Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 5324–5331

polymer

www.elsevier.com/locate/polymer

Influence of a nucleating agent on the crystallization behaviour of isotactic polypropylene and elastomer blends

N. Fanegas [a], M.A. Gómez [a,*], C. Marco [a], I. Jiménez [a,b], G. Ellis [a]

[a] *Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*
[b] *Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain*

Received 9 April 2007; received in revised form 29 June 2007; accepted 2 July 2007
Available online 30 July 2007

Abstract

The influence of a nucleating agent on the crystallization behaviour of isotactic polypropylene (iPP), in their blends with poly(styrene-*b*-ethylene butylene-*b*-styrene) (SEBS), and a metallocenic ethylene–octene copolymer (EO) was investigated by DSC, optical microscopy and real-time small and wide angle X-ray scattering (SAXS and WAXS) experiments using synchrotron radiation. In non-nucleated iPP/SEBS blends, the crystallization of the iPP matrix occurred in the presence of the styrenic domains which induced a nucleating effect on the process, as observed in the synchrotron experiments. The metallocenic elastomer did not affect the crystallization behaviour of iPP in the iPP/EO blends in non-isothermal experiments, however, the development of crystallinity in the elastomer was restricted. In the nucleated isotactic polypropylene/elastomer blends a significant increase in the crystallinity and the crystallization rate of the iPP matrix was observed due to the presence of the nucleating agent. However, the nucleating efficiency of the additive was strongly affected by the nature and content of the elastomeric component. The nucleating agent efficiency was higher in the presence of the ethylene–octene component than the styrenic elastomer.

Keywords: Isotactic polypropylene/elastomer blends; Nucleating agents; Crystallization

1. Introduction

Isotactic polypropylene, iPP, is one of the most important commercial thermoplastics with excellent properties. However, a great disadvantage which limits its application range is its low impact strength, especially at low temperature. A large number of studies have been carried out over the years to improve its toughness, and blending with an elastomer is one of the main methods used [1–4]. The elastomers which have been employed in this type of blends are mainly ethylene–propylene rubber (EPR) and ethylene–propylene–diene terpolymer (EPDM) [5–12], although styrene–ethylene butylene–styrene triblock copolymer (SEBS) [13–18] and recently metallocenic ethylene–octene copolymers (EO) [19–22] have also been tested.

It is well established in polymer blends that the incorporation of one component in order to improve a certain property may result in the detriment of another. It is often necessary to add several components in order to achieve an optimum balance of all the application properties. In the case of these polypropylene blends, the enhancement in toughness by blending with elastomers is accompanied by a decrease of stiffness [2]. However, the improvement of both the impact resistance and the stiffness of isotactic polypropylene has a practical importance in order to extend its range of applications. Several strategies have been used to achieve a balance between both properties and adding an inorganic filler or another semicrystalline polymer are amongst those most studied [23–26].

On the other hand, the crystallization of iPP is controlled by the nucleation stage, and the addition of specific additives or nucleating agents to shorten the induction time of crystallization and accelerate the formation of crystalline nuclei is a technique commonly used in the polymer industry to shorten injection-moulding cycle times, thus reducing production

---

* Corresponding author.
E-mail address: magomez@ictp.csic.es (M.A. Gómez).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.07.004

costs. Furthermore, such agents generate smaller spherulites and increase crystallinity, thus improving the optical and mechanical properties. In previous studies [27–31], we have analyzed the influence of a series of nucleating agents on the structure, morphology, crystallization behaviour and mechanical properties of isotactic polypropylene. An organic phosphate derivative has been found to have a very high nucleating efficiency achieved even at very low concentrations which provoked an important increase in the flexural modulus [27,31]. In this regard, the use of a nucleating agent as a third component in the isotactic polypropylene/elastomer blends appears to be a promising alternative to achieve a good balance of properties, although only very few studies have appeared [32,33].

From the numerous published works on isotactic polypropylene/elastomer blends, there are few details available on the crystallization behaviour of the matrix, and in most cases the main interest is in the mechanical performance of the blends. However, in the presence of a nucleating agent which can significantly modify the crystallization behaviour of iPP, it seems very important to consider the effect of both the additive and the elastomer on the capacity of the matrix to crystallize.

The aim of this work is to investigate the influence of an organic phosphate derivative as a nucleating agent of the monoclinic phase of iPP in the crystallization process of iPP/SEBS and iPP/EO blends. The crystallization behaviour of the non-nucleated blends was determined under different crystallization conditions and as a function of the elastomer concentration, for comparison with the nucleated iPP/elastomer blends. This study is part of a broad project related to the development of high impact resistance and high modulus materials based on iPP and the influence of different parameters on these properties.

2. Experimental

2.1. Materials

The matrix was based on a commercial grade iPP provided by REPSOL-YPF (Móstoles, Madrid, Spain) with an isotacticity of 95% determined by solution NMR and a viscosity average molecular weight of 164,700. The characterization has been described elsewhere [27]. The elastomers used were SEBS provided by Dynasol (Madrid, Spain) and a metallocenic ethylene–octene copolymer (EO) provided by Dow Chemical Iberica (Tarragona, Spain). The SEBS elastomer had a 30% weight styrene content and the following molecular weight characteristics as determined by GPC; $M_w = 85{,}000$, $M_w/M_n = 1.45$. The EO elastomer had a 40% weight octene content and $M_w = 71{,}000$ and $M_w/M_n = 2$, also determined by GPC.

The nucleating agent used was methylene-bis-(4,6-di-*tert*-butylphenyl) phosphate sodium salt, ADK STAB NA 11 UH, provided by Asahi Denka Kogyo K.K. (Tokyo, Japan), designated as NA11.

Blends were prepared from the melt in a Haake Rheocord 90 system at 210 °C and 50 rpm. Blending was carried out during 5 min until the torque was stabilized. Blends were prepared with and without nucleating agent, for elastomer contents of 10, 20, 30 and 50% in weight. In the case of blends nucleated with NA11, the iPP was previously melt blended with the additive at 0.1 wt% and subsequently blended with the elastomer.

