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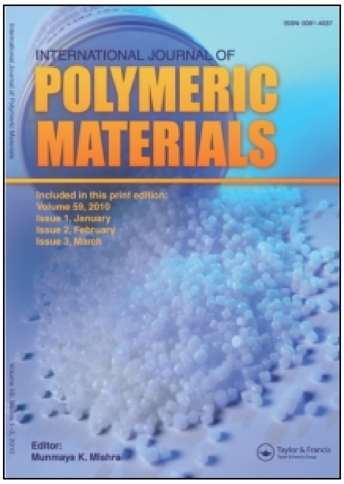

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NON-ISOTHERMAL CRYSTALLIZATION AND MELTING BEHAVIOR OF POLY(PROPYLENE)-POLY(ETHYLENE VINYL ACETATE) [PP/EVA] AND POLY(PROPYLENE)-(ETHYLENE-PROPYLENE) [PP-EP/EVA] BLENDS

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NON-ISOTHERMAL CRYSTALLIZATION AND MELTING BEHAVIOR OF POLY(PROPYLENE)-POLY(ETHYLENE VINYL ACETATE) [PP/EVA] AND POLY(PROPYLENE)-(ETHYLENE-PROPYLENE) [PP-EP/EVA] BLENDS

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The melting behavior of PP/EVA and PP-EP/EVA blends non-isothermally crystallized was studied. The morphology of blends was evaluated in terms of crystal habits, spherulitic structure and melting characteristics. For PP and EVA homopolymers the observed crystal habits were α-monoclinic and orthorhombic corresponding to PP and PE crystals since this last is a part of the EVA copolymer. Two types of α-crystals were associated to the experimental data and they were designated as low (LPα-C) and high (HPα-C) perfection α-crystals. These crystals were relatively unaffected in nature after blending the PP or the PP-EP with the EVA copolymer. Nevertheless, crystallinity decreased and the spherulitic structure changed. In differential scanning calorimetry [DSC] heating traces two partially overlapped endothermic signals were observed during heating of the non-isothermally crystallized specimen. The low temperature endotherm (I) was associated to melting of LPα-C structures while the high temperature endotherm (II) was related to two different melting processes, one corresponding to HPα-C structures and the other to recrystallized or reorganized material. The shifting of endotherm I to lower temperatures was considered an effect of interfacial interactions in the crystalline zones between the LPα-C of PP and the orthorhombic crystals of EVA. Modulated differential scanning calorimetry [MDSC]

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traces corroborated that recrystallization is higher in PP/EVA blends the opposite being the case in PP-EP/EVA blends. Differences in the multiple melting between PP/EVA and PP-EP/EVA blends are discussed in terms of molecular interactions.

Keywords: multiple melting, PP/EVA blends, MDSC, non-isothermal crystallization, morphology

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INTRODUCTION

Physical and chemical interactions between PP and EVA have been recently studied [1 – 6]. McEvoy and Krause determined the formation of EVA influxes entering into the PP phase, resulting in a mechanical interlocked interface. This increased the adhesion between the two components [1] and improved the impact strength of PP [2]. Although PP and EVA are immiscible polymers, it has been proposed that partial miscibility between these two polymers occurs in the molten state [3]. More recently, the existence of compatibility regions in PP/EVA blends depending on the EVA concentration has been determined [4, 5]. In this last case, a decrease in the melting point of PP suggested the presence of interactions in crystalline zones while the shifting in the glass transition temperature of both PP and EVA was associated with amorphous phases [6].

Multiple melting phenomena have been observed in many polymers, and several hypotheses have been proposed to explain it. One of these [7] establishes that multiple endotherms are related to melting of structures existing prior to DSC heating while the other [8, 9] establishes that endotherms are due to melting of already existing crystals and melting of recrystallized or reorganized material. In particular, it has also been proposed that in the melt recrystallization process of PP, a transformation from the α-form to a reorganized α-form is involved [10]. A phase change from the β-form to a stable α-form was also proposed for this polymer [11].

