The Effect of Addition of Different Elastomers upon the Crystalline Nature of PP

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ABSTRACT: Thermal and morphological studies have been performed on polymer blends based on ethylene–octene copolymer (PEE)/PP and ethylene–propylene–diene copolymer (EPDM)/PP. The thermal and morphological behavior of PEE, EPDM, PEE/PP, and EPDM/PP systems were analyzed by differential scanning calorimetry (DSC) and polarizing light microscopy, respectively. It was observed that the behaviors of crystallization kinetics of PEE/PP and EPDM/PP blends were similar. It was also observed that addition up to 10–20% (w/w) of elastomers resulted in increasing of spherulite size. The heat of fusion (ΔH_f) and crystallinity degree of PEE/PP and EPDM/PP systems decreased when the elastomer contents were increased. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3530–3537, 2001

Key words: elastomers; crystallization kinetics; PP

INTRODUCTION

Considerable work has been carried out to improve the impact strength of polypropylene (PP) by incorporation of elastomers.[1–4]

The literature[5] shows that unmodified PP has a regular structure with a relatively ordered spherulitic texture. Addition of an impact modifier, such as EPDM, results in a less regular spherulitic texture with less sharp spherulite boundaries. Not only the spherulite structure but also the size of the spherulite is changed markedly by the incorporation of the rubbery phase. It has also been commented on that the reduction of the average spherulite size may imply that the impact modifier is an effective nucleating agent for PP crystallization.[5,6] Thus, the aim of this work was to carry out a study of thermal behavior of the PEE/PP and EPDM/PP blends by using DSC and light microscopy to explain the similar mechanical behavior of both systems, earlier reported elsewhere.[7]

EXPERIMENTAL

Materials and Blend Preparation

Commercial grades were available for the following polymers—polypropylene (PP), ethylene–octene copolymer (PEE), and ethylene–propylene–

Table I   Characteristics of Polymers Samples Used

Material	PP	PEE	EPDM
Manufacturer	POLIBRASIL S.A.	DOW CHEMICAL	NITRIFLEX
Designation	KM6100	EG8100	EP57C
Density at 23°C (g/cm^3)[a]	0.917	0.887	0.874
Hardness (Shore A)[b]	73.6	60.0	46.2
Melt Index (g/10 min)[c]	2.1	2.0	—
Mooney Viscosity ML 1+3@100°C	—	42.1	99.0

[a] Measured in our laboratory by ASTM D792.
[b] Measured in our laboratory by ASTM D2240.
[c] Measured in CENPES/PETROBRÁS laboratory by ASTM D1238.
[d] Measured in Nitriflex laboratory by ASTM D1646.

diene terpolymer (EPDM). The material specifications are listed in Table I.

A Wortex single-screw extruder, Model H210, was used for melt blending the PEE/PP and EPDM/PP blends, containing different weight percents of elastomers. Table II shows the material compositions prepared in the extruder.

The screw speed was set at 80 rpm, and the temperature profile in the extruder from the feed to the metering zone was set at 220°C.

Measurements

A Perkin-Elmer DSC-7 apparatus was used to determine the thermal behavior of PP, PEE/PP, and EPDM/PP blends. The melting and recrystallization behavior of the pure polymers and PP blends was analyzed at a heating rate of 10°C min^{-1} and cooling rate of 10°C min^{-1}.

The isothermal crystallization of PP, PEE, EPDM, PEE/PP, and EPDM/PP blends was obtained by the following methodology: about 10 mg of each sample was heated to 210°C, remaining at this temperature for 10 min. The heating rate used was 20°C min^{-1}. Nitrogen atmosphere was employed during the experiment. This procedure

was carried out to eliminate the thermal history of the sample. The material was then cooled from 210 to 122°C. After 10 min, the sample was rapidly cooled to 40°C and heated immediately using the following heating rates: 10 and 20°C. The degree of crystallinity of the PP blends was evaluated by the ratio between the enthalpy of fusion of the blend and the enthalpy of fusion of the perfectly crystalline PP ($\Delta H_{PP} = 209$ J/g).[8]

To study the nucleation behavior by optical microscopy, sections of the samples were cut out from the extrudates. The sections were placed on microscope support glasses and covered with pieces of cover glass. The systems (plate/sample/plate) was heated at 210°C and kept at this temperature for 1 min to allow all the crystallites to melt. Then, the sample was cooled from 210 to 130°C. This procedure only permits the PP crystallization. The spherulites growth was recorded by a camera coupled to the microscope. The radius of spherulites was determined from the micrographs taken by using a polarizing microscope, Model Olympus BX 50.