2.2. Physical properties

The thermal stability of all samples was studied by thermogravimetric analysis with a Mettler TA-4000/TG-50 thermobalance in nitrogen and oxygen atmosphere and at a heating rate of 20 °C min^{-1}.

The thermal properties were analyzed under dynamic conditions in a Mettler TA-4000 differential scanning calorimeter (DSC) calibrated with indium ($T_m = 156$ °C, $\Delta H_m = 28.45$ J g^{-1}). The experiments were carried out in a nitrogen atmosphere using 10–12 mg of sample sealed in an aluminum pan. Dynamic crystallization experiments were carried out on all samples by cooling to −150 °C at a cooling rate of 10 °C min^{-1}, after melting the samples at 210 °C for 5 min to erase the thermal history. All samples were heated to 210 °C at 10 °C min^{-1} after crystallization. The transition temperatures were taken as the peak maxima in the calorimetric curves. The crystallinity (X_c) of iPP in the blends was determined from the crystallization exotherms by using the following relation:

$$X_c = \frac{\Delta H_{c,iPP}}{\Delta H^{o}_{m,iPP} w_{iPP}} \quad (1)$$

where $\Delta H_{c,iPP}$ is the apparent crystallization enthalpy of iPP, w_{iPP} is the weight fraction of iPP in the blends and $\Delta H^{o}_{m,iPP}$ is the enthalpy corresponding to the melting of a 100% crystalline sample, taken as 177.0 J g^{-1} [34]. The degree of crystallinity of the EO elastomer was calculated using Eq. (1) with the reference value of polyethylene $\Delta H^{\circ}{}_{m,PE} = 288.4$ J g^{-1} [35].

Isothermal crystallization was undertaken in a Perkin Elmer DSC7/UNIX/7DX system. The samples were first heated at 210 °C for 5 min to eliminate the previous thermal and/or mechanical history and subsequently cooled at 64 °C min^{-1} to the predetermined T_c. The crystallization curves were recorded as a function of time.

Simultaneous wide and small angle X-ray patterns were recorded using synchrotron radiation at the A2 beam line at Hasylab, DESY (Hamburg, Germany). The details of the instrument are given elsewhere [36]. Monochromatic radiation of 0.15 nm wavelength was used. The SAXS and WAXS curves were detected with two linear Gabriel detectors. The SAXS detector was placed at a distance of 235 cm from the sample and was calibrated with the different orders of the long spacing of rat-tail cornea ($L = 65$ nm). The WAXS detector was placed to cover a 2θ range from about 10° to 32° and was calibrated with the crystalline diffraction peaks of PET. In order to consider the change of the intensity of the primary beam during the scattering measurements, the scattering intensity was divided by the intensity of the primary beam detected by an ionisation chamber in relative units. The background scattering obtained when no sample was present in the beam was subtracted from all measured experimental data after an appropriate correction for absorption. Lorentz correction of the SAXS data was performed by multiplying the intensity by s^2, where $s = 2\sin\theta/\lambda$, 2θ is the scattering angle and λ is the wavelength. The long period (L) was obtained from the maximum of the SAXS curve.

Thermo-optical analysis was carried out in transmitted visible light by using a Reichert Zetopan Pol polarizing microscope and a Mettler FP-80HT hot stage with a Nikkon FX35A 35 nm SLR camera.

3. Results and discussion

The thermal stability of all samples was determined to confirm that no thermal degradation took place during the different thermal cycles applied in the analysis of the crystallization behaviour. The nucleated and non-nucleated blends showed an intermediate thermal stability between pure iPP and the elastomeric component. The thermal stabilities of the nucleated systems were similar to the non-nucleated ones. All these results indicated that the preparation of the blends did not affect the thermal stability of the components.

The crystallization behaviour of isotactic polypropylene in the iPP/elastomer blends was investigated by DSC under isothermal and non-isothermal conditions. Firstly, the non-nucleated iPP/SEBS and iPP/EO blends will be commented on. Subsequently the influence of the nucleating agent on the crystallization process of iPP in the iPP/SEBS and iPP/EO blends will be shown.

The crystallization behaviour of the iPP matrix in the binary blends was analyzed as a function of the nature and content of the elastomeric component and the thermal treatment. Fig. 1 shows the crystallization exotherms obtained under dynamic conditions at a cooling rate of 10 °C/min after melting at 210 °C, for iPP/SEBS and iPP/EO blends and their individual components. Isotactic polypropylene shows an exotherm at 113 °C corresponding to a crystallinity of 57% (Fig. 1a and 1b). The metallocenic elastomer (Fig. 1a) presents an exotherm located at 45 °C with a very low enthalpy which corresponds to a crystallinity of 11%, indicating that in spite of the high comonomer content in this elastomer there are sufficiently long sequences of ethylenic units able to crystallize. In a subsequent heating cycle a very broad and weak endotherm centered around 60 °C was observed which corresponded to the melting of very small and poorly ordered crystals. In the iPP/EO blends the crystallization of both iPP and EO components are observed (Fig. 1a) and the crystallization takes place at very similar temperatures for all compositions (Table 1). The metallocenic elastomer does not affect the crystallization temperature of polypropylene in these blends, although a small decrease in crystallinity is observed (Table 1). However, the development of crystallinity in the elastomer is restricted by increasing the iPP content as is clearly shown in Table 1.

