

NMR, Differential Scanning Calorimetry, and Fourier Transform Infrared Characterization of the Crystalline Degree and Crystallite Dimensions of Ethylene Runs in Isotactic Polypropylene/Ethylene–Propylene Copolymer Blends (iPP/EP)

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ABSTRACT: High-resolution solid-state ¹³C-NMR, differential scanning calorimetry, and Fourier transform infrared spectroscopy were used to compare the very low crystalline degree and crystallite dimensions of ethylene runs in a series of isotactic polypropylene/ethylene–propylene copolymer blends exhibiting a range of properties. Results obtained from the three techniques on samples with the same thermal history are in a satisfying qualitative agreement. They show that the morphology of the polyethylene domains is only very slightly dependent on the viscosity ratio of the two blend components. On the opposite, it is largely governed by the ethylene content of the ethylene–propylene copolymer. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3165–3172, 1999

Key words: ethylene–propylene copolymer; isotactic polypropylene; blends; infrared spectroscopy; solid-state NMR; crystallinity

INTRODUCTION

The enhancement of isotactic polypropylene (iPP) impact properties by introduction of a finely dispersed rubbery ethylene–propylene copolymer (EP) phase is a well-known process that is widely commercialized. The preparation of such blends (iPP/EP) directly in the polymerization reactors by means of a two-stage process with Ziegler–Natta catalysts gives rise to products that exhibit

a particularly good compromise between stiffness and toughness at low temperature. The mechanical properties of these materials are not only governed by the semicrystalline character of the iPP phase. The proportion and chemical composition of the elastomer component are also important parameters. Besides, as a consequence of the heterogeneity of active sites in Ziegler–Natta catalysts, some small crystalline ethylene runs exist in the elastomer phase.^{1,2} These inclusions stiffen the rubbery material. They also modify surface hardness,³ scratch resistance, tensile elongation,⁴ and impact behavior⁵ of compression molded samples and stress whitening⁶ behavior of injection

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Table I Percentages (w/w) of Ethylene Units in the EP Copolymer (%C2), Number Average Sequence Lengths for Methylene Sequences Containing Two Carbons at Least (n^{2+}), Ratios of the Viscosity of the EP Copolymer to the Viscosity of the iPP Polymer ($[\eta]_{EP}/[\eta]_{iPP}$), Percentages of EP Copolymer in the Blend (%EP), and Melt Flow Index (MFI)

	% C2	n^{2+}	$[\eta]_{EP}/[\eta]_{iPP}$	% EP	MFI (g/10 min)
PP/EP 7	58	8.9	1.40	12.4	5.9
PP/EP10	58	8.1	2.24	14.7	6.8
PP/EP14	57	8.6	0.76	12.1	5.2
PP/EP15	62	10.0	1.21	30.5	2.7
PP/EP16	55	8.7	1.25	30.0	2.5
PP/EP17	45	7.0	1.24	28.7	2.6
PP/EP18	37	5.7	1.15	24.3	2.9
PP/EP19	38	5.7	1.84	26.2	3.0

molded products. Therefore, a deeper understanding of structure–property relationships in these iPP/EP materials requires a precise knowledge of the morphology of the EP copolymer in the blends.

The present paper is devoted to the comparison of the crystalline degree and crystallite dimensions of ethylene runs in a series of iPP/EP blends exhibiting a range of properties. In these samples whose global crystallinity is largely dominated by the iPP component, X-ray diffraction does not allow to investigate small ethylene domains. On the opposite, the selectivity of differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and high-resolution solid-state ^{13}C -NMR allows us to study independently the behavior of each blend component. Results obtained from these three techniques will be reported hereafter.