Table II   PEE/PP and EPDM/PP Compositions

Elastomer (wt %)	Sample PEE/PP	Sample EPDM/PP
0	A′	A′
5	A	A*
20	B	B*
40	C	C*
60	D	D*
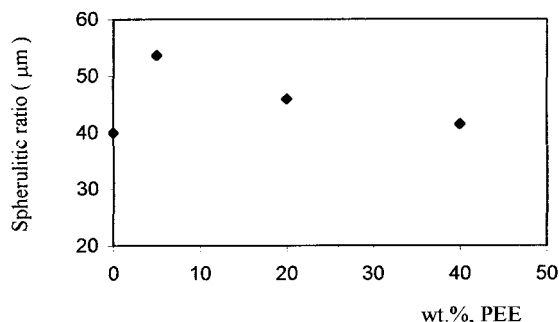
Figure 1   PP spherulite size vs. PEE content.

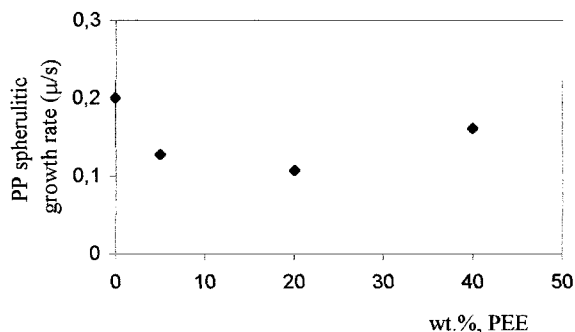**Figure 2** Growth rate of PP spherulites vs. PEE content.

Figure 4 PP spherulite size vs. EPDM content.

RESULTS AND DISCUSSION

Evaluation of Crystallization Behavior of Elastomer/PP Blends by Optical Microscopy

The effect of the PEE/PP blend composition on the size and the growth rate of the spherulites are shown in Figures 1 and 2, respectively.

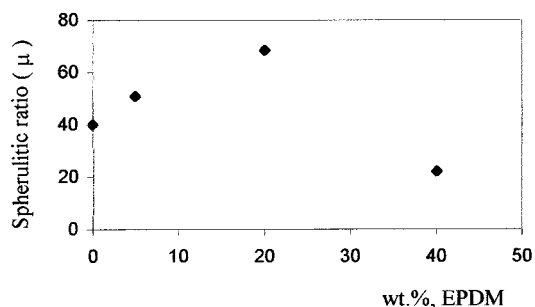Figure 1 shows that in sample A (5 wt % of PEE) an increase in the spherulite size occurred,

but as the elastomer content increased, a slight decrease in the crystal size was observed, indicating a tendency to occur a phase separation of the blend components.