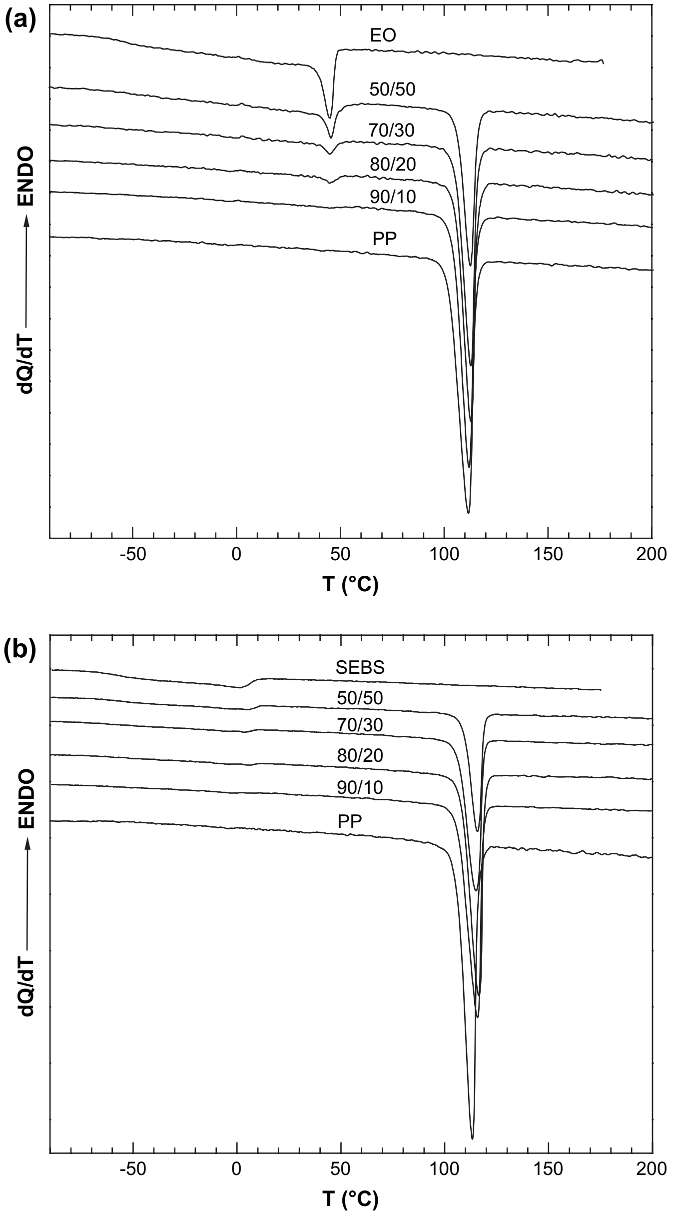

Fig. 1. Crystallization exotherms of iPP/EO (a) and iPP/SEBS (b) blends cooled at 10 °C min^{-1} for the compositions indicated.

Regarding the curves for the blends with the styrenic elastomer of Fig. 1b, one can first observe that SEBS shows a weak exotherm that extends from 0 to −50 °C which corresponds to very low levels of crystallinity of the ethylenic blocks of the elastomer. In the blends, a small increase in the crystallization temperature of iPP in the iPP/SEBS blends with respect to pure iPP is observed in the figure, with the data being presented in Table 1. This small nucleating effect will be analyzed in more detail in the crystallization experiments carried out under isothermal conditions.

The glass transitions of iPP and the EO and SEBS elastomers in the blends are not observed. In the pure metallocenic elastomer a transition at −50 °C is detected. In the SEBS elastomer the T_g of the ethylenic block is observed at −50 °C, although that corresponding to the styrenic block is not observed at high temperature. The T_g and all the relaxations of these blends were analyzed by DMA and have been reported elsewhere, together with the mechanical behaviour of the materials [37].

Table 1
Crystallization temperatures (T_c) and crystallinity (X_c) of iPP/SEBS and iPP/EO blends

Elastomer (wt%)	T_c (°C)		X_c[a] (wt%)	
	iPP	Elastomer	iPP	Elastomer
iPP/EO				
0	113		57	
10	113	45	53	1
20	113	45	55	7
30	112	45	55	9
50	113	45	52	11
100		45		11
iPP/SEBS				
0	113		57	
10	115		54	
20	117		53	
30	115		54	
50	116		54	

[a] X_c = Crystallinity determined on cooling scans.

