Morphology, Crystallization, and Thermal Behavior of Isotactic Polypropylene/Polystyrene Blends: Effects of the Addition of a Graft Copolymer of Propylene with Styrene

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ABSTRACT: Optical microscopy, differential scanning calorimetry, and small-angle X-ray scattering techniques were used to study the influence of crystallization conditions on the morphology and thermal behavior of samples of ternary blends constituted by isotactic polypropylene (iPP), atactic polystyrene (aPS), and a novel graft copolymer of unsaturated propylene with styrene (uPP-g-PS) with the purpose of assessing the uPP-g-PS capability to act as a compatibilizer for iPP/aPS materials. It was shown that the presence of the uPP-g-PS copolymer affects the interfacial tension between the iPP and aPS phases in the melt state, with the aPS particle size and the particle-size distribution being, in fact, strongly modified. In samples of iPP/aPS/uPP-g-PS blends, isothermally crystallized from the melt at a relatively low undercooling in a range of the crystallization temperature of the iPP phase, the addition of the uPP-g-PS copolymer induced a drastic change both in the aPS mode and the state of dispersion and in the iPP spherulitic texture and inner structure of the spherulite fibrils. In particular, the phase structure developed in the iPP/aPS/uPPg-PS materials was characterized by a crystalline lamellar thickness of the iPP phase comparable to that shown by the plain iPP. The extent of the induced modifications, that is, the degree of compatibilization achieved, resulted in a combined effect of composition and undercooling. Also, relevant thermodynamic parameters of the iPP phase, such as the equilibrium melting temperature (T_m) and the folding surface free energy (σ_e) of the lamellar crystals, were found to be influenced by the presence of the uPP-g-PS copolymer. A linear decrease of the T_m and σ_e values with increasing uPP-g-PS content was, in fact, observed. Such results have been accounted for by an increase of the presence of defects along the iPP crystallizable sequences and by the very irregular and perturbed surface of the crystals with increasing copolymer content. The observed decrease in T_m values revealed, moreover, that, in the iPP/aPS/uPP-g-PS blends, the iPP crystal growth occurs under comparatively lower undercooling, in line with higher crystalline lamellar thickness shown by SAXS investigation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1429-1442, 1999

Key words: polypropylene; propylene-*g*-styrene copolymer; polystyrene; morphology; crystallization

INTRODUCTION

A novel graft copolymer of unsaturated propylene with styrene (uPP-g-PS) was added to binary

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blends of isotactic polypropylene (iPP) and atactic polystyrene (aPS) to assess the effectiveness of such a copolymer as a compatibilizer for iPP/aPS materials. In previous work¹ dealing with solution-cast samples, it was shown that the uPPg-PS addition can provide iPP/aPS-compatibilized materials and that the extent of the achieved compatibilization is composition-dependent. Blends

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Sample	$ar{M}_n$ (g/mol)	$ar{M}_w$ (g/mol)	${ar M}_w/{ar M}_n$	η (dL/g)	% PS (wt/wt)	$\mathop{T_g}_{(^\circ\mathrm{C})}$	T'_m (°C)	X_c
iPP	78,700	509,000	6.5	2.0	_	7	164	0.47
aPS	74,300	291,000	3.9		100	115		
uPP-g-PS				1.4	35	11 118	142	0.20

Table I Molecular Characteristics of the Starting Polymers Together with Glass Transition Temperature (T_g) , Apparent Melting Temperature (T'_m) , and Crystallinity Index (X_c)

of iPP and aPS exhibited the coarse domain morphology characteristic of immiscible polymer systems. By adding 2% (wt/wt) of the uPP-g-PS copolymer, a very broad particle-size distribution was obtained, even though the particles appeared coated by a smooth interfacial layer as expected according to a core-shell interfacial model. With increasing uPP-g-PS content (5% wt/wt), a finer dispersion degree of particles, together with morphological evidence of interfacial adhesion, was found. With further increase of the uPP-g-PS amount (10% wt/wt), the material showed such a homogeneous texture that no domains of the dispersed phase were detected by the scanning electron microscopy technique for magnification lower than $30,000 \times$. The type of interface developed in such iPP/aPS/uPP-g-PS blends was accounted for by an interfacial interpenetration model. It should be emphasized that the addition of the uPP-g-PS copolymer also modified the iPP morphology strongly. The SAXS studies showed that the phase structure generated in the iPP/ aPS/uPP-g-PS blends was characterized by a crystalline lamellar thickness (L_c) and an interlamellar amorphous layer thickness (L_a) higher than those shown by plain iPP; the higher the copolymer content, the higher the L_c and L_a . It should be remarked that considerably larger increases were found in the L_a values. Such results have been accounted for by assuming that a cocrystallization phenomenon between propylenic sequences of the uPP-g-PS copolymer and iPP occurs and that during such a process the PS chains grafted into copolymer sequences remain entrapped in the iPP interlamellar amorphous layers, where they form their own separated domains.

