Composites based on PP/EPDM blends and aramid short fibres. Morphology/behaviour relationship

M. Arroyo[a,*], R. Zitzumbo[b], F. Avalos[c]

[a]*Instituto de Ciencia y Tecnologia de Polímeros, C.S.I.C. Juan de la Cierva 3, 28006 Madrid, Spain*
[b]*Ciatec A. C. Omega no. 201, Fracc. Delta, C.P. 37540 León, Guanajuato, Mexico*
[c]*Univ. Aut. Coahuila. Blv. Carranza y Cárdenas, 25000 Saltillo, Coahuila, Mexico*

Abstract

The effect of both a thermoplastic elastomer (EPDM) and short aramid fibres on polypropylene (PP) crystallization kinetics and tensile behaviour has been investigated. The results have shown that PP/EPDM blends are non-miscible in the melt, and, at low EPDM percentages in the blend (<25%), the particles of EPDM act as nucleating agents and co-crystallize with PP. However, at higher percentages, the EPDM obstructs the mobility of PP chains and hence decreases the PP crystallization rate. Aramid fibres are effective nucleating agents for PP crystallization, giving rise to the phenomenon of PP transcrystallinity on their surface. The tensile behaviour of the blends and composites are in intimate relation with the morphological characteristics of these materials. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Composites; PP/EPDM blends; Aramid short fibres

1. Introduction

Due to the wide range of properties as a function of their composition and production technique used, blends of polypropylene (PP) and ethylene–propylene(-diene) EP(D)M copolymers and terpolymers permit the design of "tailored" materials [1] and have been widely investigated during the last decade.

Polypropylene is a versatile material with very interesting characteristics which make it a high consumption polymer. However, due to its relatively high transition temperature, it has poor impact behaviour, especially at low temperatures. In order to improve this deficiency, different impact modifiers, such as poly-isobutylene [2], poly-isoprene [3], natural rubber [4], ethylene–propylene-diene terpolymers [3,5], etc. have been used. The most effective impact modifiers have resulted to be the EPDMs with percentages of about 25–30% in volume. However, little research has been carried out on PP/EPDM blends with a wide composition range [6,7] in order to investigate the effect of the different components on the morphology of the blends, mainly to analyse the effect of EPDM on PP crystallization [1,8–10].

On the other hand, the crystallization kinetics of semi-crystalline thermoplastic polymer matrices are deeply modified in the presence of fibres [11]. Furthermore, in semicrystalline thermoplastic composites, crystallization and transcrystallization around the reinforcing fibres have a critical influence on their mechanical properties due to the improvement of the adhesion at the polymer/fibre interface [12].

The main goal of the present study is to investigate the crystallization of PP in the presence of low and high EPDM percentages in the blend. Furthermore, the effect of aramid fibres on the PP crystallization kinetics and the morphological/mechanical behaviour relationship of the blends and composites are also investigated.

2. Experimental

2.1. Materials

Isotactic polypropylene (PP) (melt flow index: 2.9 at 190°C and 5 kg, and density: 0.905 g/cm^{-3}) was supplied by Repsol Química S.A. under the trade name Isplen PP-050. Ethylene–propylene-diene rubber (EPDM), in pellets, medium molecular weight, with ethylidene norbornene as termonomer (4.5%), ethylene content of about 68%, medium cure rate, was supplied by Bayer under the trade name Buna EPT 6470 P (Mooney viscosity: 55 ± 5 MU, ML (1 + 8), 125°C. Density: 0.86 g/cm^3). Aramid short fibres (6 mm long) were supplied by Akzo Nobel under

* Corresponding author. Tel.: +34-91-562-2900; fax: +34-91-564-4853.

Table 1
Composition of the studied materials

Material	PP (%)	EPDM (%)	Aramid fibre (%)
1	100	0	–
2	90	10	–
3	75	25	–
4	50	50	–
5	25	75	–
6	0	100	–
7	100	0	10
8	75	25	10
9	50	50	10
10	25	75	10
11	0	100	10
12	100	0	20
13	75	25	20
14	50	50	20
15	25	75	20
16	0	100	20

the trade name Twaron 1080. The fibres were adequately washed in order to eliminate their water-repellent treatment.

2.2. Preparation and rheological behaviour of blends and composites

The pellets of PP and EPDM were previously weighed and physically blended in order to prepare the compounds as compiled in Table 1. The compounding was carried out in a Haake Rheocord 9000 internal mixer with two Banbury type rotors, at 190°C and 50 rpm for 23 min. Along this period of time a constant value of the torque was obtained for the homopolymers, blends and composites. Reinforced blends were prepared following the same procedure, and, in this case, the fibres were incorporated into the internal mixer 5 min after the initiation of the PP/EPDM blends plastification. The rheological behaviour of the materials was analysed through the torque vs time diagrams.

The compounds were compression moulded in a Collins Press, at 200°C, in order to obtain plaques of 3 mm thickness.

2.3. Thermal analysis

The thermal analysis of the materials was carried out in a Perkin Elmer DSC-7 scanning calorimeter, previously calibrated with indium and the base line adjusted in a temperature range of 50–200°C. Samples of about 5–7 mg were taken from the moulded plaques. Melt temperatures and degree of crystallinity of the samples were determined as follows: the samples were heated to 200°C at a heating rate of 10 K/min and maintained at this temperature for 5 min in order to eliminate any previous thermal history and then rapidly cooled to the crystallization temperature, T_c, and maintained at that temperature till the time necessary for the complete crystallization of the matrix. The heat evolved during the isothermal crystallization (ΔH_c) was recorded as a function of time, at different crystallization temperatures.