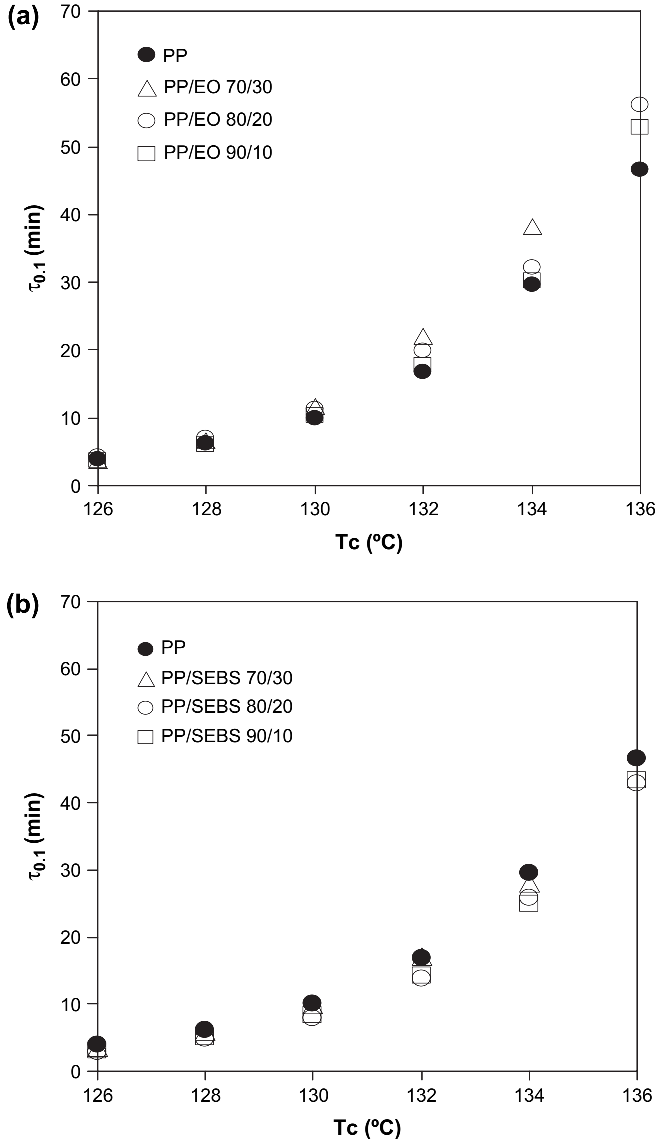

Fig. 2. Evolution of $\tau_{0.1}$ with the temperature of crystallization for (●) iPP and (a) iPP/EO blends at the following concentrations: 90/10 (□), 80/20 (○), 70/30 (△) and (b) iPP/SEBS blends at the following compositions: 90/10 (□), 80/20 (○), 70/30 (△).

The crystallization behaviour of the iPP component in the iPP/SEBS and iPP/EO blends was also investigated by DSC under isothermal conditions. Overall crystallization rates (G), considering both stages of the crystallization process, that is, nucleation and growth, can be calculated as:

$$G \approx \mathrm{Ln}(\tau_i)^{-1} \qquad (2)$$

over the time scale necessary for the crystallization of polymers, where G can be directly determined from the time necessary to reach a preestablished degree of crystalline transformation (i) denominated τ_i, and from its variation with T_c, for a predetermined molecular weight. Fig. 2 shows the changes in the time necessary to reach 10% of crystalline transformation $\tau_{0.1}$ for each T_c as a function of the elastomer content in iPP/EO blends (Fig. 2a) and iPP/SEBS blends (Fig. 2b). It is observed that $\tau_{0.1}$ increases exponentially with temperature in all cases. It is important to remark that in iPP/SEBS blends (Fig. 2b) an increase in the crystallization rate is observed, i.e. a decrease in $\tau_{0.1}$, for each T_c with respect to pure iPP. This increase in crystallization rate was already pointed out in the non-isothermal DSC experiments and the results indicate that the SEBS elastomer is exerting a nucleating effect on the crystallization process of the polypropylenic matrix in the blends. This behaviour has been found in iPP blends with other polymers in the crystalline state such as, for example, nylon 6 [38] or in the nematic phase such as Vectra [39]. It has also been observed in iPP blends with other elastomers such as EPR, although in this case the nucleation was related to partial compatibility between components [32,40]. In a very recent study [18], DSC results showed that the presence of SBS and SEBS had a nucleating effect causing an increase in the crystallization temperature of iPP, in agreement with our results. On the other hand, the iPP/EO blends showed a decrease in crystallization rate for each T_c compared with pure iPP (Fig. 2b).

The morphology of iPP/SEBS and iPP/EO blends has been previously studied by scanning electron microscopy, SEM [37]. It was found that in all cases the blends consisted of two separate phases indicating that both polymers were inmiscible, the elastomeric domains appearing as spherical droplets in the iPP matrix. In iPP/SEBS blends the size of the SEBS domains varied between 1 and 2 µm, with very low influence of elastomer concentration on domain sizes, indicating a low tendency to coalescence. In iPP/EO blends, the EO droplets showed a wide dispersion of sizes ranging from 1 to 6 µm and increasing size with elastomer content. At the highest EO content (50%) a co-continuous morphology was observed.

Although EO and SEBS are not miscible with the iPP matrix, from the DSC results it has been observed that the crystallization behaviour of polypropylene is different depending on the nature of the elastomer. These differences were enhanced when the crystallization behaviour was studied under shear conditions [41]. SEBS has been observed to have a nucleating effect on the crystallization of the iPP matrix, even if at the crystallization temperatures used in this work the SEBS elastomer is above its glass transition temperature, T_g. The explanation of the nucleation phenomena can be related to the structure of the block copolymer, as will be shown from the synchrotron results.

Simultaneous SAXS/WAXS measurements using synchrotron radiation were performed under isothermal and non-isothermal conditions in order to investigate in more detail the crystallization process of the iPP/elastomer blends. Fig. 3 shows the development of the SAXS and WAXS diffractograms of iPP/SEBS (70/30) blend on cooling from the melt at 10 °C min^{-1}. In Fig. 3a the Lorentz corrected SAXS intensity is plotted versus the scattering vector, *s*. The progress of the iPP crystallization in the blends is observed from the growth of the SAXS long period peak at about 0.055 nm^{-1} which corresponds to the lamellar structure of the matrix. A sharp SAXS peak at about 0.03 nm^{-1} is also observed in all patterns which correspond to the styrene blocks in SEBS in a cylindrical microdomain structure. This peak did not disappear in the temperature range in which the thermal cycles were performed. However, it will decrease in intensity and finally it will not be observed at the order–disorder transition of the block copolymer at much higher temperature (around 350 °C) [42]. Therefore, the crystallization of iPP in the iPP/SEBS blends took place in the presence of styrenic domains which imposed an effect on these processes. From the position of the SAXS peaks it is possible to determine an average long period, $L = 1/s_{\max}$ in the blends. A value of 17 nm was obtained for pure iPP and a very similar value was obtained for iPP in the blends. Regarding the average distance between styrenic domains, the value changes from 30 to 33 nm during the cooling process. The progress of the crystallization was also observed from the growth of crystalline reflections on the WAXS diffractograms. In Fig. 3b, it can be seen that the characteristic reflections of the α form of iPP developed on cooling the iPP/SEBS (70/30) blend from the melt.

