Quiescent Crystallization Kinetics and Morphology of i-PP Resins for Injection Molding. III. Nonisothermal Crystallization of the Heterophasic and Grafted Polymers

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ABSTRACT: The quiescent nonisothermal crystallization kinetics of heterophasic and grafted polypropylene resins was measured. Differential scanning calorimetry, polarized light optical microscopy, Fourier Transform infrared spectroscopy, dynamic mechanical thermal analysis and scanning electron microscopy were used to study this kinetics. It was observed that a modified Hoffman and Lauritzen equation could be used to describe the nonisothermal growth rate, G_n , of some of the heterophasic and grafted polymers. The heterophasic samples with the highest amount of ethylene and the maleic anhydride grafted polymer did not show similarity between their G_n and their isothermal crystallization rate, G. The G_n s of the heterophasic and grafted polymers were higher than the G_n s of the homopolymers. The heterophasic polymer showed several secondary crystallization peaks that were associated to the crystallization of ethylene-rich copolymers and other copolymers with different amounts of polypropylene comonomer. Some of the heterophasic samples showed a distribution of rubber particles in the spherulite. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1741–1753, 1999

Key words: heterophasic polypropylene; grafted polypropylene; nonisothermal crystallization; morphology; crystallization kinetics

INTRODUCTION

In the second part of this work,¹ the nonisothermal crystallization kinetics of isotactic polypropylene resins (i-PP) was studied as a function of their weight-average molecular weight M_w . A modified Hoffman and Lauritzen equation was used to describe the increase of the spherulitic radius with time; the agreement between the theoretical radius and the experimental one was excellent. It was also found that the nonisothermal crystallization growth rate G_n of all the samples was similar to the corresponding isothermal rate G; and also, like G, G_n was dependent on the M_w . A prior isothermal nucleation procedure (PIN) was used, and it was found to be valid; its use allowed us to obtain data at higher temperatures and cooling rates than the ones found in the literature.

In this work, we will continue to study the nonisothermal crystallization kinetics of i-PP resins, as a function of the amount of ethylene, the so-called heterophasic copolymers, and the amount of grafting, using the same experimental procedure as in Part II of this work.¹

THEORETICAL BACKGROUND

Materials

Heterophasic copolymers of i-PP, PP-EPR, are toughened thermoplastics, with a high impact

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Heterophasic Samples	% Ethylene (w/w) in the Synthesis	Melt Flow Index (g/10 min)	% Ethylene Copolymer–Rubber
C1	6.8	5.7	_
C2	10.3	5.7	_
C3	13.0	5.4	6.4 - 38.3
C4	9.0	1.0	_
Grafted			Melt Flow Index
Samples	% MA, Final (w/w)	% AA, Final (w/w)	(g/10 min)
PPgAM1	0.18		190.0
PPgAM2	0.54		4.7
PPgAM3	0.18		5.0
PPgAA		6.0	

Table 1 Resins Used in This wor	able I	I Resins	s Used in	n This	Work
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strength. They consist mainly of an i-PP matrix in which particles of ethylene–propylene rubber (EPR) are embbedded. The discrete rubber particles absorb and dissipate the impact energy by inhibiting crack propagation. Early studies² have shown that no crazes nucleate from any rubber particle with a diameter smaller than 0.5 μ m. Recent studies³ on the effect of the size distribution of these particles on the impact strength of the i-PP have shown that this size distribution needs to be broad and that the broader the distribution, the better the toughening of the i-PP at low temperatures.

The heterophasic polymer can be made either by postreactor blending or by a two-reactor system^{4,5}; in this last case, i-PP is made in a first reactor, while the EPR is made in a second reactor. The i-PP is blended sequentially with the EPR by adding the i-PP into the second reactor while the EPR is still being polymerized. Therefore, PP–EPR is a mixture of i-PP, EPR, and partially crystalline copolymers.

i-PP can also be grafted with a maleic anhydride monomer (MA) or an acrylic acid monomer (AA), in order to obtain reactive centers^{6,7} in the main chain that will allow the interaction of nonpolar i-PP with polar polymers like polyesters and polyamides and inorganic fillers. The grafted polymers are used mainly as compatibilizing agents in blends and composites, and usually in small quantities.