In the present article, we report the results of studies aimed at establishing the influence of the crystallization conditions on the morphology of the phase and interphase developed after complete iPP crystallization from the melt state under controlled crystallization conditions in film samples of binary iPP/aPS and ternary iPP/aPS/ uPP-g-PS blends isothermally crystallized at a relatively low undercooling in a range of crystallization temperatures of the iPP phase. The combined effect of undercooling and composition on the kinetic and thermodynamic parameters related to the isothermal crystallization process of the iPP phase was also investigated.

EXPERIMENTAL

Materials

The starting polymers used in this study were an iPP (HS005) made by Himont, an aPS made by Rapra (Shawbury, UK), and an uPP-g-PS copolymer synthesized in the Himont Scientific Laboratories according to methods patented by Cecchin et al. from Himont.^{2,3} The molecular characteristics of the plain starting materials are reported in Table I together with their glass transition temperature (T_g) , apparent melting temperature (T'_m) , and crystallinity index (X_c) .

Blending and Sample Preparation

All the investigated samples were obtained using the solvent-casting method. The blend components were dissolved in a common solvent, *o*-dichlorobenzene, at a total polymer concentration of 3% by weight and at 135° C. Thin films were then obtained by *o*-dichlorobenzene casting carried out under a vacuum at 135° C for 3 h. iPP/aPS (80/20 wt/wt) binary blends and iPP/aPS/uPP-*g*-PS ternary blends containing 2, 5, and 10% (wt/wt) of the graft copolymer were prepared.

Techniques

Differential Scanning Calorimetry

The thermal behavior of the thin films of plain iPP and binary and ternary blends isothermally

crystallized at 126, 130, 134, and 138°C was analyzed using a differential scanning calorimeter (DSC) with a Mettler TA 3000 instrument equipped with a control and programming unit (microprocessor Tc 10). The apparent melting temperatures (T'_m) and the crystallinity indeces (X_c) were determined following this procedure: The film samples (about 9 mg), heated from room temperature to 200°C at a rate of 10°C/min and kept at this temperature for 10 min in order to destroy any trace of crystallinity, were rapidly cooled to the desired crystallization temperature (T_c) after complete crystallization. Such samples were again heated at 200°C at a rate of 10°C/min. The observed melting temperatures (T'_m) and the apparent enthalpies of melting (ΔH^*) were obtained from the maxima and the area of the melting peaks, respectively. The crystallinity indices (X_c) of iPP and of the blends were calculated by applying the following relations:

$$X_{c}(iPP) = \Delta H^{*}(iPP) / \Delta H^{0}(iPP)$$
(1)

$$X_c(\text{blend}) = \Delta H^*(\text{blend}) / \Delta / H^0(\text{iPP})$$
 (2)

where $\Delta H^*(iPP)$ is the apparent enthalpy of fusion per gram of iPP in the blend; ΔH^0 (iPP) is the heat of fusion per gram of 100% crystalline iPP, from⁴ ΔH^0 (iPP) = 209 J/g; and $\Delta H^*(blend)$ is the apparent enthalpy of fusion per gram of the blend. The crystalline weight fractions referring to the iPP phase in the blends $[X_c(iPP)]$ were calculated from the following relation:

$$X_c(iPP) = X_c(blend)/W(iPP)$$
(3)

where W(iPP) is the weight fraction of iPP in the blends.

Optical Microscopy

Thin films of plain iPP and binary and ternary blends isothermally crystallized at 126, 130, 134, and 138°C according to the same procedure used to study the isothermal crystallization process of the iPP phase by the DSC were observed using optical microscopy (OM). A Zeiss optical polarizing microscope fitted with a Mettler hot stage was used; optical micrographs were taken with crossed and parallel polarizers. The radial growth rates (G) of the observed iPP spherulites were calculated by measuring the spherulite size (R) as a function of time; the photomicrographs were taken on the print and G was calculated as the slope of the straight lines obtained by plotting R against the time. The Zeiss microscope was also used to observe the melts of binary and ternary blends at 200°C and were kept at this temperature for 10 min.