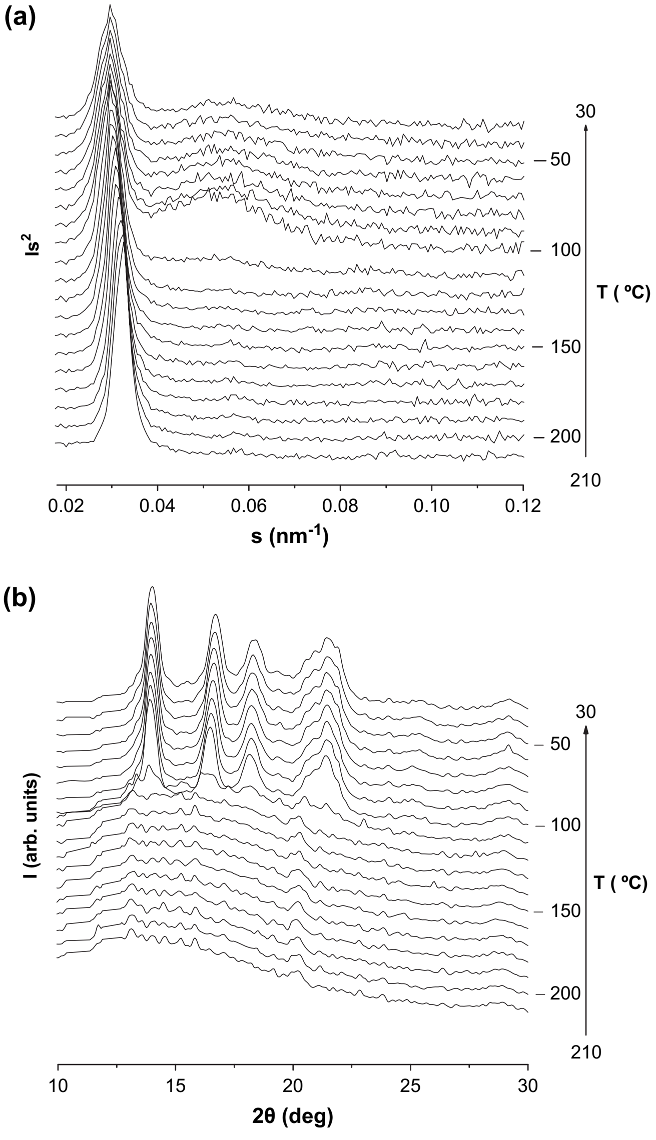

Fig. 3. Development of (a) Lorentz corrected SAXS and (b) WAXS patterns during non-isothermal crystallization of iPP/SEBS (70/30) blend on cooling from 210 to 30 °C at 10 °C min^{-1}.

The crystallization behaviour of iPP in the iPP/EO blends was also studied by simultaneous SAXS/WAXS experiments. The crystallization of iPP took place at much higher temperature than that at which the EO elastomer crystallizes. The development of crystallinity in the metallocenic elastomer was not observed from the WAXS patterns due to the low crystallinity of EO and the overlapping of reflections with those of iPP. However, it could be detected from the changes in position and width of the SAXS maxima. For a cooling scan, the SAXS shows the appearance of the PP long spacing at 110 °C, followed by a widening of the SAXS peak at 50 °C when the EO crystals are formed. This is shown in Fig. 4a for the PP and EO references and for a 50/50 blend at room temperature after the cooling scan. The metallocenic elastomer shows a very broad SAXS peak due to very poor crystals with an average long period of 14 nm compared with a narrower SAXS peak of pure iPP with a long period of 17 nm. The separation of the PP and EO peaks on the SAXS is more evident when performing a new heating scan, and the development of the signal is shown in Fig. 4b. The evolution on heating of the long spacing, *L*, and the width (FWMH) of the Lorentz corrected SAXS patterns of iPP/EO (50/50) blend after crystallization on cooling from the melt at 10 °C min^{-1} is shown. The SAXS patterns of the iPP/EO (50/50) blend (also shown in Fig. 4a) narrowed and shifted in position at around 80 °C due the melting of the defective EO crystals during the heating scan (Fig. 4b).

The influence of incorporating a nucleating agent on the crystallization behaviour of iPP in the iPP/SEBS and iPP/EO blends was also studied by DSC and SAXS/WAXS measurements using synchrotron radiation under non-isothermal conditions. Table 2 shows the crystallization temperatures and crystallinities for all nucleated blends determined by DSC experiments carried out by cooling from the melt to room temperature at 10 °C min^{-1}. Significant increases can be observed in crystallinity and crystallization temperature of the iPP matrix in the nucleated blends with respect to the non-nucleated blends due to the effect of the additive. The