The experiments were carried out in nitrogen atmosphere and the isotherms were constructed by integrating the area under the exothermic peak. After crystallization the samples were heated to the melting point at a rate of 10 K/min.

The melting temperatures (T_m) and enthalpies of fusion (ΔH_m) of the composites were calculated from the maximum and the area under the endothermic peak, respectively. The crystallization degree (X_c) was determined according to the next relation: $X_c = 100 \ (\Delta H / \Delta H_0)$, where ΔH is the enthalpy of fusion of the polypropylene as calculated from the DSC results, and ΔH_0 is the enthalpy of fusion of the 100% crystalline polypropylene. In all calculations a crystal heat of fusion of 209 J/g has been taken for the polypropylene [13].

The kinetic parameters of the polymers have been calculated from the Avrami equation [14,15] which is expressed as follows:

$$\log[-\log(1 - X_c)] = n \log t + \log K_n / 2.3 \qquad (1)$$

where X_c is the crystallization degree at time t. K_n and n are the crystallization kinetic constant and the Avrami exponent, respectively. These parameters can be used to interpret qualitatively the nucleation mechanism and morphology, and overall crystallization rate of the polymers. By plotting $\log[-\log(1 - X_c)]$ vs $\log t$, a straight line is obtained whose slope and intersection with the Y-axis corresponds to the n and K_n values, respectively.

Finally, the crystallization thermodynamics and kinetics of the samples have been analysed on the basis of the secondary nucleation theory of Hoffman and Lauritzen [16] that is expressed by the next equation:

$$(1/n)\log K_n + \Delta F / 2.3RT_c$$

$$= A_0 - (4b_0 \sigma \sigma_e T_m)/(2.3 k_B \Delta H_f T_c \Delta T) \qquad (2)$$

(where $\Delta T = T_m^0 - T_c$, σ and σ_e are the free energies per unit area of the surfaces of the lamellae parallel and perpendicular to the chain direction, respectively. The equilibrium melting temperatures (T_m^0) were obtained from the melting temperature vs crystallization temperature plots (Hoffman–Weeks plots) [17]. ΔH_f is the enthalpy of fusion and b_0 is the distance between two adjacent fold planes. k_B is the Boltzmann constant. If it is assumed that the spherulite nucleus density is independent of time, ΔT, blend composition and T_m, then A_0 may be considered constant. ΔF is the activation energy for the transport process at the liquid–solid interphase and can be calculated with a high precision from the Williams–Landel–Ferry equation [18] given by the next expression:

$$\Delta F = F_{WLF} = (C_1 T_c)/(C_2 + T_c - T_g) \qquad (3)$$

where C_1 and C_2 are constants whose values are assumed to be 4.12 kcal/mol (17.24 kJ/mol) and 51.6 K, respectively (the T_g of pure PP was taken as 260 K). When plotting $(1/n) \log K_n + \Delta F / 2.3RT_c$ vs $T_m/T_c \Delta T$, the value of $4b_0 \sigma \sigma_e / k_B \Delta H_f$ can be calculated from the slope of the
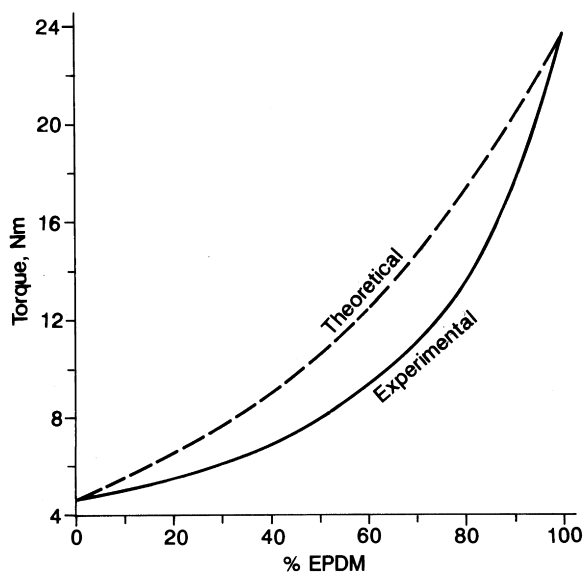
Fig. 1. Theoretical and experimental curves of torque vs EPDM percentage in the PP/EPDM blend.

straight lines, and having in mind that b_0, σ, ΔH_f, and the Boltzmann constant, k_B, have the following values given by the literature: 5.24 Å, 11 mJ/m^2, 209×10^3 J/kg, and 1.35×10^{-23} J/mol K, respectively, it is possible to calculate the value of the free energy of chainfolding of isotactic polypropylene lamellar crystals, σ_e, as a function of composite composition.

2.4. Morphological analysis

The morphology and the radial growth rates of the spherulites were studied on thin films by using an optical polarizing microscope Leika Metalographic Aristomet model, with a Mettler FP-90 automatic hot-stage thermal control. Samples were sandwiched between microscope cover glass, melted at 200°C for 10 min and then rapidly cooled to the crystallization temperature. The PP spherulitic growth was observed by taking micrographs at due intervals of time.