Small-Angle X-ray Scattering

Small-angle X-ray scattering (SAXS) studies on films of plain iPP and binary and ternary blends, isothermally crystallized at 126, 130, 134, and 138°C, were carried out using a compact Kratky camera equipped with a Braun one-dimensional positional sensitive detector. Ni-filtered CuK α radiation generated from a Philips X-ray generator (PW 1730/10) operating at 40 kV and 30 mA was used. The raw scattering data were corrected for parasitic scattering, absorption, and slit smearing using Vonk's method.⁵ The desmeared intensities were then Lorentz factor-corrected by multiplying by s^2 ($s = 2 \sin \theta/\lambda$).⁶

RESULTS AND DISCUSSION

Microscopy Studies in the Melt and Solid States

Optical micrographs, taken with parallel polarizers, of thin films of binary iPP/aPS and ternary iPP/aPS/uPP-g-PS blends melted at 200°C and kept at this temperature for 10 min to destroy any crystallinity trace are reported in Figure 1. As shown, and as expected for an immiscible system, the iPP/aPS melt exhibits phase separation with the aPS component segregated in its own spherically shaped domains, showing a relatively wide size distribution. By adding the uPP-g-PS copolymer, no homogeneous melts are achieved, with dispersed phase domains being, in fact, observed irrespective of the copolymer content in the blends (wt/wt). By visual impression, it seems that the addition of the uPP-g-PS copolymer strongly modifies the mode and state of dispersion of the minor component. As a matter of fact, the population of particles, with a size considerably larger than that shown by another population of particles, is noted. Moreover, such larger particles, most of them showing a spherical shape, seem to contain smaller domains and exhibit an average diameter noticeably larger than that exhibited by the aPS particles in the iPP/aPS melt (see Fig. 1). These findings indicate that the uPPg-PS addition modifies the interfacial tension between the iPP and aPS melts. In particular, the dispersion degree achieved indicates that the ex-



Figure 1 Optical micrographs taken at parallel polarizers of thin films of (a) binary iPP/aPS blends and (b) ternary iPP/aPS/uPP-g-PS 2% wt/wt, (c) iPP/aPS/uPP-g-PS 5% wt/wt, and (d) iPP/aPS/uPP-g-PS 10% wt/wt blends melted at 200°C.

tent of the compatibilization is not essentially the same for each PS-based particle formed. Therefore, the above morphological results could be re-

lated to an uneven dispersion of the graft copolymer and/or a different state of mixing of the uPPg-PS copolymer with iPP and aPS. It is to be recalled that the variation of the tangent δ with the temperature for such blends, reported in the previous work,¹ showed that the iPP/aPS blend possesses individual glass transition temperatures of the single components and that, irrespective of blend composition, no significant shift in such T_g values, after the addition of the uPP-g-PS copolymer, is observed. Notwithstanding these results indicating the immiscibility of the uPP-g-PS phase with both the iPP and PS phases in the amorphous condensed state, the melt morphologies exhibited by the iPP/aPS/uPP-g-PS blends show that the iPP crystal growth starts from nonhomogeneous melts.

Optical micrographs taken at crossed and parallel polarizers of thin films of iPP/aPS binary and iPP/aPS/uPP-g-PS ternary blends isothermally crystallized at 126°C are reported in Figure 2; for comparison, optical micrographs taken at crossed and parallel polarizers of the thin films of plain



Figure 2 Optical micrographs taken at crossed and parallel polarizers of thin films of (a) binary iPP/aPS blends and (b) ternary iPP/aPS/uPP-g-PS 2% wt/wt, (c) iPP/aPS/uPP-g-PS 5% wt/wt, and (d) iPP/aPS/uPP-g-PS 10% wt/wt blends isothermally crystallized at 126°C.



Figure 3 Optical micrographs taken at crossed and parallel polarizers of thin films of plain iPP isothermally crystallized at 126, 130, 134, and 138°C.

iPP at the investigated T_c are reported in Figure 3. As shown in Figure 2, the iPP/aPS blend exhibits a defined spherulitic superstructure with the aPS phase segregated in spherical-shaped domains uniformly occluded in the iPP intra- and interspherulitic regions, the comparatively lower size of the spherulites presumably indicating a migration of heterogeneous nuclei from the aPS phase toward the iPP phase. Furthermore, no amorphous interspherulitic contact regions are developed; such regions are, on the other hand, shown by the plain iPP (compare Figs. 2 and 3). By comparing the aPS mode and the state of dispersion in the solid state with that in the melt state, it is seen that the crystallization process of the iPP phase freezes the melt morphology of the aPS phase (compare Figs. 1 and 2), such an effect being reasonably related to the relatively high rate of the iPP crystallization at the examined T_c . For a T_c of 126°C, very different morphologies are developed in the ternary iPP/aPS/uPP-g-PS blends depending upon the composition, that is, upon the uPP-g-PS content (wt/wt). The observations performed at parallel polarizers clearly display that, in the blends containing 2 and 5% (wt/