Temperature modulated DSC (MDSC) provides the total heat flow and the reversing and non-reversing signals [12] involved in melting of polymers. The reversing signal is related to thermodynamic events while the non-reversing one is associated to both thermodynamic and kinetic events. Exothermic events such as crystallization are present only in the non-reversing signal, while endothermic melting is present in both signals. This allows to separate recrystallization from melting of separate lamellae in order to determine the relative contribution of different phenomena to the melting trace. The purpose of this work is to give an overall explanation to multiple melting phenomena occurring in PP/EVA and PP-EP/EVA blends after non-isothermal crystallization. The reversing and non-reversing signals in the MDSC traces were used to determine the relative contribution of phases to the melting behavior.

EXPERIMENTAL

Materials

Materials used in this work were isotactic polypropylene homopolymer (PP) from Indelpro Co., polypropylene ethylene-propylene heterophasic copolymer (PP-EP) [13] from Himont Co., and poly(ethylene vinyl acetate) (EVA) from Alcudia Co. The molecular weight of these polymers were 232000, 155000 and 55000, respectively. The melt flow index (MFI) and the density for the PP were 10.8 dg/min and 0.9003 g/cm^3, respectively. For the PP-EP copolymer an ethylene concentration of 16% was determined [5]. The MFI and density of the PP-EP copolymer were 8 dg/min and 0.9020 g/cm^3, respectively. Finally, the VA concentration [5] in the EVA copolymer was 28% and the MFI and density for this copolymer were 7 dg/min and 0.9451 g/cm^3, respectively.

Methods

PP/EVA and PP-EP/EVA blends with EVA concentration ranging from 0 to 100% were prepared as follows [4]: The as-received materials (pellets) were initially pre-mixed and then extruded and pelletized in a Werner & Pfleiderer twin screw mixer (model ZSK-30). Thin samples of pelletized blends were non-isothermally crystallized under controlled conditions using a hot stage from Mettler (FP82HT). Blends were heated up to the equilibrium melting temperature of the PP (188°C) [14], maintained for 3 min at this temperature and finally cooled up to room temperature at a rate of 10°C/min. This procedure was applied to all samples characterized by the techniques described below.

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Techniques

DSC and MDSC traces for PP/EVA and PP-EP/EVA blends were determined using a TA Instrument (model 2920) Indium calibrated. Samples were heated at 5°C/min under nitrogen atmosphere. The modulation in MDSC was 1°C each 60 s.

Wide angle X-ray diffraction (WAXD) patterns of non-isothermally crystallized samples were recorded at room temperature using an X-ray Siemmens D5000 diffractometer with Ni-filtered Cukα radiation generator. Patterns were obtained within the 2θ range of $5-35°$ at steps of 0.6°/min. Dimensions of samples were $1\,\text{cm} \times 1.4\,\text{cm} \times\ 0.07\,\text{cm}$.

Polarized optical microscopy (POM) was used to register the morphology of PP/EVA and PP-EP/EVA blends after non-isothermal crystallization. Observations were carried out at room temperature using an Olympus BX-60 microscope and micrographs were obtained using an Olympus PM-20 photographic system with magnification of 200X.

RESULTS AND DISCUSSION

Morphology of Non-Isothermally Crystallized Blends

PP/EVA and PP-EP/EVA blends non-isothermally crystallized developed particular thermal behavior. Figure 1 shows the non-isothermal crystallization thermograms of PP/EVA and PP-EP/EVA blends during cooling at 10°C/min. The exothermic peaks of PP and EVA have two ranges of variation from 100 to 120°C and from 40 to 60°C, respectively. The peaks of PP, $T_{cp,PP}$, and EVA, $T_{cp,EVA}$, show different tendencies. In PP/EVA, $T_{cp,PP}$, is about constant and $T_{cp,EVA}$, decreases when the EVA content does so. In PP-EP, $T_{cp,PP}$, moves to higher temperature with increasing EVA and $T_{cp,EVA}$ increases with the EVA content. Two main differences between PP/EVA and PP-EP/EVA blends are observed. One is the small shoulder observed at 107°C, and the other is that $T_{cp,EVA}$ in the PP/EVA blends has a tendency to increase with EVA content the opposite occurring in the PP-EP/EVA system. Therefore both systems are thermally different and these differences will be discussed in terms of melting after isothermal crystallization with modulated DSC.