In order to analyse the morphology of the composites, fracture surfaces of several samples were observed in a Jeol T330A scanning electron microscope.

2.5. Mechanical properties

The specimens for tensile testing were cut from the compression moulded plaques according to standard specifications. Tensile tests were carried out on an Instron 4301 model, equipped with a video-extensometer, at room temperature, and at a cross-head speed of 0.1 and 1.5 cm/min to measure the modulus and the tensile strength, respectively.

3. Results and discussion

3.1. Rheological behaviour

As can be seen in Fig. 1, the final constant value of the torque obtained during the preparation of the PP/EPDM blends increases as EPDM content increases. Having in mind that, in the stationary state and at the same temperature and shear rate, the value of the torque is proportional to the melt viscosity [19], it can be deduced from Fig. 1 that the viscosity of the melted blend does not follow the logarithm additive rule [20] which is expressed as follows:

$$\ln \eta_{blend} = w_1 \ln \eta_1 + w_2 \ln \eta_2 \tag{4}$$

where: w_1 and w_2 are the weight fractions and η_1 and η_2 are the viscosity of the blend components in the melt state, respectively.

As can also be seen in Fig. 1, the torque of the PP/EPDM blends does not increase linearly. However, in all cases, the torque is lower than the theoretical value as calculated from Eq. (4). This can be attributed to the immiscibility of the components of the blend in the melt state in agreement with Coran and Patel [21,22] which in previous studies on PP/EPDM blends concluded that both components are immiscible in the melt. This conclusion is also supported by the studies of Utracki and Schlund [20] which showed two different conditions to get immiscibility in blends, the lack of superposition of the viscosities of the blend in the stationary and dynamic states, and the decrease of the maximum strength at breaking in one direction extensional flow. Both conditions are in agreement with our results. The first one has been showed in Fig. 1, and the second will be discussed later.

3.2. Thermal analysis (DSC)

In order to analyse the effect of the elastomer on the PP crystallization, at different temperatures, the PP crystallinity degree, as calculated from the crystallization isotherms of the blends vs EPDM percentage, is graphically represented in Fig. 2. At any temperature, the PP crystallinity is higher in the the blends with low percentages of EPDM (<20% b.w.) than in the plain polymer. However, above this EPDM percentage in the blend, the PP crystallinity tends to decrease as EPDM content increases. From Fig. 3, it can be deduced that, at the fibre percentages that have been used in this study, the PP crystallinity decreases as fibre percentage in the composite increases. However, and as is shown in Fig. 4, at the same matrix composition, the PP crystallinity is higher in the PP/EPDM/kevlar composites than in the polymer blends.

At first, it can be thought that, at low EPDM percentages, the continuous phase is clearly constituted by the PP, and, in the melt, a discontinuous phase of softened particles of EPDM can act as a nucleating agent for the PP. Moreover, it is also well known [23–25] that fibres act as nucleating
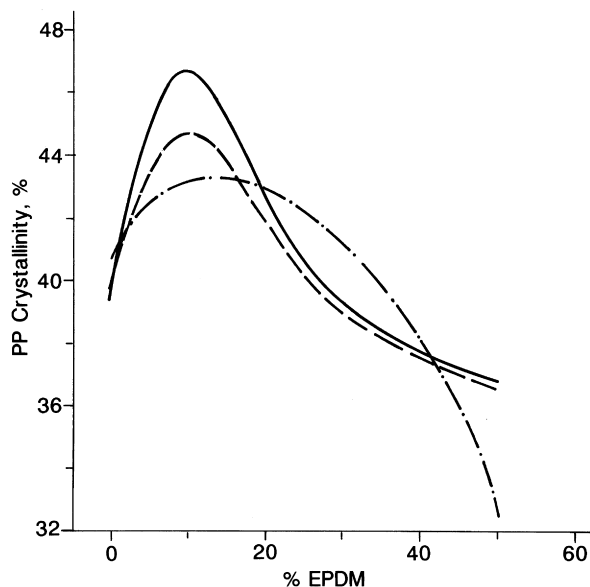
Fig. 2. PP crystallinity vs EPDM percentage in the blend matrix, at 403 K (-), 405 K (- -) and 408 K (- · -).