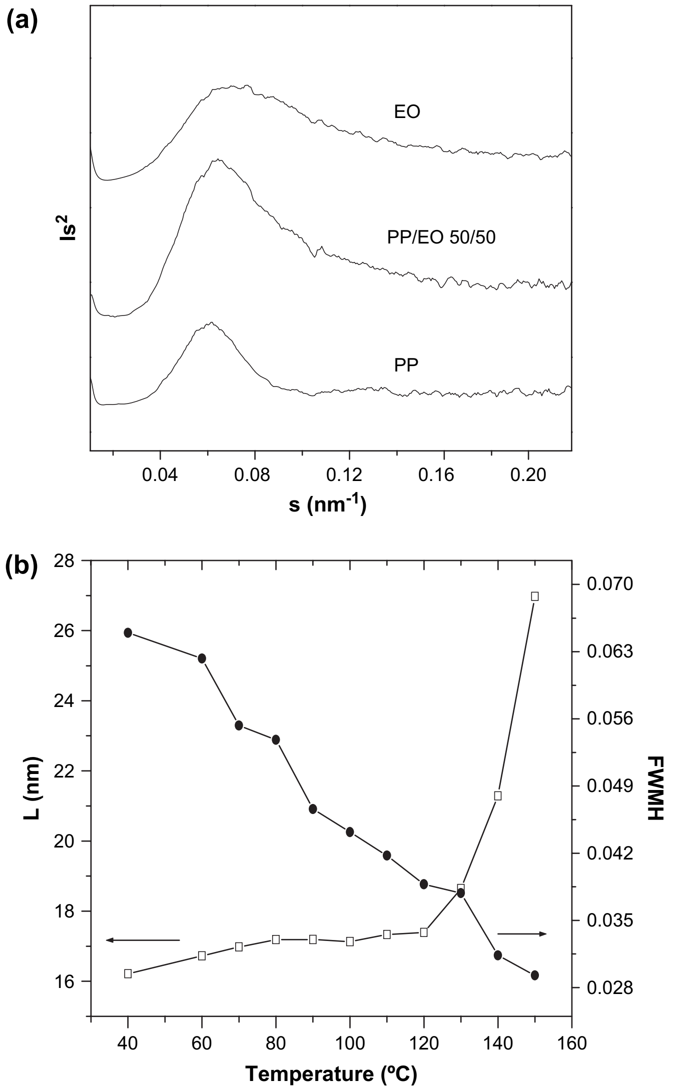

Fig. 4. Comparison (a) of the SAXS patterns of EO, iPP/EO (50/50) blend and iPP at room temperature after cooling from the melt at 10 °C min^{-1} and (b) development of the long spacing (L) and width (FWMH) of the Lorentz corrected SAXS patterns of iPP/EO (50/50) blend on heating at 10 °C min^{-1} after non-isothermal crystallization.

results clearly show that the organic phosphate derivative also exerts a very important nucleating effect on the iPP/elastomer blends, as was found for pure isotactic polypropylene in our previous work [27]. However, some differences were observed in the crystallization behaviour of the nucleated blends which can be related with the nature and content of the elastomer.

Table 2

Crystallization temperatures (T_c) and crystallinity (X_c) of nucleated iPP/EO and iPP/SEBS blends

Elastomer (wt%)	T_c (°C)		X_c[a] (wt%)	
	iPP	Elastomer	iPP	Elastomer
iPP/EO/NA[b]				
0	129		64	
10	129	41	64	0.5
20	130	43	65	2
30	130	43	60	3
50	129	44	59	9
100		45		11
iPP/SEBS/NA[b]				
0	129		64	
10	128		64	
20	128		63	
30	127		63	
50	125		60	

[a] X_c = Crystallinity determined on cooling scans.

[b] NA = Nucleating agent.

In order to analyze the nucleating efficiency of the additive in the presence of the metallocenic or the styrenic elastomer, the methodology based on the comparison with the self-nucleation of the matrix polymer proposed by Lotz et al. [43,44] was employed. The nucleation efficiency can be calculated from dynamic DSC measurements at a constant cooling rate by comparing the crystallization temperatures of the nucleated system with that of the self-nucleated matrix [43,44], regarded as the best possible nucleation efficiency because the concentration and distribution of nuclei and the nucleus–matrix interactions can be considered ideal. Given that the two extremes of the efficiency scale are the non-nucleated and the self-nucleated matrix, the nucleation efficiency, NE, can be considered as a percentage value, and is given by the following expression:

$$\mathrm{NE} = 100 \times \frac{(T_c - T_{c1})}{(T_{c2\max} - T_{c1})} \tag{3}$$

where T_{c1} and $T_{c2\max}$ are the crystallization temperatures of the non-nucleated and the self-nucleated polymer, respectively.

To apply this methodology in a rigorous manner to the nucleated blends, we should obtain the temperature of self-nucleation for each iPP/SEBS and iPP/EO blend. However, as a first approximation, we have considered $T_{c2\max}$ as the crystallization temperature of the self-nucleated iPP, with a value of

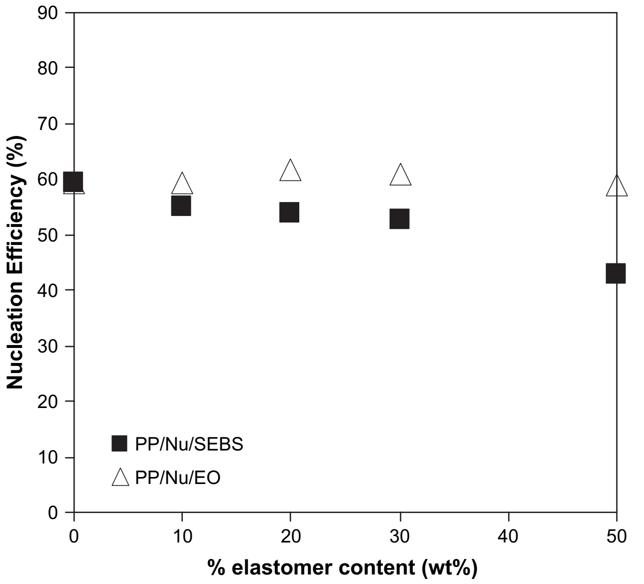

Fig. 5. Nucleation efficiency of the (△) iPP/EO blends and (■) iPP/SEBS blends as a function of the elastomer concentration.