wt) of the uPP-g-PS copolymer, the dispersion coarseness of the minor component is much finer than that developed in the iPP/aPS binary blends (the finest dispersion coarseness being achieved for a uPP-g-PS content equal to 5% wt/wt). In contrast, a wide particle-size distribution, together with large and irregularly shaped domains of the minor component, is observed for a higher copolymer content (10% wt/wt) (see Fig. 2). The comparison between the melt morphologies of the iPP/aPS/uPP-g-PS blends with the morphologies generated after iPP complete crystallization (compare Figs. 1 and 2) surprisingly shows that, for an uPP-g-PS content up to 5% (wt/wt), the iPP crystallization process provides interconnected materials more homogeneous than those of corresponding melts, as a reduced average particle size and a narrowed particle-size distribution, together with spherulites whose neatness and regularity are noticeably damaged, are found. The ternary blend containing 10% (wt/wt) of the uPPg-PS copolymer exhibits, in contrast, a regular spherulitic texture. No amorphous interspherulitic contact regions are observed in all the ternary blends irrespective of the uPP-g-PS content (wt/wt).

For all the investigated samples, a T_c of the iPP phase increase of 4.0°C (130°C T_c) induces no relevant morphological effects on both the spherulite texture and mode and the state of the dispersion of the minor component (compare Figs. 2 and 4). The blends' morphology is, on the contrary, strongly modified by further increasing the T_c (134°C) (compare Figs. 2 and 5). For the binary iPP/aPS blends, the dispersion coarseness of the aPS domains increases, suggesting that during the iPP crystallization process a coalescence phenomenon is undergone by the primary particles formed in the melt state; the presence of aPS irregular-shaped domains, indicate the deformation work performed by the spherulite growing front. Moreover, the spherulitic texture is characterized by the presence, already evidenced for the plain iPP at lower T_c , of amorphous interspherulitic contact regions, with spherulites showing size, neatness, and regularity close to that exhibited by the spherulites of plain iPP (see Fig. 5). For the iPP/aPS/uPP-g-PS ternary blends, the increased T_c results in similar morphologies almost independent of the uPP-g-PS content (wt/wt) (see Fig. 5). The neatness, regularity, and size of the spherulites of such iPP phases are, in fact, close to each other and lower than those shown by the iPP phase crystallized from the iPP/aPS melts, with no amorphous material being rejected at the spherulitic boundary regions. Note that, for the ternary blends containing a low uPP-g-PS content (2 or 5% wt/wt), the dispersion coarseness achieved by isothermally crystallizing such materials at 134°C is noticeably higher than that developed at a lower $T_c~(126~{\rm and}~130^{\circ}{\rm C})~({\rm compare}$ Figs. 2 and 4 with Fig. 5), approaching that observed in the melt state (compare Figs. 5 and 1). No relevant difference in the mode and state of the dispersion of the minor component is, on the other hand, found with increasing T_c for the ternary blends containing a high uPP-g-PS content (10% wt/wt). A further T_c increase (138°C) evidences, for all the investigated samples, a coalescence phenomenon of the domains of the dispersed phase that tend to be rejected from the crystallization front at the boundary of the spherulites and in the interspherulitic amorphous contact regions (compare Figs. 1 and 6).

Plots of the radius of the iPP spherulites crystallized from melts of the plain iPP and the binary and ternary blends against time for all the



Figure 4 Optical micrographs taken at crossed and parallel polarizers of thin films of (a) binary iPP/aPS blends and (b) ternary iPP/aPS/uPP-g-PS 2% wt/wt, (c) iPP/aPS/uPP-g-PS 5% wt/wt, and (d) iPP/aPS/uPP-g-PS 10% wt/wt blends isothermally crystallized at the 130°C.



Figure 5 Optical micrographs taken at crossed and parallel polarizers of thin films of (a) binary iPP/aPS blends and (b) ternary iPP/aPS/uPP-g-PS 2% wt/wt, (c) iPP/aPS/uPP-g-PS 5% wt/wt, and (d) iPP/aPS/uPP-g-PS 10% wt/wt blends isothermally crystallized at 134°C.