agents for the PP. However, in the present study, the PP crystallinity decreases in the presence of the kevlar fibres which indicates that this effect does not necessary imply an increase of the crystallinity. So, it is suggested that, at low EPDM percentages, the increase of PP crystallinity in the blends is due to two simultaneous phenomena: EPDM particles act as nucleating agents for the PP crystallization, and, simultaneously, the PP crystallites act as nucleating centres for the propylene segments of the EPDM. A similar crystallization mechanism was previously suggested by the authors [26].
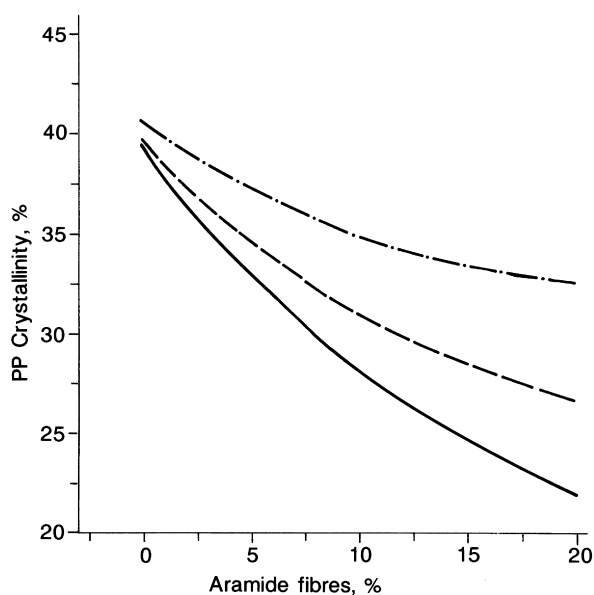
As shown in Fig. 4, in all blends and composites, a sensible decrease of the half time of PP crystallisation ($\tau_{1/2}$), at the different crystallization temperatures used in this study, is observed, as compared with the plain homopolymer, which is attributed to a nucleating effect [11] of the EPDM and kevlar fibres on the PP crystallization. In this case, the fibres show a higher ability for the nucleation than the EPDM particles. The values of $\tau_{1/2}$ depend on the crystallization temperature and blend composition. In all cases and as expected, $\tau_{1/2}$ increases with temperature. It can also be seen that, at the same matrix composition, the nucleating effect is more sensible in the composites than in the blends, and decreases as EPDM content increases which is attributed to restrictions created by the EPDM on the mobility of PP segments.

The kinetic parameters of PP crystallization in the blends and composites, as calculated from the Avrami equation (Eq. (1)), are compiled in Table 2, where k_n is the crystallization kinetic constant, n is the Avrami exponent, and $\tau_{1/2}$ the time to reach 50% of the total PP crystallization. In all cases, the value of k_n is higher in the blends and composites than in the plain homopolymer which is attributed to the nucleating effect of EPDM, at low percentages, and fibres. The increase of k_n is sensible in the PP/kevlar composites due to the higher ability of fibres to act as nucleating agents. On the other hand, k_n decreases as EPDM content in the blend increases which has been attributed to restrictions of the EPDM on the mobility of PP segments, as mentioned above, as well as to a phase inversion of the polymer matrix.

The radial growth rate of PP spherulites, as compiled in Table 3, decreases in the presence of EPDM particles and kevlar fibres but no sensible differences are observed at EPDM percentages above 25% in the blend matrix.

It is well known [14,15] that n depends on the nucleation process and the geometry of the growing crystals. According
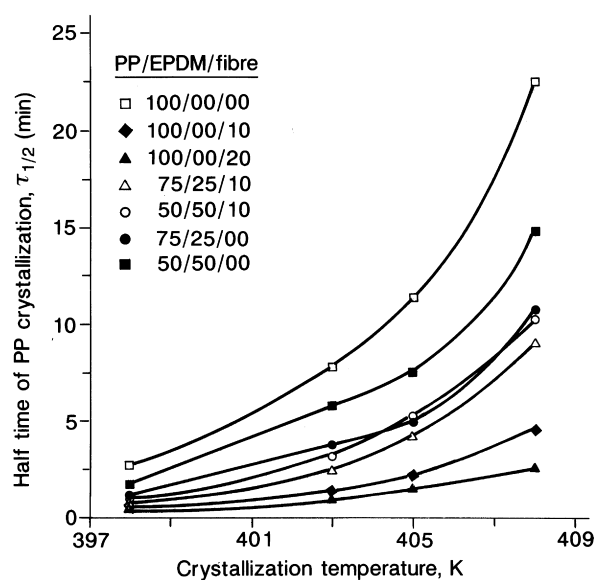

Fig. 3. PP crystallinity vs fibre percentage in the composite, at 403 K (-), 405 K (- -) and 408 K (- · -).

Fig. 4. Half time of PP crystallization ($\tau_{1/2}$) vs crystallization temperature, in different blends and composites.

Table 2
PP crystallization parameters in the studied materials

PP/EPDM /fibre	T_c (K)	K_n	n	$\tau_{1/2}$(min)	T_m (K)	T_m^0 (K)	$\sigma_e \times 10^3$ (J/m²)	Cryst.%
100/00/00	398	0.0478	2.65	2.75	438.68	476.37	176	39.4
	403	0.0026	2.72	7.86	440.80			39.4
	405	0.001	2.69	11.36	441.67			39.7
	408	0.00006	3.04	22.18	443.61			40.7
90/10/00	398	0.3765	2.95	1.23	437.77	477.20	172	43.2
	403	0.0102	3.12	3.87	439.84			46.7
	405	0.0014	3.35	6.40	440.84			44.7
	408	0.00038	3.05	11.73	442.88			43.2
75/25/00	398	0.44	2.73	1.18	438.88	468.23	147	38.4
	403	0.12	3.70	3.78	440.50			40.6
	405	0.0066	2.90	4.98	441.73			40.2
	408	0.00063	2.96	10.71	443.10			42.2
50/50/00	398	0.1669	2.61	1.73	437.62	471.65	156	37.0
	403	0.0036	3.02	5.75	439.05			36.8
	405	0.0014	3.07	7.57	440.37			36.5
	408	0.00036	2.81	14.76	442.37			32.5
75/25/10	398	1.25	2.60	0.80	439.49	461.65	125	32.6
	403	0.0711	2.52	2.47	440.78			41.8
	405	0.0168	2.59	4.21	441.73			43.8
	408	0.0015	2.80	9.03	443.01			44.8
50/50/10	i398	0.6437	2.69	1.03	439.76	467.54	145	37.3
	403	0.021	2.99	3.24	440.91			42.5
	405	0.0045	3.02	5.31	442.00			43.7
	408	0.0007	2.97	10.28	443.89			42.5
75/25/20	i398	1.61	2.25	0.69	441.39	453.76	85	24.8
	403	0.2213	2.28	1.65	442.20			35.5
	405	0.0624	2.43	2.70	442.50			39.6
	408	0.0063	2.71	5.70	443.74			41.3
50/50/20	398	0.688	2.37	1.00	438.94	464.71	135	33.2
	403	0.0239	2.91	3.19	440.14			39.5
	405	0.0047	2.97	5.38	441.			40.0
	408	0.00083	2.90	10.17	442.9703			39.3
100/00/10	i398	2.2652	2.01	0.55	439.42	459.66	104	18.3
	403	0.3313	2.22	1.40	440.98			28.1
	405	0.1312	2.19	2.14	441.76			30.9
	408	0.0256	2.16	4.63	439.53			34.9
100/00/20	398	5.017	2.36	0.43	440.58	442.66	47	12.
	403	0.767	2.01	0.95	441.09			21.9
	405	0.2873	2.09	1.53	440.98			26.7
	408	0.112	1.94	2.56	441.08			32.6