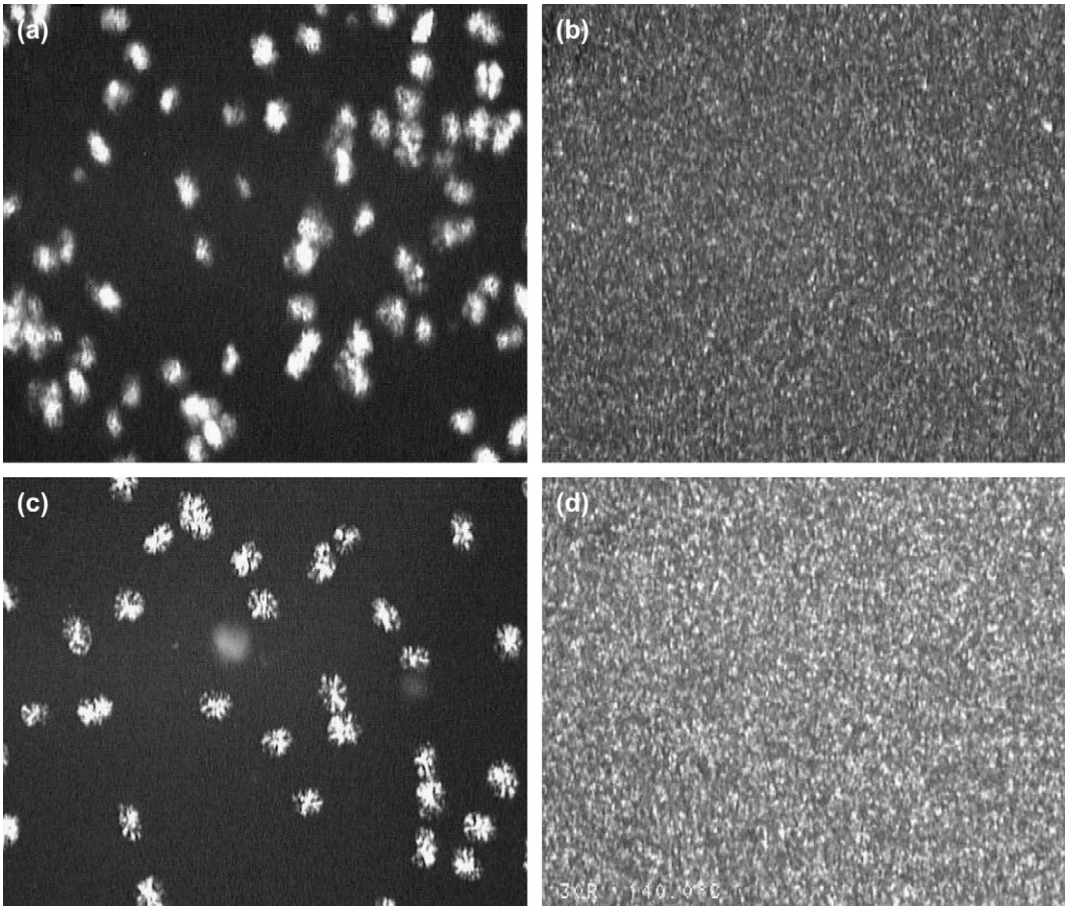

Fig. 6. Optical micrographs of (a) non-nucleated iPP/SEBS (90/10) isothermally crystallized at 132 °C, (b) nucleated iPP/SEBS (90/10) isothermally crystallized at 140 °C, (c) non-nucleated iPP/EO (90/10) isothermally crystallized at 132 °C and (d) nucleated iPP/EO (90/10) isothermally crystallized at 140 °C. The displayed area is 630 μm × 470 μm.

140 °C for a cooling rate of 10 °C min^{-1} [27], previously obtained for the same isotactic polypropylene used in this work. In order to include the influence of the elastomer on the crystallization of the iPP, T_{c1} was considered as the crystallization temperature of the non-nucleated iPP/SEBS and iPP/EO blend at each composition. Taking into account this approximation, Fig. 5 shows the comparative evolution of the nucleation efficiency in iPP/EO and iPP/SEBS as a function of the elastomer content. It is evident that the nucleation efficiency of the additive depends on the nature and concentration of the elastomer in the blends. In the presence of EO the nucleation efficiency is around 60%, regardless of the concentration of the elastomer, and identical to that obtained for nucleated raw iPP. However, in the case of the iPP/SEBS blends the nucleating efficiency of the additive decreases with SEBS concentration to a minimum value of 38%. In the presence of the styrenic elastomer the nucleation effect of the agent seems to be less efficient probably due to a poorer dispersion of the additive in the heterogeneous iPP/elastomer system.

Despite the different behaviour of the nucleation efficiency for the blends with different elastomers, in both cases there is a significant increase in crystallinity in the nucleated blends. A maximum value of 64% has been obtained compared with 52–57% in the non-nucleated blends. This increase in the degree of crystallinity in the nucleated iPP/elastomer blends results in a significant increase of their flexural modulus with respect to the non-nucleated blends. However, the impact strength remains at high values in the nucleated blends depending on composition and nature of the elastomer. The influence of the metallocenic and styrenic elastomer on the mechanical properties of the nucleated blends will be described elsewhere [37].

The development of structures during non-isothermal crystallization processes and the subsequent melting of the nucleated blends were also studied by SAXS/WAXS using synchrotron radiation. The increase in crystallinity and crystallization rate of the iPP matrix due to the presence of the nucleating agent was also observed in these experiments. The WAXS patterns of the nucleated blends only showed the crystalline reflections of α form, as was observed in the non-nucleated case, hence the WAXS curves are similar to those of Fig. 3b, with the only difference that the transition temperature is now shifted in agreement with the DSC data of Table 2. The lamellar morphology of iPP in the blends was also determined from the position of the SAXS maxima, and an increment in L was observed from 17 nm in the non-nucleated to 22 nm when the nucleating agent was added during non-isothermal experiments.

The influence of both the dispersed components on the morphology of the nucleated blends was investigated by optical microscopy. An increase in concentration of crystalline nuclei induced by the nucleating agent was observed in nucleated iPP/elastomer blends as shown in Fig. 6.

4. Conclusions

It has been shown that the crystallization behaviour of isotactic polypropylene is different in iPP/SEBS blends compared with iPP/EO blends. Simultaneous SAXS/WAXS measurements together with DSC data demonstrated that the crystallization of iPP in the iPP/SEBS blends took place in the presence of the styrenic microdomain structure and a nucleating effect of SEBS was observed. In the case of iPP/EO blends this effect was not observed and only a reduction in the EO crystallinity was determined with increasing iPP content.