The grafting is made by molten or solution processes. In both cases, residual monomers remain in the matrix.

Nonisothermal Crystallization

As pointed out in part II of this work,¹ a modified Hoffman and Lauritzen equation was used in a recent study⁸ to fit the nonisothermal crystallization data of i-PP in dotriacontane. This equation can be written as

$$egin{aligned} G_n &= G_{on} \, \exp\!\left[rac{-U^*}{\mathrm{R}[(T_m-lpha t)-T_{\infty})}
ight] \ & imes \exp\!\left[rac{-\mathrm{K_g}\{T_m^o+(T_m-lpha t)\}}{2(T_m-lpha t)^2\{T_m^o-(T_m-lpha t)\}}
ight] \end{aligned}$$

where G_{on} is the pre-exponential factor containing quantities not strongly dependent on temper-



Figure 1 Spherulitic radii with and without the PIN procedure for sample C4 at -5° C min.



Figure 2 Experimental and calculated radii of all the heterophasic polymers: (a) sample C1; (b) sample C2; (c) sample C3; (d) sample C4.

ature, U^* is the activation energy for reptation in the melt (1500 cal/mol), R is the gas constant, T_m is the temperature at which the first measurable data is recorded, α is the constant cooling rate, T_{∞} is the theoretical temperature at which reptation ceases $\cong T_g$ -30K, T_g is the glass transition temperature, K_g is the nucleation constant, and T_m^o is the equilibrium melting temperature.

Numerical integration of this equation allows to calculate the nonisothermal spherulite radius r_{en} as a function of time because $G_n = dr_{en}/dt$. Like in part II, this approach will also be used in this work.

EXPERIMENTAL

Materials

The heterophasic and grafted polymers were kindly donated by OPP Petroquimica do Brasil. The grades used in this work are listed in Table I.

Nonisothermal Crystallization

Polarized Light Optical Microscopy

 G_n was measured by using a polarized light optical microscope, from Leica, model DMRXP, a hot stage from Linkam, model THMS600, and an attached video camera from Kappa, as already described in part II.¹ The samples were first melted at 200°C for 5 min, and then cooled at -100°C/ min down to 138°C. After the visible formation of the nuclei, the samples were again cooled down to room temperature, at -5°C/min. Tests were also run with an iron constantan thermocouple of d= 75 μ m, inserted into the samples, as also described in part II.¹

Differential Scanning Calorimetry

Thermal data was also obtained by using a differential scanning calorimeter from Perkin-Elmer, model DSC-7, under a N_2 atmosphere. The experimental conditions were already described in part II of this work.¹

Fourier Transform Infrared Spectroscopy

Films of 20–30 μ m of thickness were prepared by compression molding in a hot press at 160°C, during 30 s; after the compression, the films were cooled down to room temperature. The films were analyzed in Fourier transform infrared (FTIR) equipment from Perkin–Elmer, model Spectrum 1000, with a resolution of 2 cm⁻¹.

Dynamic Mechanical Thermal Analysis

 T_g was measured by using a dynamic mechanical thermal analyzer, from Polymer Labs. The experimental conditions were described in part I of this work.⁹

Morphology

Besides the polarized light optical microscopy (PLOM) micrographs, scanning electron micrographs of the PLOM samples were also taken by using a scanning electron microscope (SEM) from Carl Zeiss, model 940-A, after coating with gold by vacuum metallization. The rubber particles in the heterophasic samples had their average sizes and size distribution analyzed by using a MO-CHA software, 1.2.10 version, from Jandel Scientific (Corte Madera, CA), after removing the elas-tomeric phase with a chromic acid solution, as described in part I of this work.⁹

RESULTS AND DISCUSSION

Nonisothermal Crystallization

As described in part II,¹ a PIN procedure was used to measure G_n . To confirm the validity of this procedure for the heterophasic polymers, measurements were also made with and without PIN. Figure 1 shows the results for sample C4. It can be observed that the agreement between both spherulitic radii is excellent; therefore, the PIN procedure is also valid for the heterophasic polymers. It can also be observed that the PIN procedure allows to obtain data at higher temperatures than the experiments without PIN.