A full characterization of the same series of samples, including ethylene content and ethylene distribution, has been performed using deconvolution of IR spectra. The results were reported, and compared with those from a parallel solution ^{13}C -NMR characterization, in a previous paper.⁷

EXPERIMENTAL

Materials

The iPP/EP samples were prepared at Solvay by a two-stage polymerization. Their compositions were determined by ^{13}C -NMR in 1,2,4-trichlorobenzene solution.⁷ The ethylene content and triad distribution were calculated according to Ray et al.⁸ The n^{2+} parameter is defined as the number-average sequence length for methylene sequences

containing two carbons at least. It was derived⁷ according to Randall.⁹

A viscosity ratio ($[\eta]_{Xs}/[\eta]_{Xi}$) can be derived from the intrinsic viscosities (measured in tetraline solution at 140°C) of the “xylene soluble” ($[\eta]_{Xs}$) and “xylene insoluble” ($[\eta]_{Xi}$) fractions of the polymer. The soluble fraction is obtained by recrystallization at room temperature after complete dissolution in xylene. The soluble and insoluble fractions are known to be representative respectively of the amorphous (EP) and of the crystalline (PP) parts of the whole polymer, thus, $[\eta]_{Xs}/[\eta]_{Xi} \approx [\eta]_{EP}/[\eta]_{iPP}$.

The percentages (w/w) of EP copolymer in the blend (%EP), and the percentage of ethylene units in the EP copolymer (%C2), the n^{2+} parameter, ($[\eta]_{EP}/[\eta]_{iPP}$), and melt viscosity index (MFI) are given in Table I for the different samples under study.

It must be noticed that the iPP/EP samples considered differ either by the viscosity ratio between the two components (PP/EP7 to 14), or by the ethylene content in the EP rubber (PP/EP15 to 18) or by both (PP/EP19).

High-Resolution Solid State ^{13}C -NMR

The high-resolution solid-state ^{13}C -NMR experiments were conducted at 75.47 MHz using a BRUKER CXP 300 spectrometer, with quadrature detection and a single radio frequency coil which was double tuned for both ^{13}C and ^1H . Experiments were carried out using the well-known techniques of proton dipolar decoupling (DD) magic-angle sample-spinning (MAS) and either direct polarization (DP) or cross polarization (CP). The matched spin-lock cross-polarization transfers were carried out with ^{13}C and ^1H mag-

netic field strengths of 62 kHz. The samples were contained in Al₂O₃ rotors. The spinning speed was around 4000 Hz. Spin-temperature inversion techniques allowed the minimization of baseline noise and roll.¹⁰

The pulse sequence used for the $T_{1\rho}$ (¹H) determination was the delayed-contact cross-polarization pulse sequence described by Stejskal et al.¹¹

According to Clayden,¹² the lamellar thicknesses of the crystalline ethylene runs in the samples were determined from the ratio of the proton magnetization (M) after two spin-lock times τ_{sl} , chosen as 1 and 5 ms:

$$R_i = \frac{M_i(\tau_{sl} = 5 \text{ ms})}{M_i(\tau_{sl} = 1 \text{ ms})} \quad (1)$$

where $i = a$ and $i = c$ indicate the amorphous and crystalline phases, respectively. As a fixed contact time of 1 ms was used, which, according to Clayden¹² is treated as part of the overall ¹H spin-lock time, no additional delay was used in the case of the 1-ms delayed contact, whereas a 4-ms delay was used for the case of 5-ms delayed contact experiment.

Qualitative information on the crystallinity of the sample was derived from the C/A ratio where C and A are the heights of the lines assigned to carbons located in small crystalline and amorphous ethylene runs, respectively, in the MAS/CP/DD ¹³C-NMR obtained by using a 1-ms contact time. The contribution to the 30-ppm line, which is due to the partial overlap from the intense 26 ppm-line, corresponding to iPP carbons, was suppressed by modeling the 26-ppm peak with the lineshape observed on the 5-ms delayed contact cross-polarization ¹³C-NMR spectrum, which does not contain any contribution from the amorphous ethylene runs, and subtracting it from the 1-ms contact time cross-polarization ¹³C-NMR spectrum.

Fourier Transform IR

The samples used for the FTIR investigations were films obtained by compression molding: the polymer was introduced in a metallic mold between two aluminum foils. It was pressed between two flat mold plates at 200°C and a 10-ton pressure for 30 s. Then, the molten sample was rapidly quenched in water. The film thicknesses were of the order of 100 μm in order to get a suitable absorbance in the 680–800 cm^{-1} region.

FTIR spectra were recorded using a Perkin-Elmer 1760 X spectrometer. The resolution was 1 cm^{-1} . Ten scans were signal averaged.