Figure 2 shows that, in the composition range analyzed, the variation in the growth rate of the spherulites was not significant; just a tendency to have an increase in the growth rate above 40 wt % of PEE was observed. Choudhary and coworkers[10] reported that the increase of the rate of crystallization in the presence of an EPDM elas-
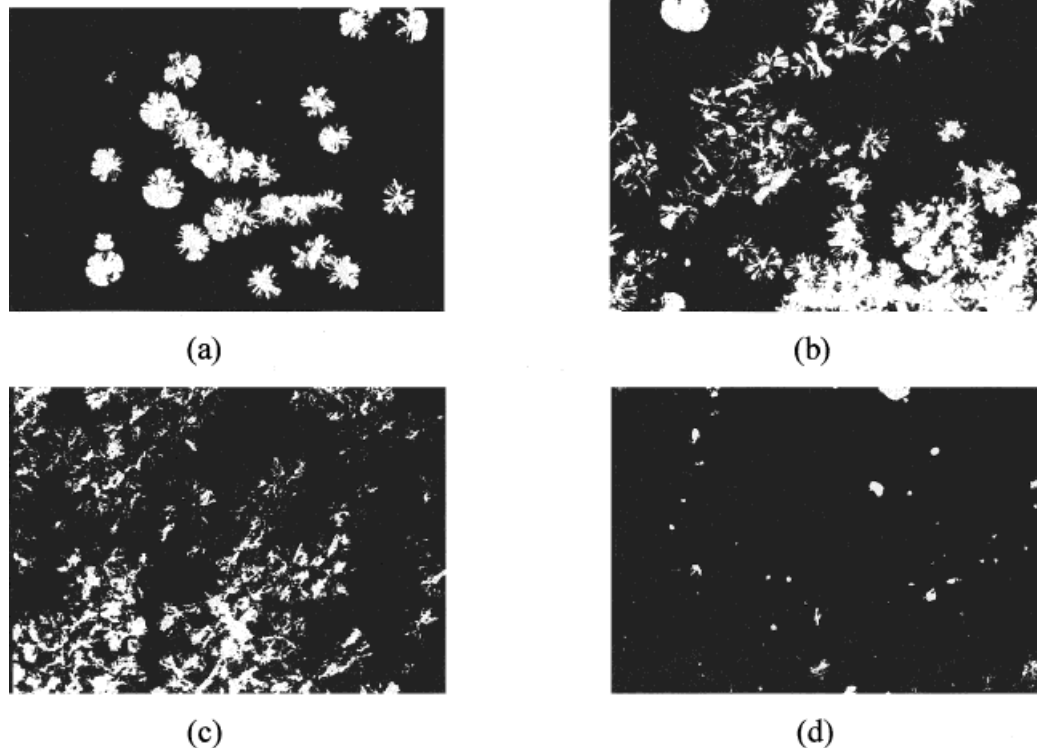

(a)

(b)

(c)

(d)

Figure 3 Micrographs of optical microscopy of PEE/PP blends (a) A, (b) B, (c) C, and (d) D.
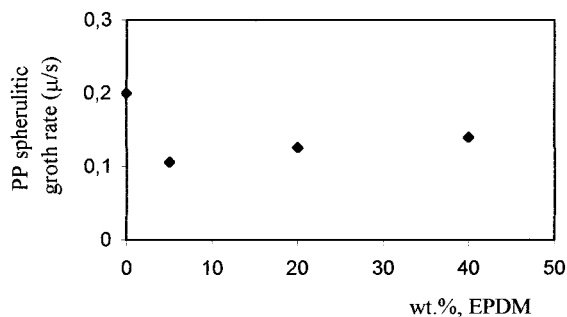
Figure 5 Growth rate of PP spherulites vs. EPDM content.

tomer may be due to the enhanced mobility of the PP segments, thereby leading to better alignment in the crystal lattice.

Figure 3 presents the spherulitic morphology of PEE/PP systems, with different contents of the elastomer. It can be observed that sample C (40 wt % of PEE) presents spherulites less perfect in relation to the previous samples. Sample E (60 wt % of PEE) presents only "points" of crystallization.

Figures 4 and 5 show that the EPDM/PP and

PEE/PP systems present similar crystallization kinetics behavior, i.e., low elastomer contents caused an increase in spherulite size, and subsequent increments of EPDM provoked a decrease in the crystal size, also indicating an occurrence of phase separation of the blend components (Fig. 4). Figure 5 shows that as in the PEE/PP systems, the variation in the growth rate of the spherulites was also not significant in the composition range analyzed.

Figure 6 shows the spherulitic morphology of EPDM/PP systems. It can be observed that sample C* (40 wt % of elastomer) presents spherulites less perfect than the samples with lower content of elastomer. Sample E* (60 wt % of EPDM) also presents only "points" of the crystallization.