to our results, the value of n in the plain homopolymer and in the PP/EPDM blends is about 3 which corresponds to heterogeneous nucleation, followed by a tridimensional spherulitic growth [27,28] in a spherical form. Small

Table 3
Radial growth rate of PP spherulites in the studied materials

Material PP/EPDM/fibre	Radial growth rate of PP spherulites (μ/s)
100/00/00	4.8
90/10/00	4.5
75/25/00	4.0
50/50/00	4.0
100/00/fibre	4.5
75/25/fibre	4.3
50/50/fibre	4.1

variations of the Avrami exponent can be due to experimental errors and specific errors of the Avrami model [14,15], as well as to the existence of both primary and secondary crystallization in the material [29]. A primary crystallization is characterized by the prevalence of nuclei and a relatively faster growth of lamellar crystals, while a secondary crystallization process is the result of the crystallization of the component with more difficulty to crystallize and/or of the increment in the perfection of existing crystallites [28,30].

On the other hand, for the PP/kevlar composites, the value of n is about 2, which is an indication of a bidimensional crystal growth [27,28] in the form of disks. For the fibre percentages investigated, the value of k_n increases as fibre content in the composite increases which is attributed to the strong nucleating effect of the fibres on the PP crystallization. It has been previously shown that glass fibre [11] and some mineral fillers [31,32] tend to increase the
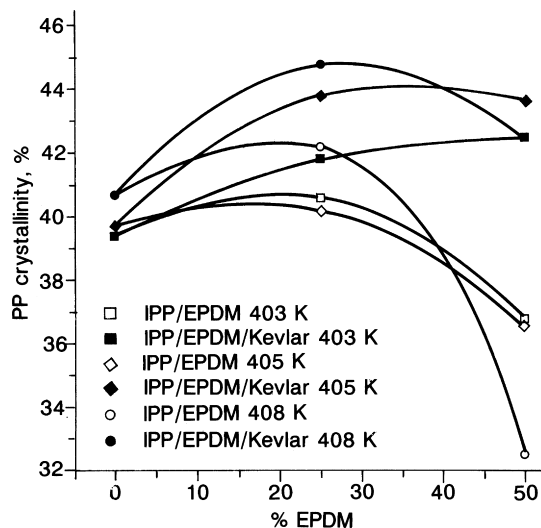
Fig. 5. PP crystallinity vs EPDM percentage in PP/EPDM blends and composites (10% aramide fibres), at different temperatures.

crystallinity degree of PP due to their nucleating effect. In the present work, the increase of PP crystallinity cannot be only attributed to the EPDM particles acting as nucleating agents, but also, to the possibility of EPDM crystallization
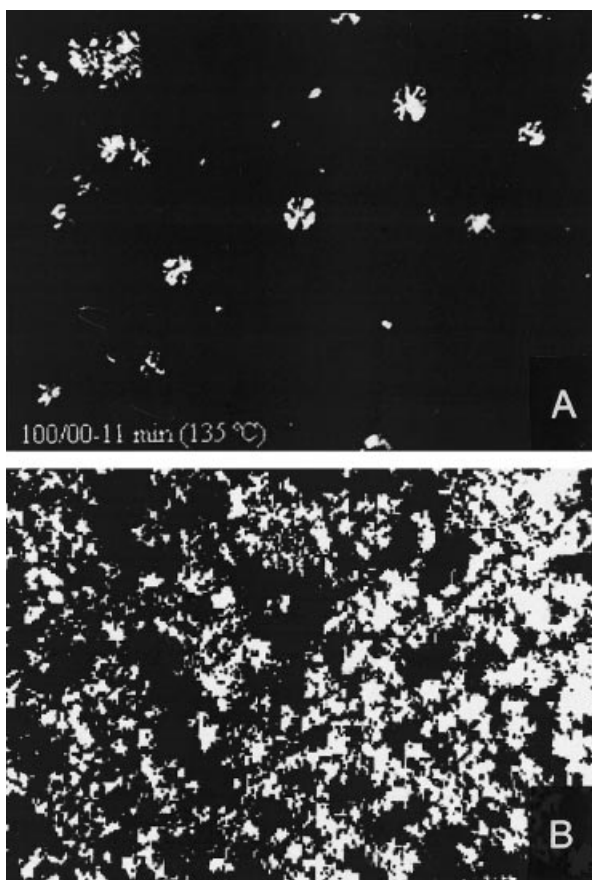

Fig. 6. Micrographs of PP crystallization (A) in plain polymer; and (B) in the presence of 10% EPDM, at 408 K (both micrographs were taken 11 min after reaching the sample crystallization temperature.

induced by PP particles, as was previously suggested by Slusarski et al. [1,8]. These authors concluded that PP particles could act as nucleating centres for propylene monomer units of the EPDM in such a way that the originally amorphous EPDM starts to crystallize.