The numerical integration of eq. (1) allowed to calculate r_{en} as a function of time. Figure 2 shows both radii, experimental and calculated, of the



Figure 3 Experimental and calculated radii of sample PPgAM2.

heterophasic polymers. It can be seen that the agreement between both radii is excellent for sample C4, good for samples C2 and C3, and poor for sample C1. In this last case, the experimental radius was higher than the calculated one at the early stages of the crystallization process. Sample C1 had the smallest amount of ethylene of all the samples; we assumed that the lower the amount of ethylene in the synthesis, the lower the amount of EPR; therefore, probably at the early stages of crystallization, the EPR particles were trapped intraspherulitically due to its small amount or bigger sizes, and the experimental radius was higher than the expected. At the intermediate and final stages of the crystallization process, there was no more EPR particles, and the crystallization process was only of the i-PP alone.

Figure 3 shows both radii for sample PPgAM2. The agreement is excellent. It seems that the MA grafting, due to its small amount, does not influence the diffusion and reptation of the whole PP chain during the crystallization process.

After the G_{on} best value was obtained, it was possible to calculate a theoretical G_n as a function of temperature by using eq. (1). These results for the heterophasic samples are shown in Figure 4. G, from Carvalho and Bretas,⁹ and G_n (derivative) are also shown for comparison. G_n (derivative) was calculated as the derivative of the experimental radius versus time curves. It can be observed that for samples C2 and C4, the agreement between G, G_n (derivative), and G_n (theoretical) was excellent, thus confirming the general trend observed in the homopolymers in part II of this work.¹ For sample C1, G_n (derivative) was lower than G_n (theoretical); therefore, eq. (1) did



Figure 4 G_n (derivative), G_n (theoretical), and G of all the heterophasic samples: (a) sample C1; (b) sample C2; (c) sample C3; (d) sample C4.

not describe with accuracy the nonisothermal crystallization of this sample. This was expected because, as shown in Figure 2, the calculated



Figure 5 G_n (derivative), G_n (theoretical), and G of sample PPgAM2.

radius did not superimpose to the experimental one. For this sample, G_n (derivative) was found to be similar to G. For sample C3, G_n (derivative) was higher than G_n (theoretical); again, eq. (1) did not describe with accuracy the nonisothermal crystallization of this sample. However, in this last case, both G_n s were found to be lower than G. We attributed this behavior to experimental errors.

Table II	Values	of G _{on}	as	Found	by	Fitting
Equation	(1)					

Sample	G_{on} (µm/min)	G_{on}/G_o
C1	$2.047~ imes~10^{13}$	1.25
C2	$7.840~ imes~10^{12}$	1.07
C3	$2.180~ imes~10^{14}$	0.83
C4	$4.080~ imes~10^{12}$	1.10
PPgAM2	$2.275~ imes~10^{13}$	1.34