Evaluation of the Crystallization Behavior of Elastomer/PP Blends by DSC

The crystallization kinetic behavior of polymers is generally evaluated in terms of the crystallized material fraction, $\chi(t)$, as a function of time, t, generating curves called crystallization exotherms.
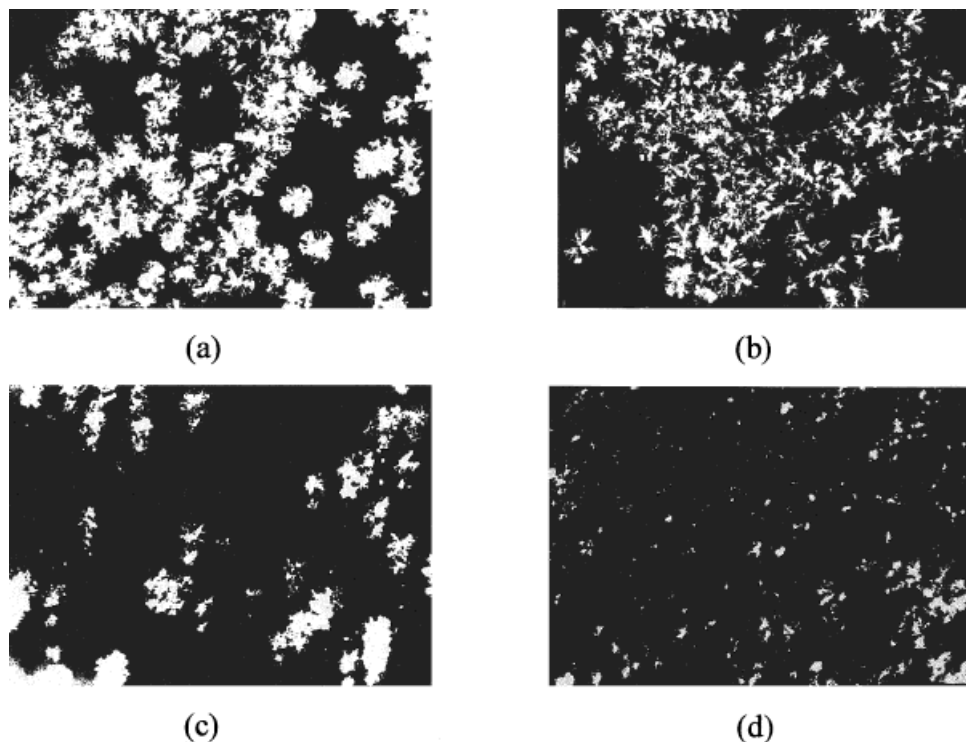

Figure 6 Micrographs of optical microscopy of EPDM/PP blends (a) A*, (b) B*, (c) C*, (d) D*.
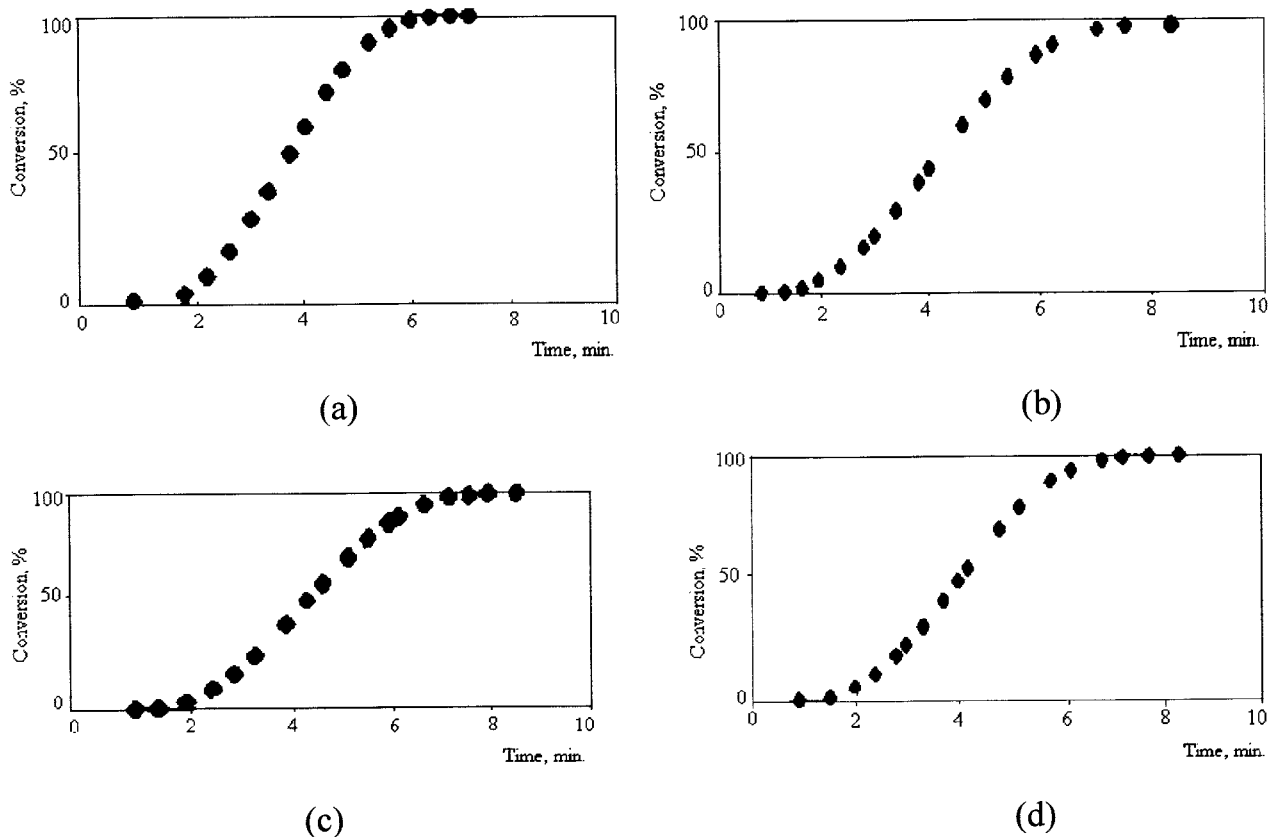
(a)

