Influence of copolymer composition on phase structure and crystallization of poly(ethylene oxide)/poly(ethylene-*co*-vinyl acetate) blends

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The influence of copolymer composition and crystallization temperature on the kinetics of crystallization and the morphology of poly(ethylene oxide)/poly(ethylene$_{1-y}$-*co*-vinyl acetate$_y$) 80/20 wt/wt blends was analysed. It was found that the morphology and the crystallization rate are strongly dependent on the copolymer composition, y (mole fraction). In particular, for blends containing the copolymer with low content of vinyl acetate (VAc) ($y \leqslant 0.43$), the non-crystallizable material segregates into spherical domains in intraspherulitic regions. The spherulite growth rate G is slightly depressed and the overall crystallization rate is independent of the copolymer composition in the blends. For blends with high VAc content ($y \geqslant 0.56$), there is no evidence that the copolymer forms segregated domains. For these blends, G and the overall crystallization rate are markedly depressed with respect to that of the pure poly(ethylene oxide) (PEO). The results obtained were accounted for by assuming that the copolymers with $y \geqslant 0.56$ were miscible with the PEO, whereas those with $y \leqslant 0.43$ formed a two-phase separated system with the PEO.

(Keywords: copolymer; poly(ethylene oxide); poly(ethylene-*co*-vinyl acetate); blends; phase structure; crystallization; kinetics; morphology)

INTRODUCTION

To our knowledge, for crystallizable component/non-crystallizable copolymer blends, the influence of copolymer composition on the crystallization parameters and phase structure has not been studied. On the other hand, for homopolymer/copolymer amorphous blends, the dependence of miscibility on copolymer composition is very well known[1-3]. Miscibility in these blends is often due not to any specific interaction between the two polymers but rather to a repulsion between the different monomer units of the copolymer. In a previous work[4] we have reported the results of a miscibility study of poly(ethylene oxide)/(poly(ethylene-*co*-vinyl acetate) (PEO/EVAc-1) blends as a function of temperature and blend composition. (For the composition of EVAc-1, see *Table 1*.) It was found that mixtures of PEO and EVAc-1 were miscible up to about 220°C and underwent phase separation at higher temperatures. The application of Flory's equation-of-state theory predicted a lower critical solution temperature (*LCST*).

It is the purpose of this paper to report the influence of copolymer composition on the crystallization kinetics and the morphology of poly(ethylene oxide)/poly(ethylene-*co*-vinyl acetate) (PEO/P(Et$_{1-y}$-*co*-VAc$_y$) blends, keeping the blend composition constant at 80/20 wt/wt. It is interesting to note that the two limiting polymers of the copolymer, polyethylene (PE) and poly(vinyl acetate) (PVAc), present very different miscibility extents with PEO. It is reported, in fact, that PEO is miscible at the molecular level with PVAc, whereas it is immiscible with PE[5-10]. In our blends, probably there could be a copolymer composition at which a miscibility/immiscibility boundary is found.

EXPERIMENTAL

Materials and blend preparation

The molecular characteristics of the polymers are reported in *Table 1*. PEO and EVAc copolymers were supplied by Fluka AG (Germany) and by Kuraray (Japan) respectively. All the copolymers used were found by d.s.c. to be amorphous. The binary blends PEO/EVAc

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Table 1 Molecular characteristics of polymers[a]

						Copolymer composition (VAc content)	
Polymer	Code	M_w (10^{-3})	M_n (10^{-3})	M_v (10^{-3})	T_g (°C) (±2°C)	Weight fraction	Mole fraction
Poly(ethylene oxide)	PEO	20	–	20	−44	–	–
Poly(ethylene-*co*-vinyl acetate)	EVAc-1	200	67	–	20	0.87	0.69
	EVAc-2	160	55	–	8	0.83	0.61
	EVAc-3	170	60	–	1	0.79	0.56
	EVAc-4	220	66	–	−14	0.70	0.43
	EVAc-5	240	93	–	−29	0.50	0.25

[a] M_w, M_n and M_v are expressed in g mol^{-1}

Table 2 Glass transition temperature T_g and nucleation density N of blends

Sample	T_g (°C) (±2°C)	N (mm^{-3})
PEO	−44	1.8
Blend 1	−6	6.3
Blend 2	−10	6.5
Blend 3	−15	5.8
Blend 4	−13 −43	5.4
Blend 5	−13 −43	6.1

80/20 wt/wt were prepared by casting a 10% (wt/vol.) solution of the preweighed mixture of PEO and EVAc in chloroform onto flat Petri dishes at room temperature.