crystallization temperatures investigated give straight lines, indicating that, irrespective of composition, the concentration of propylenic crystallizable sequences at the growth front is constant during the crystallization process. For high undercooling, the values of the radial growth rate (G) of the iPP spherulites depend on the blend composition, whereas with reduced undercooling, such values are almost constant, approaching those calculated for the plain iPP (see Fig. 7). In particular for high undercooling, the spherulites of the iPP phase, grown from the iPP/aPS/uPPg-PS melts and containing 5% of the copolymer (wt/wt), show a G value lower than that found both for the spherulites grown from the melts of plain iPP and the spherulites grown from the remaining ternary melts. Such a finding could be accounted for by a comparatively higher molecular entanglement concentration influencing the activation free energy for the transport process through the liquid–solid interface (ΔF^*) according to the well-known Turnbull-Fisher equation



Figure 6 Optical micrographs taken at crossed and parallel polarizers of thin films of (a) binary iPP/aPS blends and (b) ternary iPP/aPS/uPP-g-PS 2% wt/wt, (c) iPP/aPS/uPP-g-PS 5% wt/wt, and (d) iPP/aPS/uPP-g-PS 10% wt/wt blends isothermally crystallized at 138°C.

and/or by the phenomena of rejection, occlusion, and deformation of the dispersed domains by the growing spherulites according to Galeski and Martuscelli.⁸ Insofar as the particular activation of the free energy for the transport process through the liquid-solid interface is concerned, it is, moreover, to be taken into account that the problem of the conversion to surface nucleation and lamellar growth, earlier treated by Turnbull and Fisher, requires consideration of a number of new features, such as accounting for the work of chain folding, the quite different nature of the transport mechanism (reptation) in the polymer melt, the effect of the chain length, the segmental nature of the polymer chain, and questions related to the substrate length and the nature of a surface nucleus on a bladelike structure.⁹ For high undercooling, the remaining ternary blends show G values higher than that exhibited by the plain iPP (see Fig. 7). It could be therefore hypothesized that, for high undercooling, the rate of transport of the iPP crystallizable sequences in

the iPP/aPS/uPP-g-PS melts can be retarded or promoted, depending upon a combination of thermodynamic and kinetic effects related to the phase nature and concentration in the immediate regions of the growing lamellae and to the mode and state of dispersion of the minor component in the melt state.

DSC Studies

The thermograms of isothermally crystallized samples of plain iPP and its binary iPP/aPS and ternary iPP/aPS/uPP-g-PS blends show, for all investigated crystallization temperatures, a single endothermic peak when heated from room temperature up to 200°C. The temperatures corresponding to the maxima of such peaks (T'_m) are reported in Table II. The crystallinity indices of the blends (X_c) and of the iPP phase $[X_c(iPP)]$ for the T_c investigated are reported in Tables III and IV, and respectively. As shown in Tables II-IV and as expected, the apparent melting temperature values and crystallinity indices of all the investigated samples tend to increase with increasing crystallization temperature. For a given T_c , the following results are remarked upon:

- The T'_m values shown by the iPP phase crystallized from the binary iPP/aPS and ternary iPP/aPS/uPP-g-PS blends are within experimental error independent of the composition, that is, such values are comparable to that exhibited by the plain iPP.
- The crystallinity indices of the iPP/aPS binary blends are considerably lower than that exhibited by the plain iPP, the extent of such a decrease becoming larger with reduced undercooling (see Table III).
- The iPP/aPS/uPP-g-PS ternary blends show X_c values that are composition-dependent, that is, such values tend to decrease with increasing uPP-g-PS content (wt/wt).
- The X_c values of the iPP phase crystallized from the iPP/aPS binary blends are lower than that shown by the plain iPP, indicating that the presence in the melt state of segregated aPS domains (see Fig. 1) interferes with the iPP crystallization process.
- The X_c values of the iPP phase crystallized from the iPP/aPS/uPP-g-PS ternary blends are comparable to that shown by the plain iPP. Taking into account that, at the investigated T_c , the copolymer propylenic sequences cannot crystallize,⁸ such findings could suggest, in agreement with the morphological results, a



Figure 7 Plots of the radial grow rate (*G*) of iPP spherulites isothermally crystallized from melts of plain iPP, binary iPP/aPS, and ternary iPP/aPS/uPP-g-PS as a function of the crystallization temperature (T_c).

compatibilization effect of the uPP-g-PS copolymer in reducing the aPS dispersion coarseness. Smaller particles can be, in fact, more easily ejected by the iPP crystallizing front.