The FTIR data analysis was performed by using the method described in a previous paper.⁷

Differential Scanning Calorimetry

The DSC traces were obtained using a PERKIN-ELMER DSC-7 series apparatus. The first run was performed from room temperature to 220°C at a 10°/min heating rate. Then, samples were successively annealed for 10 min at 220°C and cooled at a 10°/min cooling rate down to room temperature. The melting temperature T_m was defined as the temperature of the maximum of the melting endotherm. The crystallinity was derived from the area under the corresponding melting peak, using $\Delta H = 290 \text{ J/g}$.

Transmission Electron Microscopy

The transmission electron microscopy (TEM) samples were trimmed and subsequently stained with RuCl₃ × H₂O in NaClO during 8 h. RuCl₃ preferentially oxidizes the amorphous regions which will appear darker on the TEM images. Sixty nm thick sections were then cut at room temperature with a diamond knife. The microscope was a Philips CM301 apparatus operated at 80 kV.

RESULTS

As described in the preceding paper,⁷ the ethylene crystallinity can be determined from FTIR spectra using a suitable calibration curve. Results thus obtained are summarized in Table II, together with data from DSC experiments.

As shown in the MAS/CP/DD ¹³C-NMR spectrum obtained by using a 1-ms contact time for the iPP/EP system (Fig. 1), two lines are observed at 30.0 and 33.1 ppm for the methylene carbons of the ethylene sequences. By comparison with the polyethylene ¹³C-NMR spectrum,¹³ they can be assigned to carbons located in small amorphous and crystalline ethylene runs, respectively. This assignment is supported by the direct polarization ¹³C-NMR spectrum with a short repetition time (1 s; Fig. 2), which discriminates against the crystalline areas, and the CP pulse sequence with a very short contact time (20 μs ; Fig. 3), which discriminates against the amorphous carbons.¹⁴

Table II Melting Temperatures T_m and Crystallinities of Ethylene Runs as Measured by DSC and FTIR

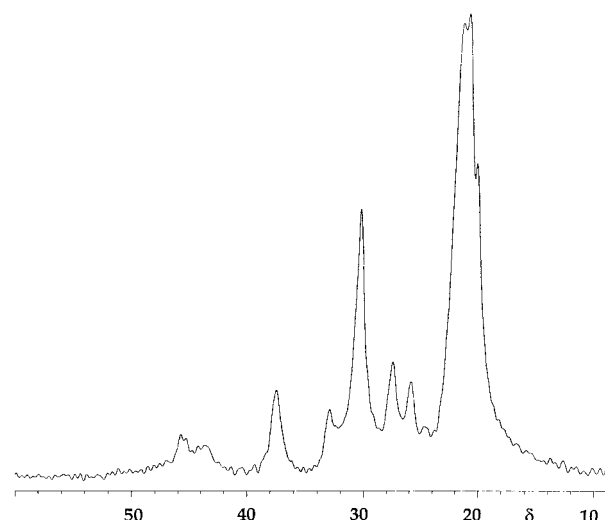
	T_m (°C)	PE Crystallinity (%)	
		DSC	FTIR
PP/EP 7	120.1	0.39	1.8
PP/EP10	115.0	0.19	1.5
PP/EP14	119.5	0.25	1.6
PP/EP15	119.6	1.21	4.6
PP/EP16	117.8	0.79	3.4
PP/EP17	116.3	0.42	2.3
PP/EP18	115.2	0.15	1.3
PP/EP19	114.4	0.03	1.4

As an example, the $T_{1\rho}$ (^1H) decays of the amorphous and crystalline ethylene runs in PP/EP7 are shown in Figure 4. The R_a , R_c , and C/A ratios are listed in Table III for all the samples together with the thicknesses, La and Lc , of the amorphous and crystalline lamellae calculated by using data reported by Clayden.¹²