When a nucleating agent which induces crystallization of the monoclinic phase of isotactic polypropylene was present in iPP/SEBS and iPP/EO blends, the nucleating efficiency of the additive depends on the concentration and nature of the elastomer. A significant increase in crystallinity was observed in both types of blends. However, whilst in the presence of the ethylene–octene elastomer the significant increase in crystallization temperature of the iPP matrix was maintained, in iPP/SEBS blends this temperature, i.e., the crystallization rate, decreased as SEBS content increased. All the changes in crystallinity, crystallization behaviour and morphology observed in the nucleated blends will have an important impact on the mechanical performance of the materials.

Acknowledgements

Financial support from the Spanish Ministry of Education and Science, MEC (MAT 2002-03831) is gratefully acknowledged. N.F. also acknowledges the MEC for a FPI studentship. The work performed at the synchrotron facility in Hamburg (Hasylab, DESY) was supported by contract RII3-CT-2004-506008 (IA-SFS) of the European Commission and the authors thank Dr. S. Funari for his technical assistance. V. Ruiz Santa Quiteria, L. Fraga and J.M. Arribas from REPSOL YPF and J. Nieto from Dow Chemical are gratefully acknowledged for providing the raw polymers and characterization details.

References

[1] Karger-Kocsis J, editor. Polypropylene: structure, blends and composites, vol. 2. London: Chapman & Hall; 1995.
[2] Karian HG, editor. Handbook of polypropylene and polypropylene composites. New York: Marcel Dekker Inc.; 1999.
[3] Liang JZ, Li RKY. J Appl Polym Sci 2000;77:409.
[4] Galeski A. Prog Polym Sci 2003;28:1643.
[5] Wu S. Polym Eng Sci 1990;30:753.
[6] Choudhary V, Varma HS, Varma IK. Polymer 1991;32:2534.
[7] D'Orazio L, Mancarella C, Martuscelli E, Sticott G. Polymer 1993; 34:3671.
[8] Mehrabzadeh M, Burford RP. J Appl Polym Sci 1996;61:2305.
[9] Van der Waal A, Mulder JJ, Oderkekt J, Gaymans RJ. Polymer 1998; 39:6781.
[10] Van der Waal A, Gaymans RJ. Polymer 1999;40:6067.
[11] Naiki M, Matsumura T, Matsuda M. J Appl Polym Sci 2002;83:46.
[12] Bedia EL, Astrini N, Sudarisman A, Sumera F, Kashiro Y. J Appl Polym Sci 2000;78:1200.
[13] Gupta AK, Purwar SN. J Appl Polym Sci 1984;29:1595.
[14] Gupta AK, Purwar SN. J Appl Polym Sci 1986;31:535.
[15] Stricker F, Thomann Y, Mülhaupt R. J Appl Polym Sci 1998;68:1891.
[16] Mäder D, Bruch M, Maier R-D, Stricker F, Mülhaupt R. Macromolecules 1999;32:1252.
[17] Bassani A, Pessan LA. J Appl Polym Sci 2002;86:3466.
[18] Abreu FOMS, Forte MMC, Liberman SA. J Appl Polym Sci 2005; 95:254.
[19] Kukaleva N, Jollands M, Cser F, Kosior E. J Appl Polym Sci 2000; 76:1011.
[20] McNally T, McShane P, Nally GM, Murphy WR, Cook M, Miller A. Polymer 2002;43:3785.
[21] Premphet K, Paecharoenchai W. J Appl Polym Sci 2002;85:2412.
[22] Prieto O, Pereña JM, Benavente R, Cerrada ML, Pérez E. Macromol Chem Phys 2002;203:1844.
[23] Hornsby PR, Premphet K. J Appl Polym Sci 1998;70:587.
[24] Premphet K, Horanont P. Polymer 2000;41:9283.
[25] Obater Y, Sumitomo T, Ijitsu T, Matsuda M, Nomura T. Polym Eng Sci 2001;41:408.
[26] Chaffin KA, Bates FS, Brant P, Brown GM. J Polym Sci Polym Phys 2000;58:108.
[27] Marco C, Gómez MA, Ellis G, Arribas JM. J Appl Polym Sci 2002; 84:1669.
[28] Marco C, Ellis G, Gómez MA, Arribas JM. J Appl Polym Sci 2002; 84:2440.
[29] Marco C, Gómez MA, Ellis G, Arribas JM. J Appl Polym Sci 2002; 86:531.
[30] Marco C, Ellis G, Gómez MA, Arribas JM. J Appl Polym Sci 2003; 88:2261.
[31] Marco C, Ellis G, Gómez MA, Arribas JM. Recent Res Devel Appl Pol Sci 2002;1:587.
[32] Jang GS, Jo NJ, Cho WJ, Ha CS. J Appl Polym Sci 2002;83:201.
[33] Zhang X, Xie F, Pen Z, Zhang Y, Zhang Y, Zhou W. Eur Polym J 2002;38:1.
[34] Li JX, Cheung W, Demin L. Polymer 1999;40:1219.
[35] Mandelkern L, Fatou JG, Denison R, Justin J. J Polym Sci Polym Lett 1965;3:803.
[36] http://www-hasylab.desy.de/science/groups/saxs-group/
[37] Fanegas N, Gómez MA, Jiménez I, Ellis G, Marco C, García-Martínez JM. Poly Eng Sci, in press.
[38] Marco C, Ellis G, Gomez MA, Fatou JG, Arribas JM, Campoy I, et al. J Appl Polym Sci 1997;63:2665.
[39] Torre F, Cortazar MM, Gómez MA, Ellis G, Marco C. Polymer 2003; 44:5209.
[40] Martuscelli E, Silvestre C, Bianchi L. Polymer 1983;24:1458.
[41] Fanegas N, Azzurri F, Alfonso GC, Gómez MA, Marco C. In preparation.
[42] Chun SB, Han CD. Macromolecules 1999;32:4030.
[43] Fillon B, Wittmann JC, Lotz B, Thierry A. J Polym Sci Polym Phys Ed 1993;31:1383.
[44] Fillon B, Thierry A, Lotz B, Wittmann JC. J Therm Anal 1994;42:721.