(b)

(c)

(d)

Figure 7 Isothermal of crystallization at 122°C of the samples: (a)A′, (b) A, (c) B, (d) C.

The crystallized material fraction was obtained by the integration of the area under the crystallization peak in predetermined time intervals, by the equation:

$$\chi(t) = \int \frac{dH}{dt}\, dt \Big/ \int \frac{dH_T}{dt}\, dt \qquad (1)$$

where dH/dt is the heat flow rate, and $\chi(t)$ is the fraction, wt %, of the crystallized material in t time.
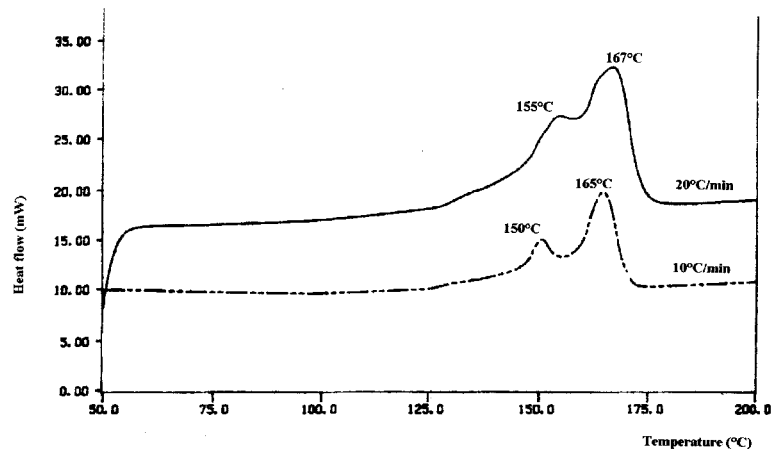
For as much as the integrals represent areas, eq. (1) can be transformed to eq. (2):

$$\chi(t) = A_t/A_\infty \qquad (2)$$

Figure 7 shows the crystallization exotherms of PP and PEE/PP blends. As can be observed, the exotherms present sigmoidal forms that, according to the literature,[11] characterize a crystallization process without any descontinuity, which is typical of a phase transformation in polymers.

Table III   Isothermal Crystallization Parameters ($t_{1/2}$ and ΔH_f) to PP and PEE/PP Blends

Sample	$t_{1/2}$ (min)	ΔH_f (J/g)
A′	3.5	93
A	4.1	71
B	4.2	53
C	4.0	36

Table IV   Heat of Fusion (ΔH_f) and Crystallinity Degree (χ_c) of PP and PEE/PP Blends

Heating Rate (°C/min)	A′ ΔH_f (J/g)	A′ χ_c (%)	A ΔH_f (J/g)	A χ_c (%)	B ΔH_f (J/g)	B χ_c (%)	C ΔH_f (J/g)	C χ_c (%)
20	88.6	42.4	83.6	40.0	74.4	35.6	64.6	30.9
10	84.8	40.6	82.5	39.5	63.9	30.6	62.1	29.8