The WAXD patterns of PP/EVA and PP-EP/EVA blends are shown in Figure 2. For the PP homopolymer, a typical diffraction pattern of the α-monoclinic form [15] is shown in Figure 2a. For the corresponding blends, the diffraction pattern of the α-form remains but the intensity of peaks decreases with an increase in EVA concentration. The pattern of the EVA copolymer shows the diffraction peaks corresponding to polyethylene [16], which is part of the EVA copolymer [17]. The WAXD pattern of PP-EP can also be associated to the α-monoclinic form of PP. However, it can be

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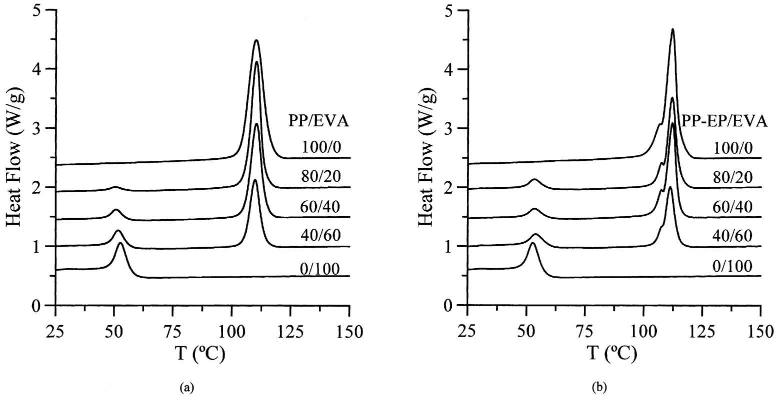

FIGURE 1 DSC traces during cooling at 10°C/min. of (a) PP/EVA and (b) PP-EP/EVA blends.

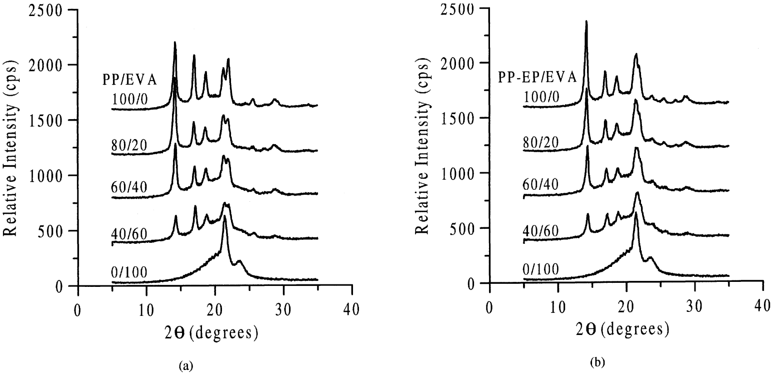

FIGURE 2 WAXD patterns at room temperature of non-isothermally crystallized (a) PP/EVA and (b) PP-EP/EVA blends.

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observed that the intensity of the signal at 21.3° is higher compared with that of PP. The enhancement of the signal at this angular position must be due to the presence of polyethylene crystals in the PP-EP copolymer, which as a consequence makes a double reflection to look as one. As in the case of PP/EVA blends, the α-form remains but the intensity of crystalline reflections decreases with increase in EVA. Figure 3 shows the relative crystallinity (X_c) as a function of the EVA concentration for all blends. As expected and due to copolymerization, the X_c is always higher for PP/EVA blends compared to PP-EP/EVA blends.

The spherulitic structure of PP/EVA and PP-EP/EVA blends is shown in Figures 4 and 5, respectively. For PP a familiar spherulitic pattern is

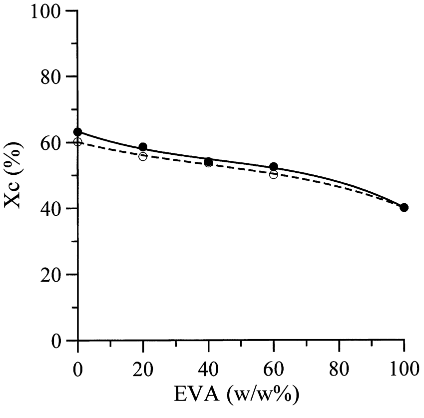

FIGURE 3 Relative crystallinity at room temperature of non-isothermally crystallized PP/EVA (full) and PP-EP/EVA (dashed) blends as function of EVA content.