Small-Angle X-ray Scattering Studies

Typical Lorentz-corrected desmeared patterns for isothermally crystallized samples of binary iPP/ aPS and ternary iPP/PS/uPP-g-PS blends are shown in Figure 8. As shown, such SAXS profiles exhibit well-defined maxima. By applying Bragg's law, the long period (L) of the iPP phase was calculated from the peak position. Assuming a two-phase model for the iPP spherulite fibrils, consisting of alternating parallel crystalline lamellae and amorphous layers, the crystalline la-

Table II Apparent Melting Temperatures (T'_m) for Plain iPP and iPP Crystallized from Its Blends as a Function of the Crystallization Temperature (T_c)

	T_m' (°C)			
Sample	$T_c = 126$ °C	$T_c = 130^{\circ}\mathrm{C}$	$T_c = 134$ °C	$T_c = 138^{\circ}\mathrm{C}$
iPP	164	166	169	171
iPP/aPS	163	165	167	170
iPP/aPS/uPP-g-PS graft 2% (wt/wt)	163	165	167	169
iPP/aPS/uPP-g-PS graft 5% (wt/wt)	163	165	166	169
iPP/aPS/uPP-g-PS graft 10% (wt/wt)	163	164	166	169

		Χ	ζ_c	
Sample	$T_c = 126$ °C	$T_c = 130^{\circ}\mathrm{C}$	$T_c = 134$ °C	$T_c = 138$ °C
iPP	0.50	0.52	0.53	0.54
iPP/aPS	0.37	0.38	0.40	0.41
iPP/aPS/uPP-g-PS graft 2% (wt/wt)	0.38	0.40	0.41	0.42
iPP/aPS/uPP-g-PS graft 5% (wt/wt)	0.38	0.38	0.39	0.40
iPP/aPS/uPP-g-PS graft 10% (wt/wt)	0.36	0.36	0.38	0.40

Table III Crystallinity Indices (X_c) of Plain iPP, iPP/aPS, and iPP/aPS/uPP-g-PS Blends as a Function of the Crystallization Temperature (T_c)

mellar thickness (L_c) was calculated using the following relation for the *L* values:

$$L_{c} = \frac{X_{c(iPP)}L}{(\rho_{c}/\rho_{a})(1 - X_{c(iPP)}) + X_{c(iPP)}}$$
(4)

where $X_{c(iPP)}$ is the DSC crystallinity index of the iPP phase and ρ_c and ρ_a are the densities of the crystalline and amorphous iPP phases, respectively.

The thickness of the amorphous interlamellar layer (L_a) was calculated by

$$L_a = L - L_c \tag{5}$$

The long period, lamellar thickness, and amorphous interlamellar thickness of the plain iPP and the iPP crystallized from its binary and ternary blends are reported in Tables V–VII as a function of the T_c . As to be expected for both plain iPP and iPP crystallized from the binary iPP/aPS and ternary iPP/aPS/uPP-g-PS blends, the L and L_c values increase with increasing crystallization

temperature (see Tables V and VI). On the other hand, for a given T_c , there is no clear dependence of the L values upon composition. It is interesting to observe that when, for a given T_c , iPP crystallizes in the presence of aPS the phase structure developed in the binary blends is characterized by a crystalline lamellar thickness and an interlamellar amorphous layer thickness lower than and comparable to that shown by plain iPP (see Tables VI and VII). Such findings confirm that the iPP crystallization process from the iPP/aPS melts is strongly affected by the presence of the aPS domains. For the iPP phase crystallized from the ternary blends, irrespective of the T_c , no significant increases in the *L* values are found, thus indicating that the uPP-g-PS phase is not present between the iPP lamellae. Notwithstanding this, the uPP-g-PS addition results in an average crystalline thickness of the iPP phase closely approaching that exhibited by the plain iPP. The L_a values of the iPP phase can be considered to be within the experimental error (see Table VII). Such results seem to support the hypothesis that

Table IV Crystallinity Indices of iPP Phase as a Function of the Crystallization Temperature (T_c)

		X_{c}	$X_{c(\mathrm{iPP})}$	
Sample	$T_c = 126^{\circ}\mathrm{C}$	$T_c = 130^{\circ}\mathrm{C}$	$T_c = 134$ °C	$T_c = 138^{\circ}\mathrm{C}$
iPP	0.50	0.52	0.53	0.54
iPP/aPS	0.46	0.48	0.50	0.51
iPP/aPS/uPP-g-PS graft 2% (wt/wt)	0.48	0.51	0.52	0.53
iPP/aPS/uPP-g-PS graft 5% (wt/wt)	0.50	0.50	0.52	0.53
iPP/aPS/uPP-g-PS graft 10% (wt/wt)	0.49	0.50	0.53	0.56



Figure 8 Typical SAXS Lorentz-corrected desmeared profiles for isothermally crystallized samples of binary iPP/aPS and ternary iPP/aPS/uPP-g-PS blends.

the uPP-g-PS copolymer, owing to its capability to reduce the particle size, could minimize the interference of the aPS domains on the nucleation and growth processes of the iPP lamellae. By plotting the apparent melting temperature (T'_m) , obtained by DSC, versus the inverse of the crystalline lamellar thickness of the iPP phase $(1/L_c)$, straight lines can be drawn (see Fig. 9).