As can be deduced from Fig. 5, the simultaneous incorporation of EPDM and kevlar has a synergistic effect on the crystallinity degree of PP which could be an indication of the simultaneous occurrence of both phenomena above mentioned, as has been previously suggested by Zugenmaier and Amash [9]; and Karger-Kocsis and Kiss [10]. The first authors detected, through DSC measurements carried out at 120°C, a small endothermic peak ($\Delta H = 3 \times 10^3$ J/kg) which was attributed to the presence of a small amount of crystallized copolymer in the blend. On the other hand, the latter carried out some studies on PP/elastomer and PP block copolymer blends, and found, through DMA measurements, a peak at about -100°C corresponding to the PE (γ-transition which was confirmed by a DMA spectrum of the plain EPDM. So, the authors concluded that the PE segments of the EPDM (with a high PE content) could be crystallized.

Melt temperatures and enthalpies, compiled in Table 2, were measured at a heating rate of 10°C/min, and calculated from the maximum and the area under the peak, respectively. The PP melting temperature increases as crystallization temperature increases which is directly related to the size of the PP crystals. The equilibrium melting temperatures (T_m^0) were obtained from the melting temperature vs crystallization temperature plots (Hoffman–Weeks Plots) [17] and compiled in Table 2. The crystallization thermodynamics of PP in the melt have been calculated through the secondary nucleation theory of Hoffmann and Lauritzen expressed by Eq. (2), as also compiled in Table 2. As can be seen, the PP chain folding energy (σ_e) in the blends decreases as EPDM content increases, till an EPDM percentage near to 50%. From this EPDM percentage in the matrix composition, σ_e tends to increase again. It can be suggested that at low concentrations, the EPDM acts as a nucleating agent for PP. However, at high EPDM percentages ($>$50%) in the blend, the EPDM particles give rise to restrictions on PP segments mobility. On the other hand, at a constant matrix composition, σ_e decreases as fibre content in the composite increases. According to Beck [33] approach, a good nucleating agent reduces the value of σ_e. So, as can be deduced from Table 2, kevlar fibres exert a more sensible nucleating effect on PP crystallization than EPDM particles which is in agreement with the curves of Fig. 4.

3.3. Optical microscopy study

Films of plain PP and PP/EPDM blends were isothermally crystallized at 135°C by means of an optical polarizing microscope equipped with an automatic hotstage thermal control. Micrographs were taken at appropriate
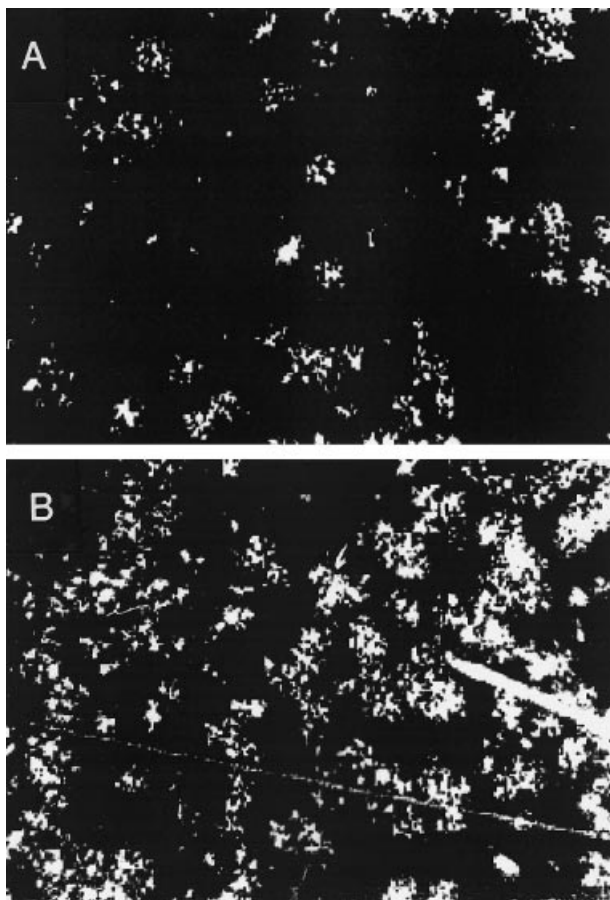
Fig. 7. Micrographs of PP crystallization in a matrix based on 50/50 PP/EPDM blend (A) in the absence of fibres; and (B) in the presence of aramid fibres, at 408 K, (both micrographs were taken 15 min after reaching the sample crystallization temperature).

intervals of time. As can be deduced from the microphotographs of Fig. 6, taken 11 min after reaching the sample crystallization temperature, the blend with an EPDM content of 10%, shows a high spherulitic density

Fig. 8. PP crystallization in the presence of aramid fibres, at 408 K (7 min after reaching the sample crystallization temperature).

as compared with the plain PP, which confirms the increase of the crystallization rate in the presence of small quantities of EPDM due to the nucleation effect of this elastomer crystallization which is in agreement with the obtained value of σ_e. This result could be related to the EPDM crystallization which also explains the increase of crystallinity in the PP/EPDM blends.