The codes of the blends used in the present work are the following:

Blend	*Code*
PEO/EVAc-1	Blend 1
PEO/EVAc-2	Blend 2
PEO/EVAc-3	Blend 3
PEO/EVAc-4	Blend 4
PEO/EVAc-5	Blend 5

To ensure complete removal of the solvent, the resulting films were kept under vacuum at 70°C for 24 h.

Radial growth rate measurements

The radial growth rates were calculated by using a polarizing microscope fitted with an automatic hot stage. The standard procedure used was the following: Blend films were sandwiched between a microscope slide and a coverglass, heated at 80°C and kept at this temperature for 10 min. The temperature was then rapidly lowered to the crystallization temperature T_c, and the blends were allowed to crystallize isothermally. The radial growth of a spherulite was finally monitored during crystallization by taking micrographs at appropriate intervals of time and measuring the size of PEO spherulites as a function of time.

Calorimetric measurements

The overall kinetics of crystallization and the glass transition temperature of the blends were analysed by differential scanning calorimetry (Mettler TA 3000). The isothermal crystallization process was studied using the following procedure: All the samples were heated at 80°C and kept at this temperature for 10 min. The samples were rapidly cooled to the desired T_c, and the heat dH/dt evolved during the isothermal crystallization was recorded as a function of time. The weight fraction X_t of material crystallized at time t was calculated from the ratio of the heat generated at time t and the heat evolved during the complete crystallization.

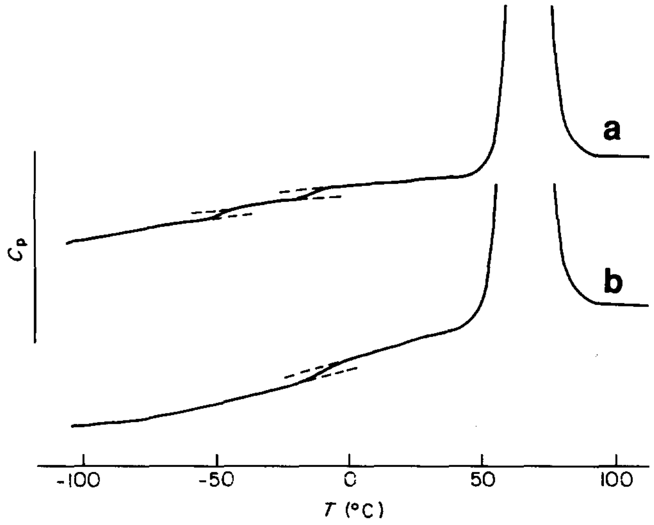

Figure 1 D.s.c. thermograms for (a) blend 4 and (b) blend 1

The glass transition temperatures were obtained by heating the samples from −100 to 100°C at a rate of 10 K min^{-1} and by recording the heat evolved during the scanning process as a function of temperature. The T_g of the sample was taken as the temperature corresponding to 50% of the transition.

RESULTS AND DISCUSSION

Glass transition temperature

In *Table 2* are reported the T_g values of the blends detected on d.s.c. thermograms, and in *Figure 1* are shown as an example only the thermograms of blend 1 and blend 4.

In the case of blend 1, blend 2 and blend 3 a single T_g is always detected (see for example the thermogram of blend 1 shown in *Figure 1b*). The appearance of a single T_g indicates that, within the limits of detection of the used d.s.c. technique, the blends are molecularly homogeneous in the amorphous phase. For blend 4 and blend 5 (see *Figure 1a*) two glass transition temperatures are present