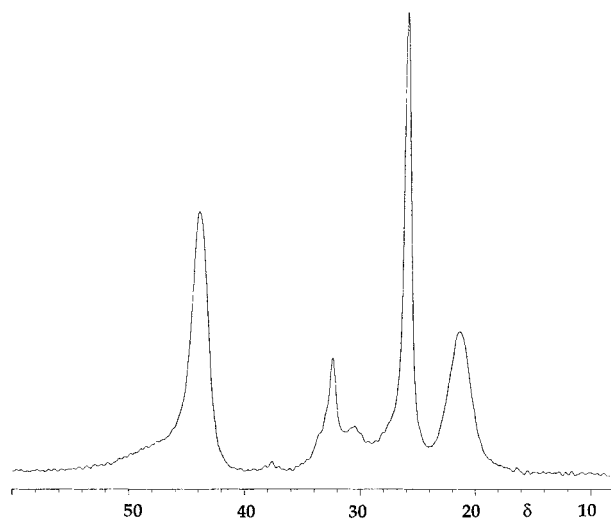
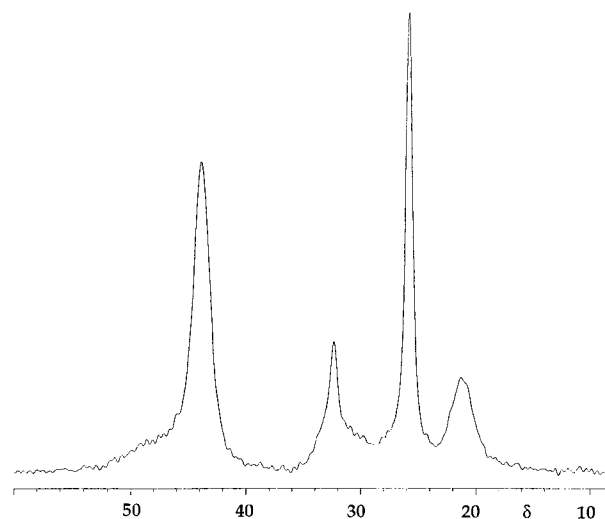
DISCUSSION

Crystallinity of Ethylene Runs in iPP/EP Samples

Particular attention has been paid to the PP/EP15 to 18 blends that differ by the ethylene content (%C2) of the EP rubber, all other param-

**Figure 2** Direct polarization MAS/DD ^{13}C -NMR spectrum of PP/EP15 sample with a 1-s repetition time.

eters being kept approximately constant (Table I). As shown in Figure 5, both FTIR and DSC data show that the amount of crystalline ethylene runs increases with the ethylene content in the EP rubber. The relationship between the PE crystallinity as measured by infrared and DSC and the methylene number-average sequence length, as measured by solution ^{13}C -NMR, n^{2+} , is shown in Figure 6. As expected, these results indicate that the ethylene content (%C2—Table I) and ethylene sequence distribution (n^{2+} —Table I) of the EP copolymer are of major importance for determining the PE crystallinity of iPP/EP blends.

**Figure 1** MAS/CP/DD ^{13}C -NMR spectrum of an iPP/EP sample obtained using a 1-ms contact time.**Figure 3** MAS/CP/DD ^{13}C -NMR spectrum of PP/EP15 sample obtained using a 20- μs contact time.

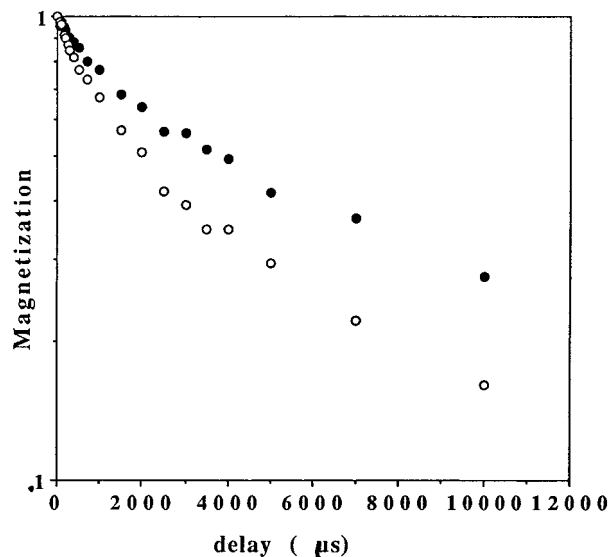


Figure 4 $T_{1\rho}({}^1\text{H})$ decays of the amorphous (○) and crystalline (●) ethylene runs in PP/EP7 sample.

The C/A ratio is qualitatively related to the relative extents of the crystalline and amorphous regions. In order to test the validity of the C/A ratio as an indicator of crystallinity, the $100C/(C + A)$ ratio was plotted as a function of the PE crystallinity as determined for the ethylene runs either from FTIR (Fig. 7) or from DSC (Fig. 8) for the PP/EP15 to 18 blends. In both cases, a very good linear relationship is observed for the samples with the same viscosity ratio, which implies that the quantity derived from the solid-state ${}^{13}\text{C}$ -NMR experiments is proportional to the degree of crystallinity.