(a)
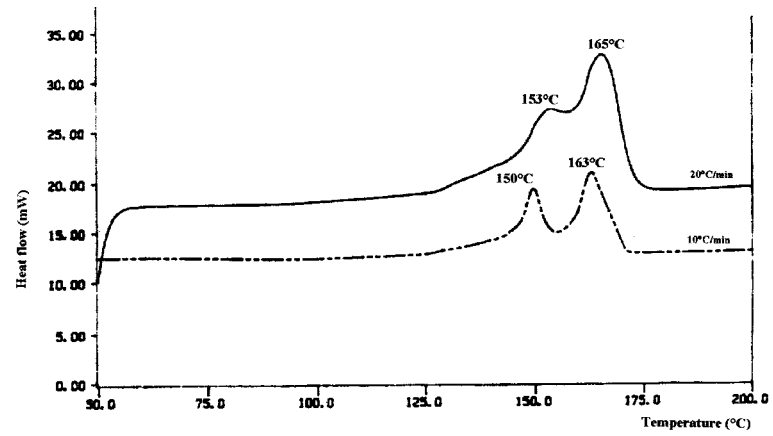
(b)
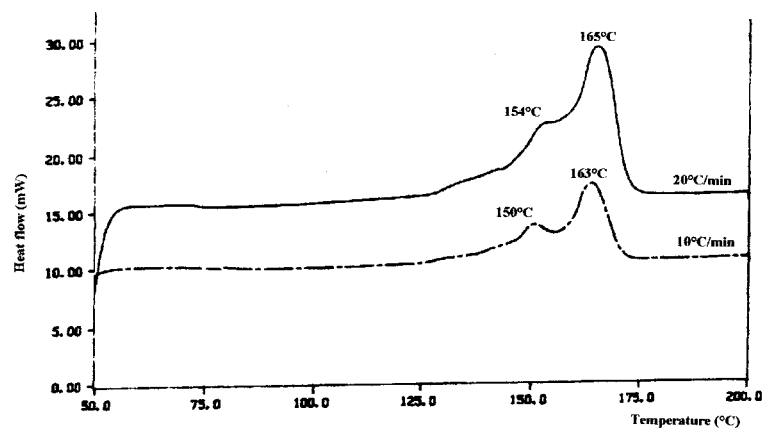
(c)

Figure 8   Fusion behavior of the samples: (a) A′, (b) A, (c) B, (d) C.

(d)

Figure 8. (*Continued from the previous page*)

This transformation proceeds in an accelerated rate, up to attaining a pseudoequilibrium state.
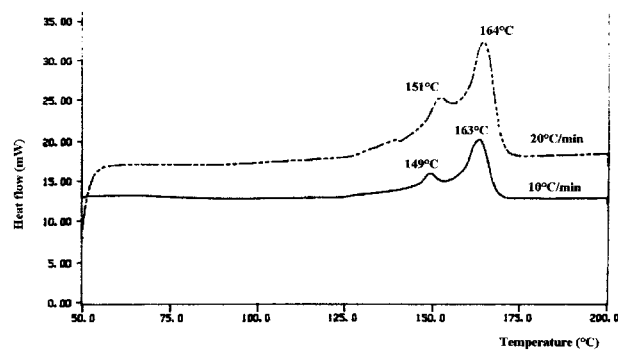
The crystallization speed was available in terms of the experimental parameter $t_{1/2}$, that is, the time (in minutes) to attain 50% conversion rate.

The $t_{1/2}$ values and the fusion heat (ΔH_f) for PP and PEE/PP blends are shown in Table III.

The results show that the crystallization speed, expressed by $t_{1/2}$ values, tend to increase with the addition of the elastomer. Therefore, the variation of the crystallization speed was not significant in the composition range analyzed. This behavior confirmed the results obtained by microscopy analysis. As expected, the ΔH_f values show that the crystallinity of the samples decreases with the increase of PEE content.

The heat of fusion (ΔH_f) and the crystallinity degree (χ_c) of PP and PEE/PP blends at the heat speeds analyzed are shown in Table IV.

Table IV shows that the crystallinity degree was not affected significantly in the heat speed range analyzed. A tendency of the crystallinity degree to decrease as the heat speed decreases was observed.