	Cooling								
	Rate	T_{c}	ΔH_c	$T_c \; (^{\circ}\mathrm{C})$	$\Delta H_c~({\rm J/g})$	$T_c~(^{\circ}\mathrm{C})$	$\Delta H_c~({\rm J/g})$	$T_c \; (^{\circ}\mathrm{C})$	$\Delta H_c~({\rm J/g})$
Sample	(C/min)	(°C; Main)	(J/g; Main)	Peak (a)	Peak (a)	Peak (b)	Peak (b)	Peak (c)	Peak (c)
C1	5	114.4	84.3	90.5	1.1				
C1	10	112.1	80.1	86.7	1.5				
C1	20	108.8	80.5	80.6	1.7				
C1	30	107.3	80.1	75.5	1.5				
C1	40	104.8	79.0	70.2	1.6				
C1	50	102.7	78.8	70.3	1.7				
C2	5	114.5	67.4	104.3	0.29	93.9	1.2	86.9	0.09
C2	10	112.0	67.0	102.4	0.52	89.9	1.3		
C2	20	109.3	72.9	97.5	0.37	85.8	$2.0^{\mathrm{b,c}}$	82.5	b,c
C2	30	106.7	67.9	82.0	$1.9^{\mathrm{a,b}}$	80.1	a,b		
C2	40	104.9	73.2	80.0	$2.2^{\mathrm{a,b,c}}$	72.1	a,b,c	65.6	a,b,c
C2	50	102.6	72.2	78.0	$2.0^{\mathrm{a,b}}$	64.5	a,b		
C3	5	114.1	71.2	92.3	1.5	83.2	0.1		
C3	10	111.8	70.9	86.9	1.9	68.8	0.03		
C3	20	108.5	69.9	84.5	2.1				
C3	30	106.2	70.7	88.4	0.03	78.4	$2.0^{\mathrm{a,b}}$	66.0	1.2
C3	40	103.6	69.6	73.6	$2.3^{\mathrm{a,b}}$	65.1	a,b		
C3	50	101.6	68.2	63.7	2.1				
C4	5	113.9	72.4	91.7	1.8				
C4	10	111.9	71.5	88.9	1.7				
C4	15	110.4	70.6	88.5	2.5				
C4	20	108.6	72.0	84.3	2.0				
C4	30	106.6	72.0	81.2	2.0				
C4	40	106.6	72.6	82.1	2.5				
C4	50	103.0	72.6	77.4	1.8				
PPgAA	5	133.1	89.3						
PPgAA	10	129.3	87.3						
PPgAA	20	124.5	89.5						
PPgAA	30	121.8	87.9						
PPgAM2	5	117.2	87.5						
PPgAM2	10	114.1	87.0						
PPgAM2	20	109.7	84.2						
PPgAM2	30	107.0	83.6						
PPgAM2	40	104.8	82.1						
PPgAM2	50	102.8	83.7						

Table III Main and Secondary Crystallization Peaks as Obtained by DSC

Peaks (a), (b), and (c) are secondary crystallization peaks.

^{a,b} Peaks (a) and (b) were superimposed; ΔH_c total = $\Delta H_c(a) - \Delta H_c(b)$. ^{a,b,c} Peaks (a), (b), and (c) were superimposed; ΔH_c total = $\Delta H_c(a) - \Delta H_c(b) - \Delta H_c(c)$.

Figure 5 shows G, G_n (derivative), and G_n (theoretical) for sample PPgAM2. In this case, both G_n s were similar; therefore, eq. (1) described the nonisothermal crystallization kinetics of this sample well. However, both G_n s were higher than G. Again, no explanation could be found for this dissimilarity. Table II shows the G_{on} values found for our samples.

It can be observed that the G_{on} s of the heterophasic and grafted polymers were higher than the G_{on} s of the homopolymers;¹ therefore, the G_n s

of the heterophasic and grafted polymers are higher than the G_n s of the homopolymers, even the ones with the highest molecular weight. It seems that the EPR particles and the MA grafting are acting as nucleating agents during the nonisothermal crystallization. Because no data could be found in the literature regarding the values of G_{on} of the heterophasic and grafted polymers, we could not compare them to test their accuracy as we did with the homopolymers.¹

Table III shows the general behavior of the



Figure 6 $(T_{onset} - T_c)$ of the heterophasic polymers as a function of the cooling rate.

crystallization temperature T_c and the crystallization heat ΔH_c of the polymers as a function of the cooling rate.

It can be observed that the first T_c , which corresponds to the crystallization temperature of the i-PP matrix of the heterophasic polymers, decreased as the cooling rate increased, as expected, independently of the amount of ethylene or kind of grafting. It can also be observed that these heterophasic polymers had more than one crystallization peak, peaks a, b, and c.