Fig. 7 shows that, at the same blend compsosition, the spherulitic density is higher in the presence of aramid fibres which is attributed not only to the nucleating effect of the fibres but also to the crystallization of PE and/or PP segments of the EPDM induced by PP crystallites. This could explain the synergistic effect of EPDM and aramid fibres on PP crystallization.

The ability of aramid fibres to PP transcrystalline growth on their surface can be suggested from Fig. 8. Transcrystallinity is the result of the high nucleating effect of the fibre surface for PP crystallization [23]. However, as is shown in Fig. 9, the PP transcrystallization is obstructed in the presence of EPDM. From Figs. 6(A), 7 and 8, it can be deduced that PP transcrystallization is more dificult as EPDM content in the blend increases which is attributed to restrictions created by the EPDM on the mobility of PP segments, as suggested above.

3.4. Mechanical properties

The tensile modulus and strength at break, as well as the elongation at break, are compiled in Table 4. As can be seen, a sensible increase of the stiffness is obtained with the addition of fibres due to the characteristics of the fibres and the transcrystallization [24,25] of PP at the fibre/matrix interface. An increase of the modulus with the addition of fibres is also observed in the EPDM probably due to a physical interaction between the fibre and this matrix. The modulus of the blends and composites decreases as EPDM content increases. So, composites with low EPDM content ($\leq 25\%$) in the matrix, can be used as substitutes of PP with an improved toughness. In contrast, blends with high EPDM percentages could be used as thermoplastic elastomers.

It can also be deduced from Table 4 that the tensile strength at break decreases as EPDM content in the matrix increases. These results indicate that both polymers are non-compatible, as was previously suggested by Utracki and Schlund [20] which indicated that there were two indirect ways of blends immiscibility: (1) the lack of viscosity super-position of the blend in the steady and dynamic state (see Fig. 1); and (2) a decrease of the maximum strength at the breaking point in an extensional flow in one direction. The strength at break of the plain PP increases as fibre content in the composite increases, which can be due to the PP trans-crystallinity induced by the aramid fibres.

The addition of aramid fibres to the EPDM gives rise to an increase of the stiffness and a decrease of the strength. It can be thought that a good contact between the fibres and the EPDM exists due to a strong mechanical adhesion created

by the different expansion coefficients of both materials. However, when the material starts to flow in a tensile test, the fibres begin to slide smoothly at the interface due to an increment of the temperature caused by the interfacial shear [23]. So, a great effort is needed to unstick the fibres from the matrix, but once the fibres are unsticked, they slide very smooth at the interface giving rise to voids in the polymer matrix which in turn decreases the tensile strength and elongation at break in the presence of fibres.

In general, the elongation at break of the blends increases as EPDM content increases, and tends to decrease with the incorporation of fibres. Only in the case of PP/EPDM blends with 10% fibre content, the elongation at break hardly varies with the EPDM content. It is suggested that this behaviour can be due to the special morphology created by the nucleating effect of both the fibres and the EPDM at this EPDM percentage.

4. Conclusions

From the above results, the next conclusions can be deduced:

- Blends of PP/EPDM are immiscible in the melt as confirmed by the torque vs time graphics and the behaviour of the strength at break of these materials.
- At low EPDM contents in the blend ($\leq 25\%$), the particles of EPDM act as nucleating agents and co-crystallize with the PP, increasing both the crystallization rate and crystallinity of the PP. However, at higher percentages, the EPDM obstructs the mobility of PP chains and hence decreases the PP crystallization rate.
- Aramid fibres are effective nucleating agents for PP crystallization giving rise to both an increase of the global rate of the crystallization process and the phenomenon of transcrystallinity with PP, which permits increasing the interaction at fibre/matrix interface and hence the mechanical behaviour of the composites.
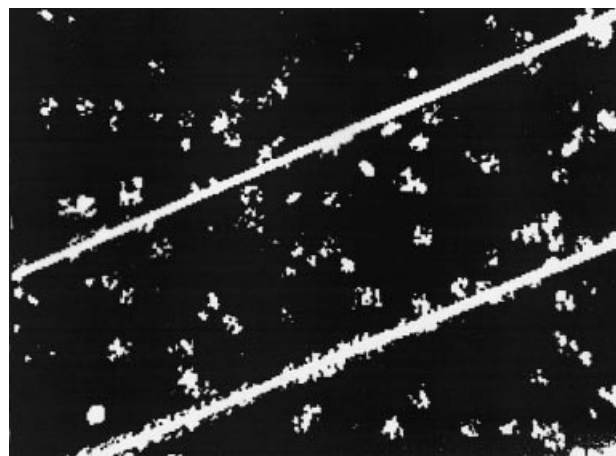

Fig. 9. PP crystallization in a matrix based on 90/10 PP/EPDM, and in the presence of aramid fibres, at 408 K (7 min after reaching the sample crystallization temperature).