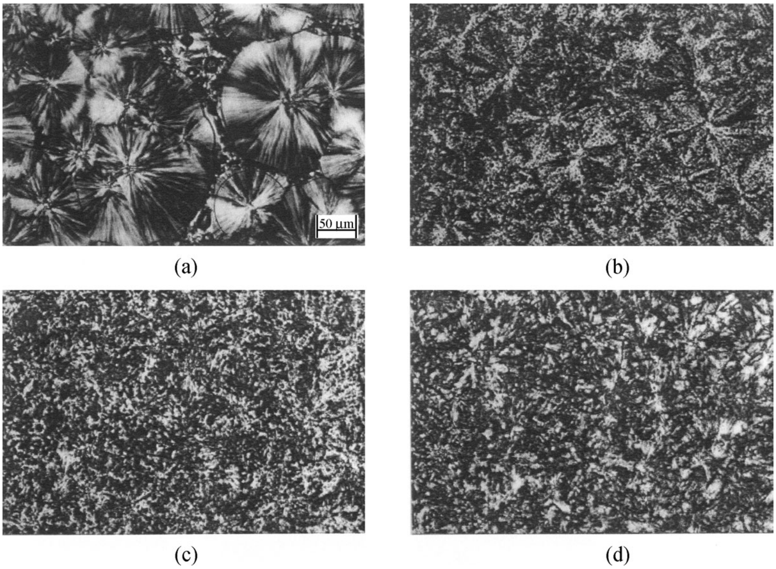

FIGURE 4 POM micrographs at room temperature of non-isothermally crystallized PP/EVA blends (a) 100/0, (b) 80/20, (c) 60/40, and (d) 40/60.

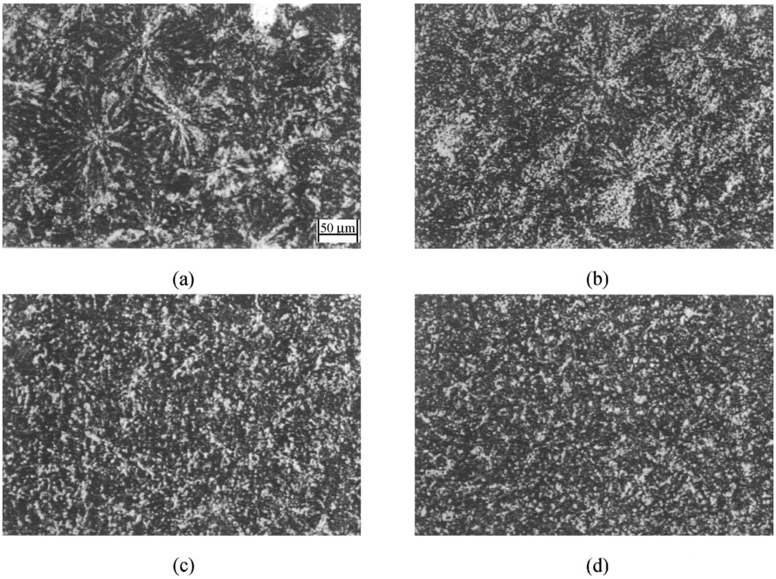

FIGURE 5 POM micrographs at room temperature of non-isothermally crystallized PP-EP/EVA blends (a) 100/0, (b) 80/20, (c) 60/40, and (d) 40/60.