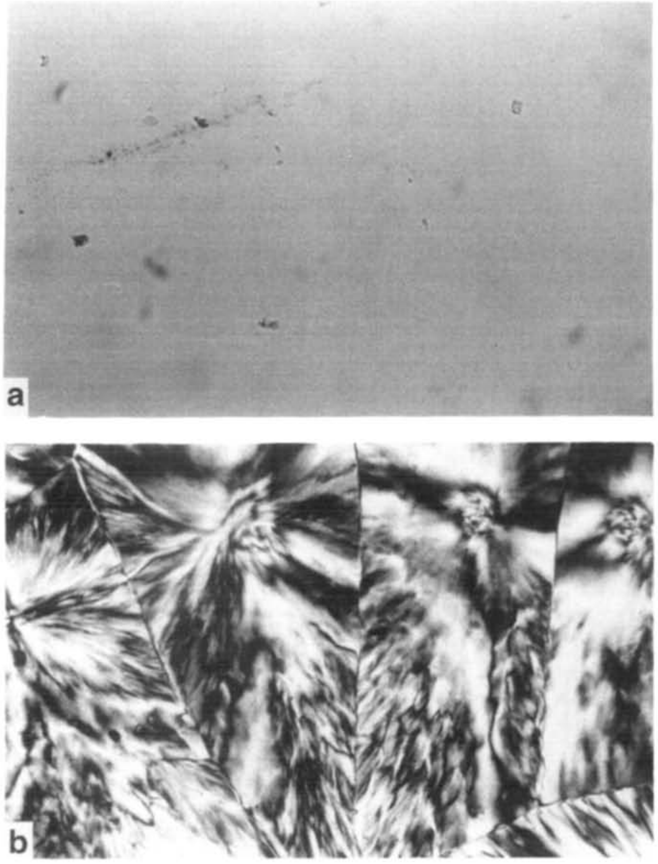

Figure 2 Optical micrographs of blend 1 film: (a) melted at 80°C; (b) isothermally crystallized at 50°C. Magnification 380 ×, reduced to 50% in printing

on thermograms, indicating probably that in the melt two amorphous phases are present, one rich in PEO and the other in copolymer, in agreement with the morphological evidence and the kinetics of crystallization results reported in the following sections.

Morphology

The morphology and the state and mode of dispersion of the minor component in the blend are dependent on the copolymer composition.

Optical micrographs of thin films of PEO/EVAc blends for different copolymer composition are reported in *Figures 2–6*. For blend 1, blend 2 and blend 3 (see *Figures 2–4*) the melt is homogeneous. After crystallization there is no evidence that the copolymer forms segregated domains in inter- and/or intraspherulitic contact zones, with dimensions exceeding the resolving power of the technique used. This result indicates that for these blends the copolymer is present in interlamellar regions, suggesting miscibility at the molecular level of the two components, in agreement with the d.s.c. data.

For blend 4 and blend 5 the melt is not homogeneous and the samples are phase separated. For blend 4 (see *Figure 5*) a modulated structure characterized by the presence of two continuous phases is present. For blend 5 (see *Figure 6*) discrete particles dispersed in a continuous matrix are visible. The particles are spherical with dimensions ranging between 20 and 120 μm.

After crystallization the particles are mainly segregated in intraspherulitic regions.