It is also of interest to compare results obtained for PP/EP14, 7, and 10. Data reported in Tables II and III show that, whatever the sample (PP/EP14, 7, and 10) or the technique used, the crystallinity of ethylene runs is very low and of the

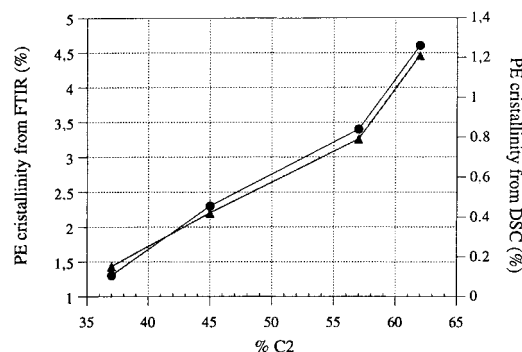


Figure 5 Dependencies of the crystallinities as determined by DSC (▲) and FTIR (●) as a function of %C2 in PP/EP15–18 blends.

same order of magnitude in the three samples. As indicated in Table I, these samples differ mainly by the values of their viscosity ratio, $[\eta]_{\text{EP}}/[\eta]_{\text{iPP}}$. Therefore, under the experimental conditions of the synthesis, the viscosity ratio appears to have no significant influence on the crystallinity of the ethylene domains. This last conclusion is supported by data obtained on PP/EP18 and 19. These two samples, whose characteristics given in Table I are very different from those of PP/EP14, 7, and 10, also differ from each other only by their viscosity ratio $[\eta]_{\text{EP}}/[\eta]_{\text{iPP}}$. In agreement with results observed for PP/EP14, 7, and 10, the solid-state NMR and FTIR measurements indicate that PP/EP18 and 19 exhibit very similar crystallinity degrees.

Crystallite Dimensions

As indicated in Table III, the thicknesses of the PE crystalline lamellae L_c are very small in all the samples considered. They correspond to crystalline domains that contain only a few ethylene monomer units. The same result is observed for

Table III C/A Ratios, R_a , R_c , and Lamellar Thicknesses of Crystalline and Amorphous Ethylene Runs

Sample	R_a	L_a (nm)	R_c	L_c (nm)	C/A
PP/EP7	0.35	0.53–0.68	0.49	0.75–0.98	0.79
PP/EP10	0.31	0.60–0.75	0.43	0.70–0.90	0.73
PP/EP14	0.28	0.51	0.40	0.80–1.00	0.79
PP/EP15	0.25	0.75–0.90	0.50	0.80–1.20	1.52
PP/EP16	0.20	0.74–1.18	0.46	0.75–1.05	1.18
PP/EP17	0.18	0.88–1.48	0.38	0.60–0.80	0.97
PP/EP18	0.18	0.88–1.48	0.32	0.53–0.75	0.82
PP/EP19	0.16	0.88–1.55	0.29	0.45–0.66	0.76

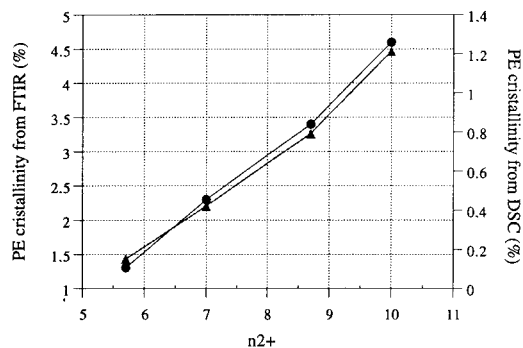


Figure 6 Dependencies of the crystallinities as determined by DSC (▲) and FTIR (●) as a function of n^{2+} in PP/EP15–18 blends.

the amorphous domains. It must be noticed that the L_a and L_c values are very close to those determined by Clayden¹² by performing the same experiments on very similar samples. These small domain dimensions are due to the random character of the EP copolymer.