Mirabella⁴ used a temperature-rising elution fractionation technique (TREF) to separate and to analyze the structure of a PP–EPR blend of MFI = 6.0 g/10 min. He found that the blend was mainly composed of 75 wt % of i-PP, 17 wt % of EPR, and 8 wt % of semicrystalline ethylenepropylene copolymers. A major component of these semicrystalline copolymers was an ethylene-rich copolymer, containing no observable propylene up to 8 wt % of propylene comonomer. Therefore, the secondary peak, the (a) peak, can be associated to the crystallization of these ethylene-rich copolymers. However, samples C2 and C3 showed other secondary peaks, peaks (b) and (c); these samples had the higher amount of ethylene, therefore, these peaks can be attributed to the crystallization of the other ethylene-propylene copolymers with different amounts of propylene comonomer.

In the grafted polymers, secondary crystallization peaks were not observed. However, it seems that the AA grafting had a strong nucleating effect on the PP because the PPgAA crystallization temperature was 20°C higher than of the PPgAM. Liberman et al.,¹⁰ in samples of PP grafted with

Table IV Melting Temperatures T_m and Heat of Fusion ΔH_m of the Samples as Measured by DSC

Sample	T_m (°C)	$\Delta H_m~({\rm J/g})$
C1	167.0 (0.5)	76.0 (0.5)
C2	165.8 (0.9)	67.7 (1.8)
C3	166.7 (0.6)	66.4 (1.0)
C4	165.7(0.4)	72.4(5.3)
PPgAM2	165.4(0.2)	74.8(3.2)
PPgAA	164.8(0.5)	90.2(2.5)
C1 C2 C3 C4 PPgAM2 PPgAA	$\begin{array}{c} 167.0\ (0.5)\\ 165.8\ (0.9)\\ 166.7\ (0.6)\\ 165.7\ (0.4)\\ 165.4\ (0.2)\\ 164.8\ (0.5)\end{array}$	$\begin{array}{c} 76.0 \ (0.5) \\ 67.7 \ (1.8) \\ 66.4 \ (1.0) \\ 72.4 \ (5.3) \\ 74.8 \ (3.2) \\ 90.2 \ (2.5) \end{array}$

The number in parenthesis is the standard deviation.

AA, observed the same nucleating effect on the PP, even after purification of the samples to eliminate the AA residual monomer; however, they confirmed the presence of polyacrylic acid (PAA) in the samples by infrared (IR) spectroscopy. Later, they prepared mechanical blends of i-PP and PAA, but no nucleating effect of the PAA on the PP was observed. Thus, they concluded that the observed nucleating effect in the AA-grafted polymers was promoted by the chemically linked PAA to the i-PP chains.

It can also be observed that sample C3 had the lowest heat of crystallization. Figure 6 shows $(T_{\rm onset} - T_c)$ of the heterophasic polymers as a function of the cooling rate. $T_{\rm onset}$ is defined as the temperature at which crystallization begins, and T_c is the main crystallization peak. Therefore, $(T_{\rm onset} - T_c)$ is a measure of the width of the crystallization peak, and it can be related to the global or overall crystallization rate. The lower this temperature difference, the narrower the crystallization peak and the higher the overall



Figure 7 FTIR spectra of the heterophasic samples.



Figure 8 FTIR spectra of the PPgAA sample.

crystallization rate. It can be observed that $(T_{\text{onset}} - T_c)$ did not vary from sample to sample, confirming that the i-PP crystallization was the same, independent of the amount of ethylene and grafting; also, as expected, this temperature difference increased with the cooling rate.

Table IV shows the melting temperature and heat of fusion of the samples.

The melting temperature of the heterophasic and grafted polymers was almost the same, independent of the amount of ethylene or kind of grafting. However, the heat of fusion increased with the decrease in the amount of ethylene due to the higher amount of i-PP. Comparing with the homopolymers,¹ the heterophasic polymers had higher melting temperatures, indicating that more perfect crystallites were developed, due to



Figure 9 Loss moduli of the heterophasic samples as a function of temperature.