Because in a blend the resulting morphology is

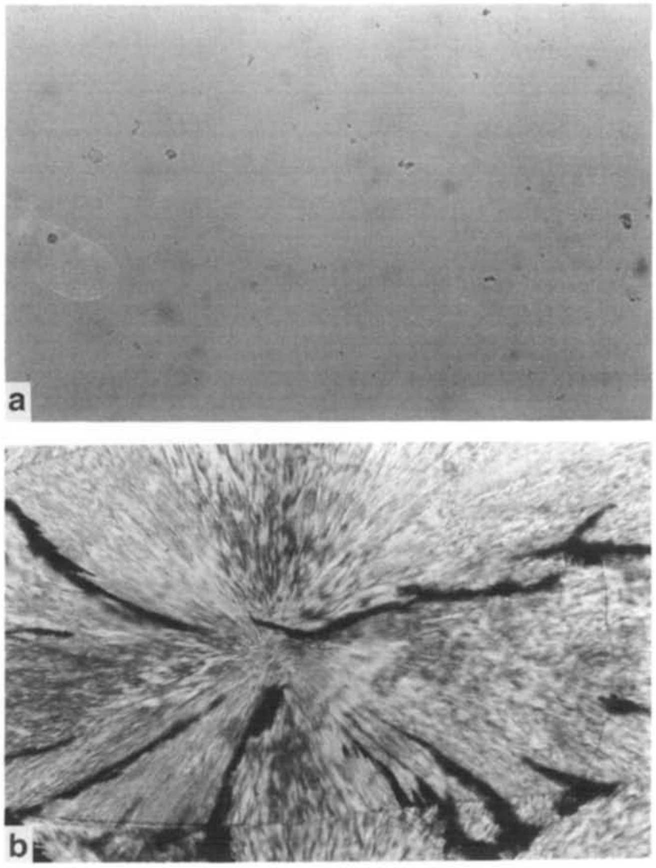

Figure 3 Optical micrographs of blend 2 film: (a) melted at 80°C; (b) isothermally crystallized at 50°C. Magnification 380 ×, reduced to 50% in printing

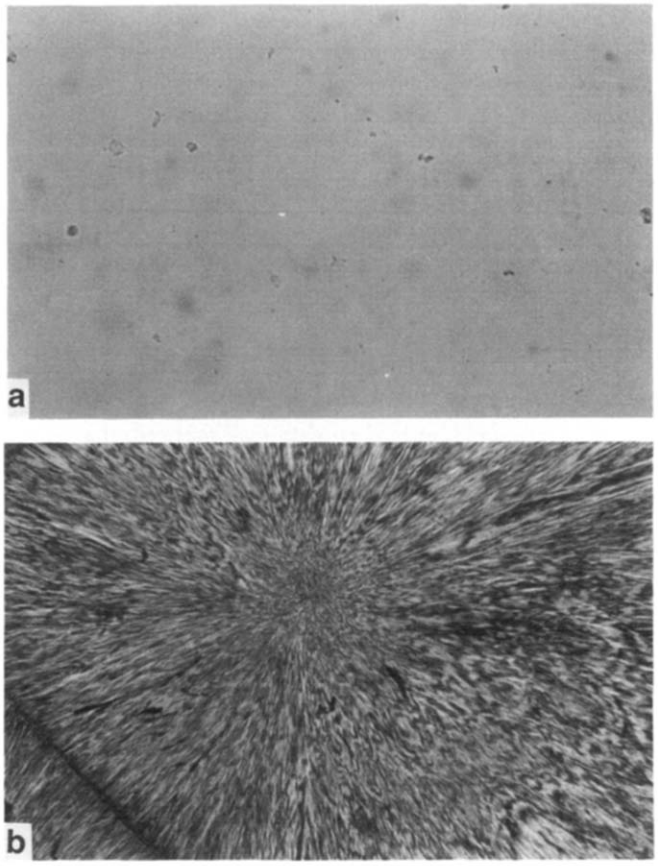

Figure 4 Optical micrographs of blend 3 film: (a) melted at 80°C; (b) isothermally crystallized at 50°C. Magnification 380 ×, reduced to 50% in printing