Transcrystallization of PP decreases as EPDM content in the matrix increases.

- The Avrami exponents of the plain PP and PP/EPDM blends are about 3 which is characteristic of heterogeneous nucleation followed by a tridimensional spherulitic growth of spherical shape.
- In the case of the composites, the Avrami exponents are about 2, which correspond to a 2D growth of the crystals.
- EPDM and fibres exert a synergistic effect on nucleating action. However, and according to the values of σ_e (free energy for chain folding of PP chains), the nucleating effect of aramid fibres is higher than the effect of EPDM particles.
- The radial growth rate of PP spherulites decreases in the presence of EPDM and fibres, and hardly varies with EPDM percentages in the matrix above 25%.
- The stiffness of the PP and EPDM increases as fibre percentage in the composite increases, and decreases as EPDM content in the matrix increases. Blends of PP/

Table 4
Tensile behaviour of the studied materials

Material PP/EPDM/aramid	Modulus (MPa)	Tensile strength at break (MPa)	Elongation at break (%)
100/00/00	876.2	17.70	134.7
75/25/00	561.2	14.28	160.2
50/50/00	184.2	9.97	297.3
25/75/00	56.7	5.11	499.9
00/100/00	8.5	8.79	1017.1
100/00/10	1740.2	23.26	17.9
75/25/10	882.2	16.70	134.2
50/50/10	282.8	9.43	112.3
25/75/10	139.3	3.95	128.7
00/100/10	15.6	3.17	271.3
100/00/20	3515.6	26.46	11.0
75/25/20	1141.0	13.40	15.5
50/50/20	341.0	8.67	20.7
25/75/20	146.6	8.72	41.1
00/100/20	31.5	6.86	71.5

EPDM with low percentages of fibre show similar stiffness to the PP with an improved toughness.

- Tensile strength at break shows a similar behaviour to the stiffness, and the elongation at break generally increases as EPDM percentage in the matrix increases, and decreases as fibre content in the composite increases.

References

[1] Slusarski L, Bielinski D, Wlochowicz A, Slusarczyk C. Polym Int 1995;36:261.
[2] Bianchi L, Cimino S, Forte A, Greco R, Martuscelli E, Riva F, Silvestre CJ. Mater Sci 1985;20:895.
[3] Karger-Kocsis J, Kalló A, Szafner A, Bodor G, Sényei Zs. Polymer 1979;20:37.
[4] Tinker AJ. Polym Commun 1984;25:325.
[5] Jang BZ, Uhlmann DR, Vander Sande JB. J Appl Polym Sci 1984;29:4377.
[6] Pukánszky B, Tüdös F, Kalló A, Bodor G. Polymer 1989;30:1399.
[7] Danesi S, Porter RS. Polym Engng Sci 1987;27(4):254.
[8] Bielinski D, Slusarski L, Wlochowicz A, Slusarczyk C, Douillard A. Polym Int 1997;44(2):161.
[9] Zugenmaier P, Amash A. J Polym Sci B: Polym Phys 1997;35:1448.
[10] Karger-Kocsis J, Kiss L. Polym Engng Sci 1987;27(4):254.
[11] Arroyo M, Lopez-Manchado MA, Avalos F. Polymer 1997;38(22):5587.
[12] Schonhorn H, Ryan FWJ. Polym Sci A-2 1968;6:231.
[13] Brandup J, Immergut EH. Polymer handbook. 3. New York: Wiley, 1988 chap. 8.
[14] Avrami MJ. Chem Phys 1939;7:1103.
[15] Avrami MJ. Chem Phys 1941;9:177.
[16] Hoffman JD. SPE Trans 1964;4:315.
[17] Hoffman JD, Weeks JJ. J Chem Phys 1962;37:1723.
[18] Williams ML, Landel RF, Ferry JD. J Am Chem Soc 1965;77:3701.
[19] Abraham D, George KE, Francis DJ. Eur Polym J 1990;26:197.
[20] Utracki LA, Schlund B. Polym Engng Sci 1987;27:20.
[21] Coran A, Patel R. US Patent No. 4297453 (1981).
[22] Coran A, Patel R. US Patent No. 4310638 (1982).
[23] Cai Y, Petermann J, Wittich H. J Appl Polym Sci 1997;65:67.
[24] Avella M, Della Volpe G, Martuscelli E, Raimo M. Polym Engng Sci 1992;32(5):376.
[25] Avella M, Martuscelli E, Pascucci B, Raimo M. Polym Engng Sci 1992;32(5):383.
[26] Avalos F, Arroyo M. Rev Plast Mod 1990;408:825.
[27] Duland Bouyahya Idrisi M. Doctoral dissertation, Lyon University, France, 1983.
[28] Mandelkern L. Crystallization of polymers. New York: McGraw-Hill, 1964.
[29] Martuscelli E, Pracella M, Crispino L. Polymer 1983;24:693.
[30] Sharples A. Introduction to polymer crystallization. London: Arnold, 1966.
[31] Ahmad Fuad MY, Mustafah J, Mansor MS, Mohd Ishak ZA, Mohd Omar AK. Polym Int 1995;38:33.
[32] Alonso M, Gonzalez A, Requejo A, Arribas M, Saja JA. Polym Test 1992;11:71.
[33] Beck HN. J Appl Polym Sci 1975;19:371.