		L	(Å)	
Sample	$T_c = 126$ °C	$T_c = 130^{\circ}\mathrm{C}$	$T_c = 134$ °C	$T_c = 138^{\circ}\mathrm{C}$
iPP	183	188	219	232
iPP/aPS	171	188	202	219
iPP/aPS/uPP-g-PS graft 2% (wt/wt)	171	175	197	225
iPP/aPS/uPP-g-PS graft 5% (wt/wt)	175	197	208	239
iPP/aPS/uPP-g-PS graft 10% (wt/wt)	171	197	197	232

Table V Long Period (L) Values for Plain iPP and iPP Crystallized from Its Blends as a Function of the Crystallization Temperature (T_c)

	L_c (Å)			
Sample	$T_c = 126$ °C	$T_c = 130$ °C	$T_c = 134$ °C	$T_c = 138^{\circ}\mathrm{C}$
iPP	87	93	111	120
iPP/aPS	75	86	96	106
iPP/aPS/uPP-g-PS graft 2% (wt/wt)	78	90	98	119
iPP/aPS/uPP-g-PS graft 5% (wt/wt)	83	94	105	121
iPP/aPS/uPP-g-PS graft 10% (wt/wt)	80	94	97	124

Table VI Crystalline Lamella Thickness (L_c) Values for Plain iPP and iPP Crystallized from Its Blends as a Function of the Crystallization Temperature (T_c)

Thus, the trend of T'_m against the L_c can be described by the following relation:

$$T'_{m} = T_{m} - \frac{2\sigma_{e}T_{m}}{\Delta H_{f}} \frac{1}{L_{c}}$$
(6)

where T'_m is the apparent melting temperature; ΔH_f , the enthalpy of the fusion of 100% crystalline iPP; L_c , the crystalline lamellar thickness; T_m , the equilibrium melting temperature; and σ_e , the surface free energy of folding. According to this equation, T_m and σ_e can be determined, respectively, from the intercept and slope of the straight lines obtained by plotting T'_m against $1/L_c$. The T_m and σ_e values, determined by this method, are reported in Table VIII. As shown in the table, the plain iPP shows T_m and σ_e values in line with those reported in the literature,⁵ whereas the iPP phase crystallized in the presence of the aPS phase or the aPS and uPP-g-PS phases show both T_m and σ_e values lower than those found for the plain iPP, confirming that the

presence of such components interferes with the iPP crystallization process. Moreover, lower T_m values of the iPP phase grown from its blends indicate that, for a given T_c , the crystal growth occurred under comparatively lower undercooling. The folding surface free energy can be expressed by the fundamental thermodynamic equation⁹

$$\sigma_e = \Delta H_e - TS_e \tag{7}$$

where ΔH_e is the folding surface enthalpy, and S_e , the folding surface entropy. The σ_e variation can be attributed to a variation of the S_e term. Therefore, the observed decrease in the σ_e values, shown by the iPP crystals grown from the iPP/ aPS and iPP/aPS/uPP-g-PS melts, is presumably due to an increase in the S_e term, that is, a higher surface disorder of the lamellar crystals. It is interesting to observe that, by plotting T_m and σ_e values of the iPP phase crystallized from its blends versus the uPP-g-PS content (wt/wt),

Table VII Interlamellar Amorphous Layer Thickness (L_a) Values for Plain iPP and iPP Crystallized from Its Blends as a Function of the Crystallization Temperature (T_c)

		L_a	(Å)	
Sample	$T_c = 126$ °C	$T_c = 130^{\circ}\mathrm{C}$	$T_c = 134$ °C	$T_c = 138^{\circ}\mathrm{C}$
iPP	96	95	108	112
iPP/aPS	96	102	106	113
iPP/aPS/uPP-g-PS graft 2% (wt/wt)	93	90	99	106
iPP/aPS/uPP-g-PS graft 5% (wt/wt)	92	103	105	118
iPP/aPS/uPP-g-PS graft 10% (wt/wt)	91	103	95	108



Figure 9 Plots of the apparent melting temperatures (T'_m) versus the inverse of lamellar thickness $(1/L_c)$ of the iPP phase isothermally crystallized from melts of plain iPP, binary iPP/aPS, and ternary iPP/aPS/uPP-g-PS.

