evolution of the relative crystallinity index as a function of temperature for GFRPA66 component in the blends at 2.5 wt % of PP-*g*-MAH and under various cooling rates.
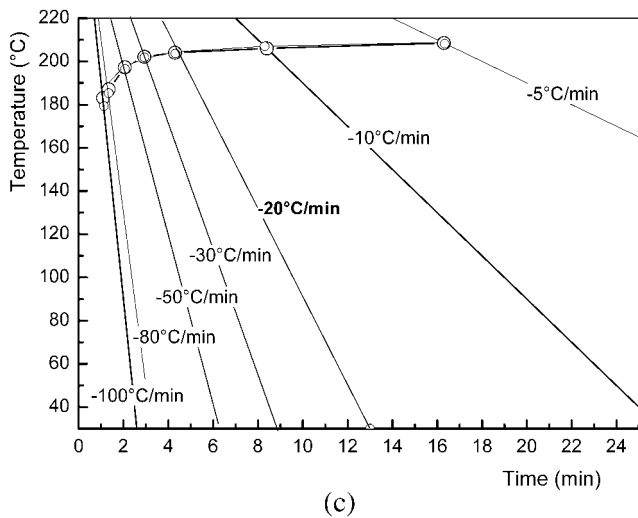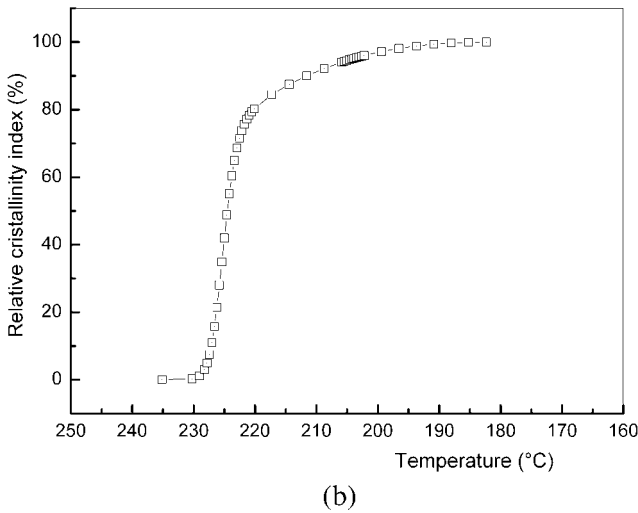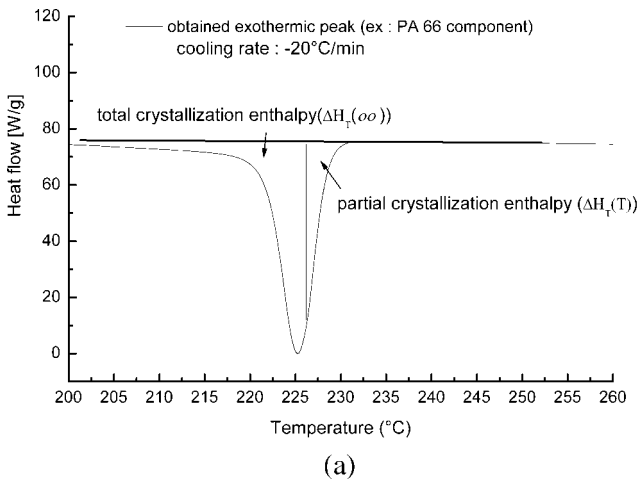
(a)

(b)

(c)

Figure 8 Illustration of methodology for the tracing of CCT diagrams.

crystallite growth predominates; this might be due to the fact that both polymers having a moderate molecular weight, allowing some molecular chain mobility
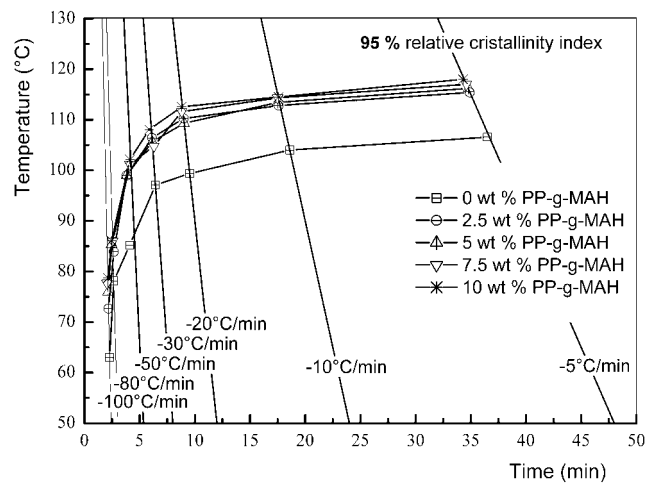