The L_a and L_c values are very similar for PP/EP14, 7, and 10, which differ mainly by the values of their viscosity ratio, $[\eta]_{EP}/[\eta]_{iPP}$. Just as for the crystallinity degree, the viscosity ratio appears to have no significant influence on the sizes of the crystalline and amorphous domains. L_c values reported in Table III show that the size of the crystalline ethylene domains, decreases progressively from PP/EP15 to PP/EP16, 17, and 18. Simultaneously, a slight increase in the dimension L_a of the amorphous regions is observed. It is interesting to notice that PP/EP15–18 samples have almost identical viscosity ratios, melt viscosity indexes, MFI, and very close contents of EP

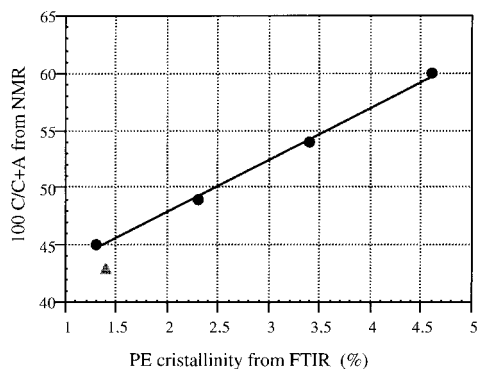


Figure 7 100 $C/(C + A)$ ratios obtained from NMR measurements versus PE crystallinity obtained from FTIR measurements [●, low viscosity ratio; ▲, high viscosity ratio].

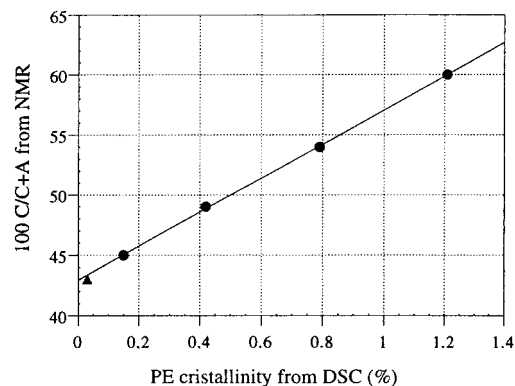


Figure 8 100 $C/(C + A)$ ratios obtained from NMR measurements versus PE crystallinity obtained from DSC measurements [●, low viscosity ratio; ▲, high viscosity ratio].

copolymer in the blend. They mainly differ by the composition of the EP copolymer whose ethylene content decreases progressively from PP/EP15 to PP/EP18. The ethylene content in PP/EP18 is about half of the ethylene content of PP/EP15. Therefore, results listed in Table III for these samples clearly demonstrate that the size of the crystalline ethylene units is strongly dependent on the ethylene content in the EP copolymer. Moreover, the NMR measurements seems to indicate that the sizes of both amorphous and crystalline ethylene domains are slightly lower for the PP/EP19 sample, which has a higher viscosity ratio, as compared to the PP/EP18 sample with the same ethylene content.

The relationships between the thicknesses of the amorphous and crystalline ethylene runs, and the ethylene content in the EP copolymers are

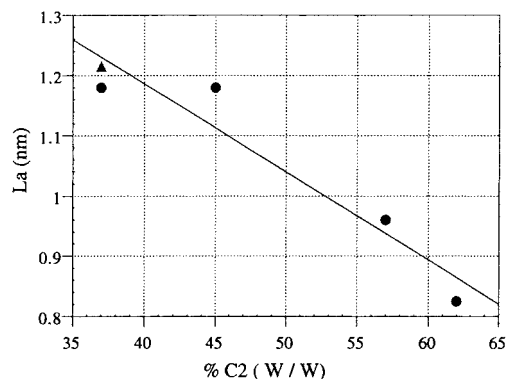


Figure 9 Dependence of the thicknesses of the amorphous ethylene runs L_a as a function of the ethylene content in the EP copolymers.