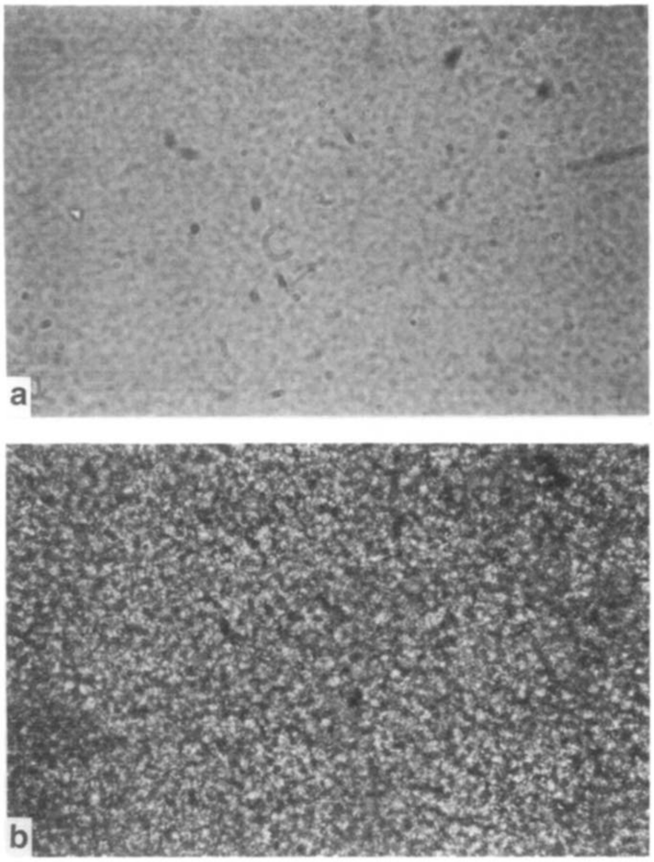

Figure 5 Optical micrographs of blend 4 film: (a) melted at 80°C; (b) isothermally crystallized at 50°C. Magnification 380 ×, reduced to 50% in printing

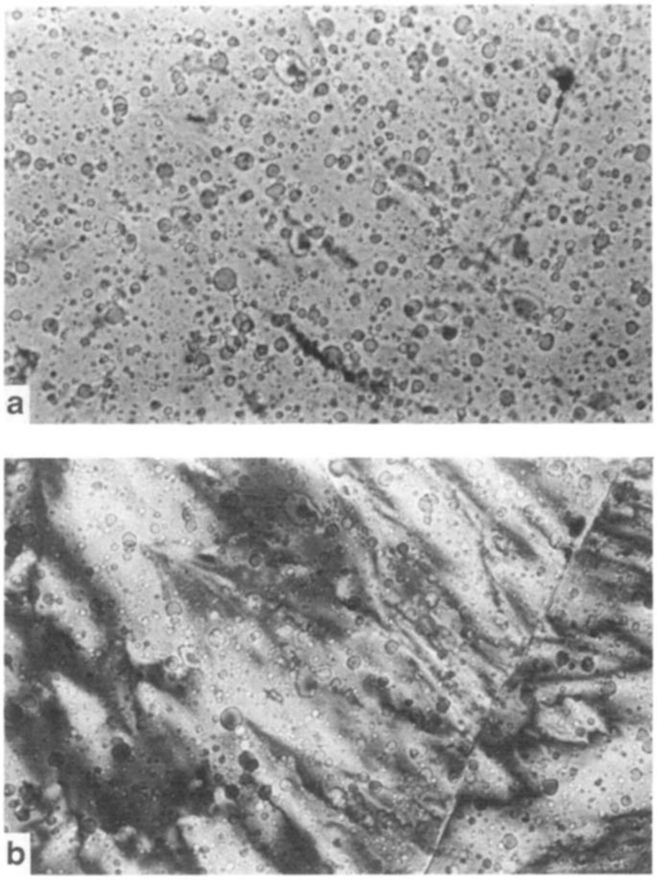

Figure 6 Optical micrographs of blend 5 film: (a) melted at 80°C; (b) isothermally crystallized at 50°C. Magnification 380 ×, reduced to 50% in printing

connected to the mechanism of phase separation, the two different morphologies observed could be an indication that the two blends underwent different demixing mechanisms: nucleation and growth for blend 5 and spinodal decomposition for blend 4[11,12].

Crystallization rate

The spherulite growth rate G, as a function of crystallization temperature for different copolymer compositions, is reported in *Figure 7*.

For all the blends at a given T_c a decrease in G with respect to the pure PEO is always observed. This decrease is dependent on copolymer composition. For blend 4 and blend 5 the decrease of G was less marked than that observed for blend 1, blend 2 and blend 3. The decrease of G for all the blends can be related to the diluent effect of the copolymer on the PEO spherulites.

For blend 4 and blend 5 phase separation is present, in agreement with the T_g data and the morphological results, so the composition of copolymer in the PEO-rich phase involved in the crystallization is lower than the nominal one.