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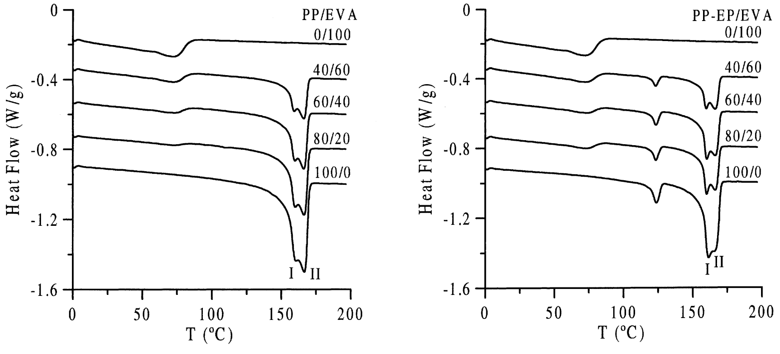
observed (Fig. 4a). For the PP/EVA blend with 20% of EVA (Fig. 4b) the structure of spherulites is less defined and their size is apparently smaller compared to PP homopolymer, a number of spots is also observed in crystalline regions. For blends with 40% of EVA or more (Figs. 4c and 4d) the spherulitic structure is completely lost and other than a higher number of spots, is not possible to resolve a spherulitic structure. The POM micrograph PP-EP shown in Figure 5a indicates that that spherulites of PP-EP copolymer are less defined than the ones of the PP, although the spherulite size is quite similar. As in the case of PP/EVA blends, the PP-EP/EVA spherulitic patterns lost definition when the EVA concentration increased (Figs. 5b–d). Overall these effects are an indication that on crystallization both blends behave in different morphological manner.

Melting Behavior by DSC

The DSC traces of PP/EVA and PP-EP/EVA blends shown in Figures 6a and 6b, indeed corroborated the different nature of each system. Two partially overlapped melting endotherms (T_I and T_{II}) are observed for PP. On the other hand PP-EP shows three melting peaks; one located around 123°C and two others partially overlapped at higher temperatures (T_I and T_{II}) such as with PP. The peak located at 123°C corresponds to the fusion of PE like-crystals from the PP-EP copolymer. It is known that when PP is crystallized at low temperature (< 112°C) the sample tends to recrystallize during heating due to some structural instability and two melting peaks are shown [10, 18]. The measured $T_{cp,PP}$ and $T_{cp,PP\text{-}EP}$ for PP and PP-EP was quite similar *i.e.*, 110°C (Fig. 1a) and 112°C (Fig. 1b) respectively and also in both systems the dominant structure was the α-monoclinic (Figs. 2a and



(a) (b)

FIGURE 6 DSC traces during heating at 5°C/min. of non-isothermally crystallized (a) PP/EVA and (b) PP-EP/EVA blends.

2b), therefore, it can be assumed that in the total DSC trace, endotherm I is associated with the melting of the low perfection α-crystals while the endotherm II is originated from the melting of the already existing high perfection α-crystals and also from the melting of recrystallized or reorganized material.

For PP, the intensity of endotherm I is lower than the one of endotherm II (Fig. 6a), but for PP-EP the endotherm II is less intense. Thus, the amount of recrystallized material should be higher for the PP/EVA blends. Also, for PP/EVA blends the ratio of intensities between endotherms I and II, as a function of EVA concentration, remains practically constant; *i.e.*, peak I is less intense than peak II for all PP/EVA blends. Nevertheless, for the PP-EP/EVA blends such ratio tends to decrease; *i.e.*, the relative intensity of endotherms I and II changes with EVA concentration. Also, in both PP/EVA and PP-EP/EVA blends, the endotherm of EVA is observed around 75°C and it is proportional to the PP concentration.

The melting points (T_I and T_{II}) of the PP α-crystals, as a function of EVA concentration, are shown in Figure 7 where it is observed that T_I of both PP/EVA and PP-EP/EVA blends, decreases with the EVA concentration although the T_I, values are slightly higher for the PP-EP/EVA blends. Also, T_I shows a more pronounced decrease in the PP-EP/EVA blends. On the other hand, the melting points T_{II} of PP/EVA and PP-EP/EVA blends are approximately constant as the concentration of EVA increases and are very close to each other. These melting results suggest that the small decrease in $T_{I,PP}$ and $T_{I,PP\text{-}EP}$ is associated with interactions