Figure 9 CCT diagrams corresponding to 95% relative crystallinity index for PP component in the blends with various amounts of PP-*g*-MAH. Straight lines express the cooling laws for seven cooling rates (5 till 100°C/min.).

are capable of crystallizing even during the cooling stage from the molten state causing the hiding of the germination step by the growth step. Similar observations have been reported elsewhere.[17–19]

The CCT diagrams bring the following informations:

The crystallization speed is maximal at the "nose" of the present diagrams where a privileged range of temperature is defined for polypropylene to be 60–80°C and between 175 and 190°C for GFRPA66.

The compatibilizing agent content 2.5 wt % is enough to reduce the time necessary to reach a given crystallization transformation ratio for the PP part in the blends considered as shown in Figure 9.

Meanwhile, no significant effect of the compatibilizer is observed on the crystallization of the matrix GFRPA66 as shown on Figure 10. This result is in
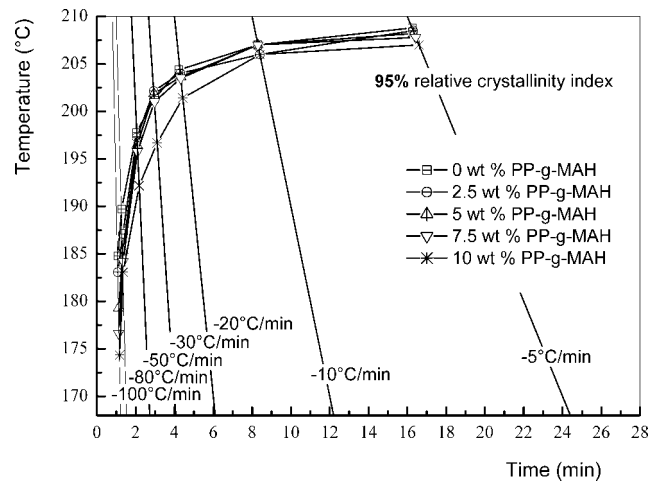

Figure 10 CCT diagrams corresponding to 95% relative crystallinity index for GFRPA66 component in the blends with various amounts of PP-*g*-MAH. Straight lines express the cooling laws for seven cooling rates (5 till 100°C/min).

agreement with those obtained by Chuah et al.[24] In fact, PA having the higher crystallization temperature (over 200°C), such that the crystallization can not be affected by the presence of PP-*g*-MAH as a compatibilizing agent having a lower crystallization temperature (about 110°C). In the range of temperatures close to the crystallization region of PA, the compatibilizer is still in liquid state like PP.

CONCLUSION

The study of the crystallization under nonisothermal conditions of reinforced polymer blends evidenced the influence of the thermomechanical history as well as the effect of a compatibilizer on the crystallization behavior of the blend constituents, namely, PP and GFRPA66. The holding time and temperature are found to be 5 min and 290°C, respectively. The presence of PP-*g*-MAH as a compatibilizing agent for PP/GFRPA6 blends caused an increase in the crystallization temperature of PP in PP/GFRPA66 blends.

The CCT curves established from the determination of no-isothermal kinetics give evidence for the changes in the crystallized fraction versus cooling rate. The CCT diagrams show a decrease in the crystallization ability of both PP and GFR PA 66 components with increasing cooling rate. CCT diagrams evidence the existence of a temperature domain between 60 and 80°C and 175–195°C where the crystallization rate is maximal for PP and GFRPA66, respectively. Such diagrams have also evidenced the existence of an abrupt change at the concentration of 2.5 wt % of compatibilizer and then levels off. However the concurrent crystallization behavior of GFRPA66 was not observable even though the amount of PP-*g*-MAH was high. Finally, such crystallization diagrams are useful to evidence the role of each components and the effect of PP-*g*-MAH as a compatibilizer on the crystallization behavior of both components in PP/GFR PA 66 reinforced blends.

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