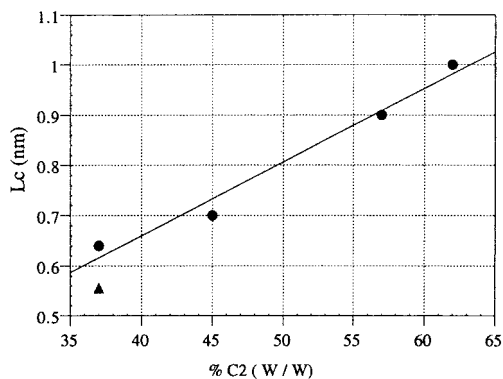


Figure 10 Dependence of the thicknesses of the crystalline ethylene runs L_c as a function of the ethylene content in the EP copolymers.

explicitated in Figures 9 and 10. Figure 10 shows that L_c exhibits a quasi-linear dependence vs % C2.

The dependence of the melting temperature T_m measured at the maximum of the DSC peak for the crystalline ethylene regions, as a function of the lamellar thickness L_c is plotted on Figure 11. Within experimental accuracy, a linear relationship is observed between T_m and L_c , according to the Gibbs–Thomson equation:

$$T_m = T_{m0} \left(1 - \frac{2\sigma_e}{L_c \Delta H} \right) \quad (2)$$

where ΔH is 280 J/cm^3 , it is possible to extract values of T_{m0} (thermodynamic equilibrium temperature) = 126°C and σ_e (surface energy associated with the crystalline phase) = 2.5 mJ/m^2 . Both values are significantly smaller than those

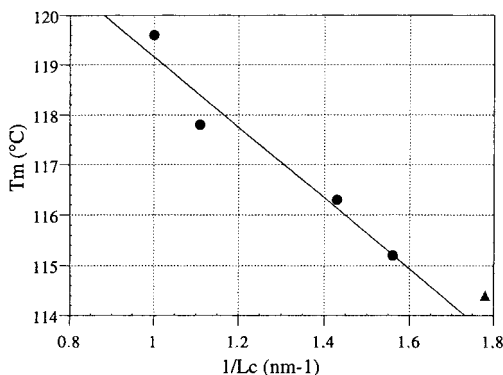


Figure 11 Dependence of the melting temperature T_m as a function of the lamellar thickness L_c [●, low viscosity ratio; ▲, high viscosity ratio].

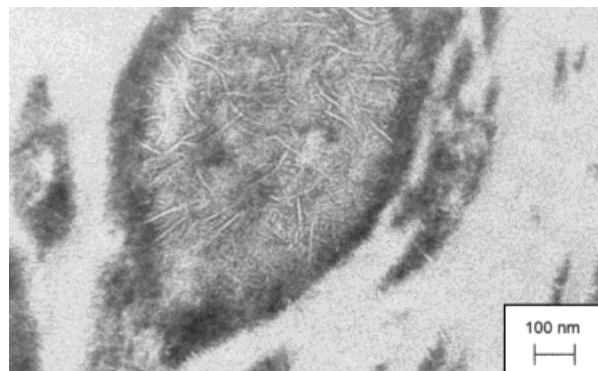


Figure 12 TEM images obtained on sections from PP/EP18 (upper) and PP/EP15 (lower) samples.

derived for pure polyethylene: $T_{m0} = 146^\circ\text{C}$ and σ_e comprised between 40 and 230 mJ/m^2 . These discrepancies could result from the very small size of the crystallites, which should be considered closer to bidimensional rather than tridimensional crystals.

Nevertheless, the use of the same equation for $T_m = 115.2$ and 119.6°C (measured respectively for PP/EP18 and PP/EP15 samples) and $\sigma_e = 9.3 \cdot 10^{-6} \text{ J/m}^2$ ¹⁵ gives a lamellar thickness range of about 8 – 10 nm which is more consistent with the observed apparent size of polyethylenic lamellae visible into the EP nodules for these two samples (Fig. 12).

This suggests that the relative values and evolution of L_c calculated according to Clayden's model¹² for the different samples are in good agreement with the theory but that their absolute values are however questionable in regard to the experimental data.

CONCLUSION

The combination of high-resolution solid-state ^{13}C -NMR, DSC, and FTIR provides an interesting

means for comparing the crystallinity of the ethylene domains in iPP/EP blends. A good correlation has been evidenced between the measurements obtained by the three techniques. The dimensions of the very small amorphous and crystalline ethylene domains that are found in these materials were evaluated by high-resolution solid-state ^{13}C -NMR. Results thus obtained have shown that the morphology of the ethylene domains is nearly independent on the value of the viscosity ratio. On the opposite, it is largely governed by the ethylene content of the EP copolymer.

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