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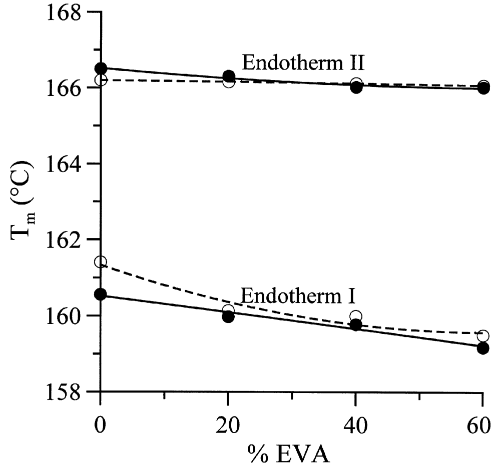

FIGURE 7 Melting points of i-PP for (a) PP/EVA (full) and PP-EP/EVA blends (dashed).

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in the crystalline zones [5, 6]. If we assume that the pronounced decrease observed in PP-EP/EVA blends is related to interfacial interactions between the ethylene moieties existing in both PP-EP and EVA copolymers, it is probably that interactions occur between low perfection α-crystals of PP and PE-like crystals from the EVA copolymer. The low perfection α-crystals of the PP-EP copolymer seem to have more stability than the ones of pure PP (see Fig. 7), even though the relative amount of these crystals is smaller due to the presence of ethylene and propylene sequences.

Melting Behavior by MDSC

The total MDSC traces of PP/EVA and PP-EP/EVA blends are shown in Figure 8 where it is observed that the shape of the total MDSC traces is close to the one obtained by conventional DSC. Even though the two partially overlapped peaks are not well defined as in the DSC traces, it can be assumed that the two endotherms are also present in the MDSC traces. The reversing and non-reversing heat flow of PP/EVA and PP-EP/EVA blends is shown in Figures 9 and 10, respectively. The reversing signals of PP/EVA (Fig. 9a) and PP-EP/EVA (Fig. 9b) blends are related to the partial melting of lamellae [19]. These reversing signals decrease as the EVA concentration increases. In the non-reversing signal of PP/EVA (Fig. 10a) and PP-EP/EVA (Fig. 10b) blends the recrystallization exotherm is immediately followed by a melting endotherm. More importantly however, the non-reversing trace indicates that there is higher recrystallization (exothermic peak at 152°C) in the PP/EVA blend or higher partial melting in the reversing signal as the EVA content increases. This is an indication that, as proposed before, there is more

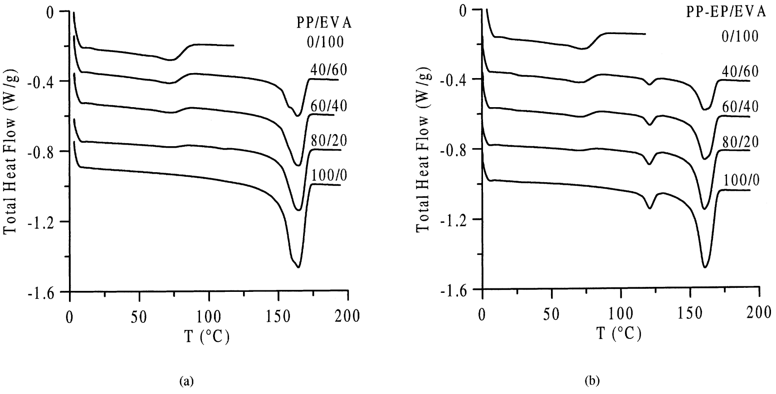
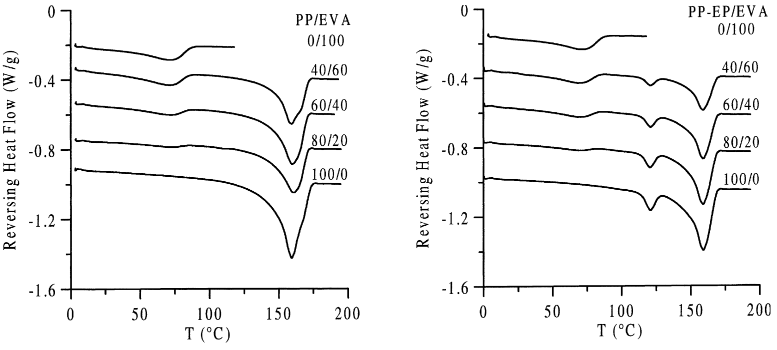
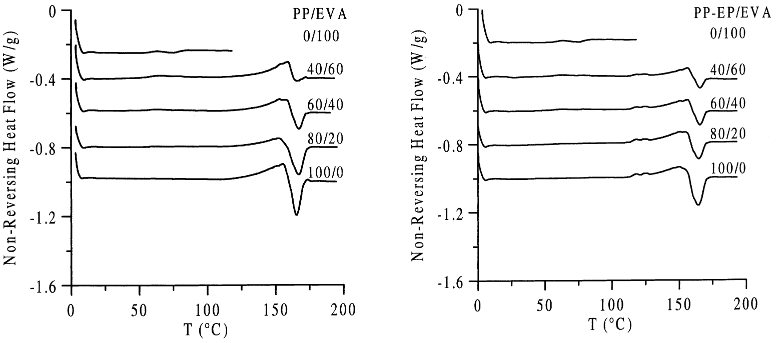