Table V T_{g} s of EPR and i-PP as Measured by DMTA

Sample	% Ethylene (Synthesis)	T_g (°C) EPR	T_g (°C) i-PP
C1	6.8	-43.6(0.57)	$\begin{array}{c} 6.31(0.46)\\ 6.45(0.40)\\ 6.05(0.38)\\ 4.86(1.79)\end{array}$
C2	10.3	-42.4(0.71)	
C3	13.0	-42.9(0.49)	
C4	9.0	-42.7(0.28)	

The number in parenthesis is the standard deviation.

their crystallization temperatures being higher than of the homopolymers.¹¹

Figure 7 shows the FTIR spectra of the heterophasic samples. The i-PP characteristic band is shown at 810 cm⁻¹. Studies¹² have shown that a band at 733 cm⁻¹ is characteristic of isolated



(a)



(b)

Figure 10 PLOM micrographs of sample C1 at different temperatures: (a) T = 134.0 °C, 200×; (b) T = 130.4 °C, 200×.



Figure 11 PLOM micrographs of sample C2 at different temperatures: (a) T = 134.8 °C, 200×; (b) T = 127.9 °C, 200×.

ethylene units between propylene sequencies, while a band at 722 cm⁻¹ occurs when two or more ethylene blocks are present. However, when ethylene crystallization occurs, this last band splits into two, one at 720 cm⁻¹ and the other at 729 cm⁻¹. It can be observed from Figure 7 that there is a well-defined peak at 720 cm⁻¹ and a shoulder at 729 cm⁻¹. Therefore, at least one of the secondary crystallization peaks observed by DSC is associated to the crystallization of ethylene sequencies in the semicrystalline ethylene– propylene copolymers.

Figure 8 shows the FTIR spectra of the PPgAA sample. The PAA characteristic bands can be observed, at 1710 and 3100 cm⁻¹, thus confirming that the grafted PAA is the one responsible for the nucleating effect. The IR spectra of the PPgAM2 sample (not shown) shows a small peak at 1785 cm⁻¹, characteristic of the carbonyl group of the

MA,⁶ the MA monomer can be in the form of a grafted monomer or a residual one.

Figure 9 shows the curves of the loss modulus E'' as a function of temperature of the heterophasic polymers. Two well-defined peaks can be observed: one, at -43° C, corresponds to the T_g of the EPR; the other, at 6°C, is associated with the T_g of the i-PP. It can be observed that the peak size associated to the EPR increased with the increase in the amount of ethylene; this is an indication that the amount of the EPR phase also increased with the increase in the amount of ethylene.

The T_g s of both phases are also shown in Table V.

It can be observed that the T_g of the EPR did not change with the increase in the amount of ethylene, or the EPR phase. Liberman et al.⁵ found that the T_g of the EPR varied with the

Figure 12 PLOM micrographs of sample C3 at different temperatures: (a) T = 130.9 °C, 200×; (b) T = 123.0 °C, 200×.

_____ 22.7 ,m

(b)

Figure 13 PLOM micrographs of sample C4 at different temperatures: (a) T = 133.5 °C, 200×; (b) T = 124.7 °C, 200×.

ethylene content in the rubber, decreasing as the ethylene content increased, up to $53-55 \mod \%$, where again, it begun to increase. Therefore, from our results, we can conclude that in our samples, the amount of ethylene in the rubber did not vary significantly, and it stays around 38%.

Morphology

Figures 10–13 show PLOM micrographs of the heterophasic samples at different temperatures. The rougher texture was observed in sample C3, probably due to its highest amount of EPR particles. Sample C4 that had the highest molecular weight of all the heterophasic samples also had a more radial and finer texture.

Figure 14 shows the follow-up of the spherulites morphology of sample PPgAM3. The dark, oily-like droplets are probably residual MA. Again, the texture was radial and fine. In Figure 15, the early stages and final stages of the nonisothermal crystallization of sample PPgAA are shown. In this case, it was not possible to measure the spherulites radius because there was no formation of well-defined, rounded spherulites. Also, the residual AA interfered with the crystallization, as can be seen in the final stages of the crystallization, Figure 15(b), where the formation of transcrystallites is observed.