The fusion behavior of PP and PEE/PP blends were also analyzed. After the crystallization at 122°C, the samples were immediately heated using the following heating rates: 10 and 20°C/min. The fusion curves of PP and PEE/PP blends are shown in Figure 8.

Figure 8 shows that in all endothermas of fusion, two fusion peaks can be observed, and that at the heating rate of 10°C/min the peaks were more defined.

The literature reported[12] that the PP peak that appears at the lower temperature is attributed to

the fusion of the crystals formed during the isothermal crystallization process. The peak that appears at the higher temperature may be attributed to the fusion of the crystals resultant from the recrystallization or reorganization processes that occur during the fusion.

Figure 8 also shows that the addition of PEE tends to shift the peaks to lower temperatures; this behavior was more accentuated in sample C, which contains higher PEE proportion.

The recrystallization or reorganization processes of the crystals can occur during the fusion of metastable crystals. At low heating rates, there is time enough for those crystals to stabilize through recrystallization or reorganization processes. This behavior may explain the fact that more defined peaks appeared at 10°C/min rate.

Figure 8 also shows that the peak temperature is a function of the heating rate. As the heating rate decreased to 10°C/min, those peaks shifted to lower temperature. An endothermal "shoulder" in all samples can be observed that were heated at 20°C/min, in a temperature range between 125 and 150°C. Probably, that "shoulder" corresponds to the β crystalline form transition that, according to the literature,[12] occurs around 143°C.

The $t_{1/2}$ values and the fusion heat (ΔH_f) to PP and EPDM/PP blends are shown in Table V.

Table V shows that the variation of the crystallization speed was not significant in the composition range analyzed. The ΔH_f values also show that the crystallinity of the samples decreases as EPDM content increases. These results show that EPDM/PP and PEE/PP blends present the same crystalization behavior.

The heat of fusion (ΔH_f) and the crystallinity degree (χ_c) of PP and EPDM/PP blends at the heating rates analyzed are shown in Table VI.

In PEE/PP systems, the crystallinity degree of EPDM/PP blends was not affected significantly at the heating rate range analyzed. Comparing the results in Table VI with the results in Table IV, it

Table V Isothermal Crystallization Parameters ($t_{1/2}$ and ΔH_f) to PP and EPDM/PP Blends

Sample	$t_{1/2}$ (min)	ΔH_f (J/g)
A′	3.5	93
A*	3.6	74
B*	3.5	65
C*	3.5	55

Table VI   Heat of Fusion (ΔH_f) and Crystallinity Degree (χ_c) of PP and EPDM/PP Blends

Heating Rate (°C/min)	A′		A*		B*		C*	
	ΔH_f (J/g)	χ_c (%)	ΔH_f (J/g)	χ_c (%)	ΔH_f (J/g)	χ_c (%)	ΔH_f (J/g)	χ_c (%)
20	88.6	42.4	85.2	40.8	76.7	36.7	68.2	32.6
10	84.8	40.6	86.7	41.5	76.5	36.6	64.6	30.9

can be observed that ΔH_f and χ_c values of both systems (PEE/PP and EPDM/PP blends) are very close.

The fusion endotherms of EPDM/PP blends present a similar behavior as those of PEE/PP systems, i.e., two peaks appeared, and at lower heating rate these peaks become better defined. It was also observed that when the heating rate was decreased, the peaks shifted to a lower temperature. A endothermal "shoulder" in all samples that were heated at 20°C/min was also observed between 125 and 150°C. For PEE/PP systems, this "shoulder" can also be related to β crystalline form transition.

Previous results[7] showed that PEE/PP and EPDM/PP systems present similar behavior relative to tensile properties and impact strength. These results can be related to the similar crystallization behavior of the PP blends that was observed in this work.

CONCLUSIONS

The results obtained by optical microscopy and DSC analysis showed that the behavior of crystallization kinetics of PEE/PP and EPDM/PP systems were similar, and that they were not significantly affected by the addition of elastomers, in the compositions analyzed in this work.

Similar thermal behaviors (fusion and crystallization) of PEE/PP and EPDM/PP blends were verified. These results corroborate the results reported previously that the PEE/PP and EPDM/PP systems present a similar mechanical behavior.[7]

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