FIGURE 8 Total MDSC traces during heating at 5°C/min. (± 1°C, 60 s) of non-isothermally crystallized (a) PP/EVA and (b) PP-EP/EVA blends.



(a) (b)

FIGURE 9 Reversing MDSC traces during heating at 5°C/min. (± 1°C, 60 s) of non-isothermally crystallized (a) PP/EVA and (b) PP-EP/EVA blends.



(a) (b)

FIGURE 10 Non-reversing MDSC traces during heating at 5°C/min. (± 1°C, 60 s) of non-isothermally crystallized (a) PP/EVA and (b) PP-EP/EVA blends.

recrystallization in the PP/EVA system under scanning. This can also be taken as an indication that in the cooling process at which the blends were subjected, the EVA copolymer perturbs the formation of high perfection α-crystals of PP, but it promotes the simultaneous formation of low perfection α-crystals or material able to recrystallize. As indicated before, PP/EVA blends show more recrystallized material than the PP-EP/EVA blends. This could be associated to two distinct processes, one related to the amount of material able to recrystallize, which could be decreased by the presence of the ethylene moieties in the PP-EP, the other to the stronger interactions between PP-EP and EVA copolymers, compared to those to PP and EVA which impedes recrystallization.

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CONCLUSIONS

Non isothermal crystallization of PP/EVA and PP-EP/EVA generated α-monoclinic structures. These were classified into high perfection α-crystals and low perfection α-crystals. The PP-EP/EVA blends also form PE-like crystals. Crystallinity of both PP/EVA and PP-EP/EVA blends decreased as the EVA concentration increased, although it was slightly higher for the PP/EVA blends. Spherulites were well defined for PP/EVA blends although the spherulitic pattern was less defined as the EVA concentration increased. This was an indication of the different nature of each sample. In the multiple melting of PP/EVA and PP-EP/EVA blends, two partially overlapped melting endotherms, named I and II, were observed. The low temperature endotherm (I) was assigned to melting of the LPα-C structures while the high temperature endotherm (II) corresponded to the melting of both recrystallized material and HPα-C structures. The peak of endotherm I (T_I) was located at lower temperatures than the one of endotherm II (T_{II}) for all PP/EVA and PP-EP/EVA blends. The shifting of T_I to lower temperatures with increasing EVA concentration suggested the presence of interactions in crystalline zones for both PP/EVA and PP-EP/EVA blends. Also, the more pronounced decrease of T_I of PP-EP/EVA blends suggested higher interactions for this blend. It was proposed that interactions occurred between the LPα-C structures of PP and the PE crystals of the EVA copolymer. For the PP/EVA blends the intensity of endotherm I was lower than the one of endotherm II, which was contrary to the observed for the PP-EP/EVA blends. This indicated that recrystallization is higher for the PP/EVA blends. MDSC results corroborated this proposition for which an explanation was that recrystallization is diminished by the presence of ethylene moieties in the PP-EP copolymer. Another possibility is that molecular interactions between the ethylene moieties of PP-EP and EVA reduce the ability of recrystallization of PP in blends of these copolymers.

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