Scanning electron micrographs of the PLOM samples were also taken; the grafted polymers did not show any different features than the ones observed by PLOM. However, the SEM of the heterophasic samples allowed to analyzed in detail their spherulites. Figure 16 shows SEM micrographs of different regions of one spherulite of sample C4 after the PIN procedure. The whole spherulite is shown in Figure 16(a); a variation in the amount of the EPR particles can be observed. In the center of the spherulite, as shown in Figure

Figure 14 PLOM micrographs of sample PPgAM3 at different temperatures: (a) T = 120.9 °C, $200 \times$; (b) T = 119.0 °C, $200 \times$.

(b)

Figure 15 PLOM micrographs of sample PPgAA at different temperatures: (a) early stages, T = 130.0 °C, $200 \times$; (b) final stages, T = 90.0 °C, $200 \times$.

16(b), there are few rubber particles. However, towards the spherulite periphery, the amount of these particles increases, as shown in Figure 16(c).

The particle size distribution of both regions are given in Figure 17. Figure 17(a) shows the particle size distribution at the center of the spherulite; it can be observed that the average particle size was 0.3942 μ m (±0.2063 μ m) from a total of 58 particles. A high percentage of these particles had diameters between 0.05 and 0.8 μ m. Figure 17(b) shows the particle size distribution at the spherulite periphery; the average particle size was $0.3472 \ \mu m \ (\pm 0.2397)$ μ m), from a total of 199 particles. A high percentage of the particles had diameters between 0.05 and 0.5 μ m. Therefore, the average particle size at the center of the spherulite is higher than the average particle size at the periphery of the spherulite, but the amount of EPR parti-

Figure 16 SEM micrographs of different regions of a spherulite of sample C4. (a) whole spherulite; (b) spherulite center; (c) spherulite periphery.

Figure 17 Size distribution of the EPR particles on different regions: (a) spherulite center; (b) spherulite periphery.

cles at the center is smaller than the amount of EPR particles at the periphery.

It seems that at all stages of the spherulite formation of sample C4, the PP crystallization growth rate was higher than the diffusion rate of rubber particles. Therefore, at the early stages of the spherulite growth, only big EPR particles, which have a low diffusion rate, were trapped intraspherulitically; at the later stages, small EPR particles, which have a high diffusion rate, were then trapped intraspherulitically. The variation in the particle size and amount of particles can be the result of the PIN procedure; the observation of spherulites without the PIN procedure by SEM is presently under way.

As already pointed out, we observed an excellent agreement between both radii of the sample C4, experimental and theoretical.

CONCLUSIONS

The following conclusions can be inferred from this work.

- 1. The PLOM nonisothermal experiments showed that the modified Hoffman and Lauritzen equation can be used to describe the nonisothermal crystallization growth rate of some of the heterophasic polymers, the ones with 9–10 wt % ethylene. The equation also describes with accuracy the nonisothermal crystallization growth rate of the grafted polymers.
- 2. Regarding the similarity between G_n and G, it was found that the heterophasic sample with the highest amount of ethylene and the MA grafted polymer did not show this similarity, probably due to experimental errors.
- 3. The PIN procedure was found to be valid, allowing to obtain data at higher temperatures than the without PIN procedure.
- 4. The G_n s of the heterophasic and grafted polymers were higher than the G_n s of the homopolymers, probably due to a nucleating effect promoted by the EPR particles and the grafted monomers.
- 5. The heterophasic polymers showed several secondary crystallization peaks that were associated to the crystallization of ethylenerich copolymers and other copolymers with different amounts of propylene comonomer.

- 6. The AA grafting had a higher nucleating effect on the PP than the MA grafting, probably due to the grafted PAA.
- 7. The heterophasic sample C4 had a distribution of EPR particle sizes in the spherulite; a small amount of bigger EPR particles were trapped in the spherulite center, while a high amount of smaller EPR particles were trapped in the spherulite periphery.

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