straight lines can be drawn (see Figs. 10 and 11), and indicating a linear dependence of such thermodynamic parameters upon the composition, that is, a linear decrease of T_m and σ_e values with an increasing copolymer content (wt/wt). Such results can be accounted for by an increase of the presence of defects and by the very irregular and perturbed surface of iPP crystals with increasing uPP-g-PS content. Work is in progress to estab-

Table VIII Equilibrium Melting Temperature (T_m) and Surface Free Energy of Folding (σ_e) Values of Plain iPP and iPP Phase Crystallized from Its Binary and Ternary Blends

Sample	T_m (°C)	$\sigma_e \ ({ m erg/cm}^2)$
iPP	189	118
iPP/aPS	185	97
iPP/aPS/uPP-g-PS graft 2% (wt/wt)	185	97
iPP/aPS/uPP-g-PS graft 5% (wt/wt)	182	90
iPP/aPS/uPP-g-PS graft 10% (wt/wt)	180	80

lish if the decrease observed is related to morphological and/or miscibility effects by investigating the influence of the crystallization conditions on the morphology and thermal behavior of the samples of the binary iPP/uPP-g-PS blends isothermally crystallized in the same T_c range of the iPP phase. Taking into account all the above results,



Figure 10 Plots of the equilibrium melting temperatures (T_m) of the iPP phase as a function of uPP-g-PS content (wt/wt).



Figure 11 Plots of the surface free energy of the folding (σ_e) of lamellar crystals of the iPP phase as a function of uPP-g-PS content (wt/wt).

the lamellar structure of the iPP phase developed in binary iPP/aPS and ternary iPP/aPS/uPP-g-PS blends is compared to that generated in plain iPP according to the schematic models reported in Figure 12.

CONCLUSIONS

Samples of blends of iPP and aPS, isothermally crystallized at 126, 130, 134, and 138°C, exhibit a coarse morphology of the aPS phase whose domains are occluded in the iPP intra- and interspherulitic contact regions. For comparatively higher undercooling, owing to the relatively high

rate of the iPP crystallization at the examined T_c , the crystallization process of the iPP phase freezes the melt morphology of the aPS phase. With reduced undercooling, the dispersion coarseness of the aPS domains increases, suggesting that during the iPP crystallization process a coalescence phenomenon is undergone by the primary particles formed in the melt state; the presence of aPS irregular-shaped domains indicate the deformation work performed by the spherulite growing front. Moreover, for a given T_c , the lamellar crystals in the iPP spherulites fibrils are characterized by an average crystalline thickness lower than that developed in the plain iPP. The addition of the uPP-g-PS copolymer is found to affect the interfacial tension between the iPP and aPS phases in the melt state, with the aPS particle size and the particle-size distribution being. in fact, strongly modified. After complete crystallization of the iPP phase at 126, 130, 134, and 138°C, the presence of the uPP-g-PS phase modifies not only the aPS mode and the state of dispersion, but also the iPP spherulitic texture and inner structure of the spherulites fibrils. The extent of the induced modifications, that is, the degree of compatibilization achieved, depends upon a combination of the composition and undercooling. For high undercooling, a comparatively higher homogeneous texture and finer dispersion coarseness is shown by the material containing the 5% of the uPP-g-PS copolymer. With reduced undercooling, a coalescence phenomenon of the domains of the dispersed phase, which tends to be rejected by the crystallization front at the bound-



Figure 12 Schematic models of the lamellar structure of the iPP phase crystallized under controlled undercooling from melts of plain iPP, iPP/aPS, and iPP/aPS/uPP-g-PS blends.

ary of the spherulites and in the interspherulitic amorphous contact regions, is observed in all the ternary blends. It is interesting to remark that, for a given T_c , the phase structure generated in the PP/aPS/uPP-g-PS materials is characterized by an average crystalline lamellar thickness comparable to that shown by the plain iPP. Moreover, relevant thermodynamic parameters of the iPP phase, crystallized from its ternary blends, are strongly affected by the presence of the uPP-g-PS phase, the observed effect being composition-dependent. As a matter of fact, the values of both the equilibrium melting temperature (T_m) and of the surface free energy of folding (σ_{e}) of the iPP lamellar crystals decrease linearly with increasing uPP-g-PS PS content in the blends. Such results have been accounted for by an increase of the presence of defects and by the very irregular and perturbed surface of iPP crystals with increasing uPP-g-PS content. The observed decrease in T_m values indicates, moreover, that, in the iPP/aPS/uPP-g-PS blends, the iPP crystal growth occurs under comparatively lower undercooling, in line with crystalline lamellar thickness values determined by SAXS investigation.

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