Supposing that the decrease in G is due only to the diluent effect, it is possible to calculate the composition of PEO-rich phase, X, in blend 4 and blend 5 through an empirical relation:

$$X=\frac{0.20(G_0-G_{0.20})}{G_0-G_x} \qquad (1)$$

where $G_{0.20}$ is the depression of G observed for blend 1, blend 2 and blend 3 caused by adding 20% of copolymer

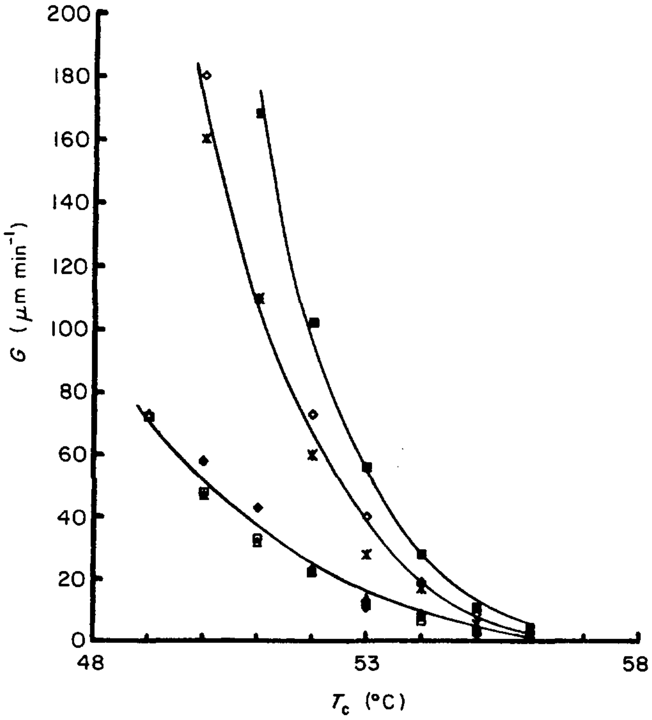

Figure 7 Spherulitic growth rate G *versus* crystallization temperature for different copolymer composition blends: ■, PEO; □, blend 1; △, blend 2; ◆, blend 3; ◇, blend 4; ✱, blend 5

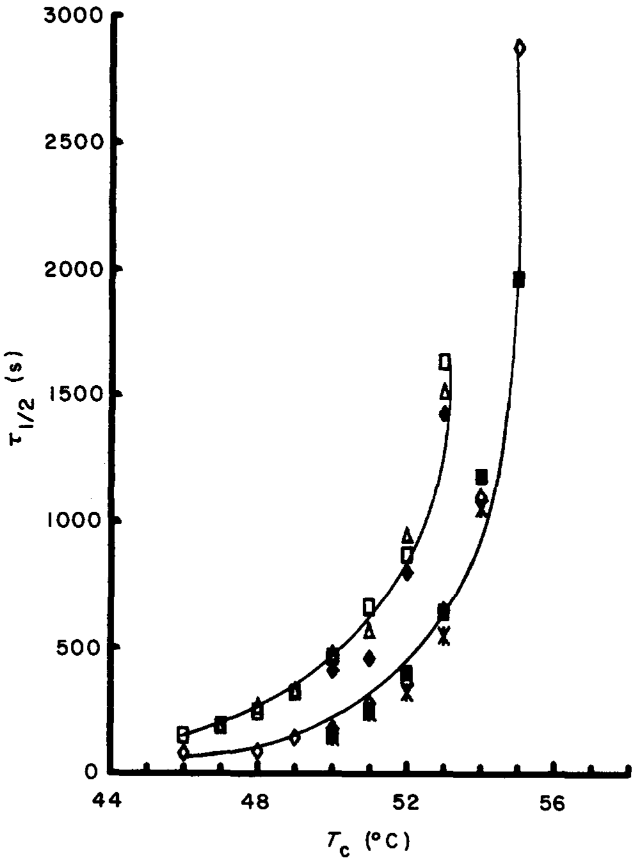

Figure 8 Half-time of crystallization as a function of T_c for PEO and blends. Symbols as in *Figure 7*

to the PEO; G_0 is the spherulite growth rate of pure PEO; G_x is the spherulite growth rate of the phase-separated blend (blend 4 and blend 5).

This empirical relation was found to be valid for any crystallization temperature. The value of $X = 0.09 \pm 0.01$ found for both blend 4 and blend 5 could indicate that the diluent effect is a function only of the amount of copolymer present in the PEO-rich phase and is hence independent of copolymer composition.

The half-time of crystallization, $\tau_{1/2}$, obtained from the isotherm of crystallization, is plotted in *Figure 8* as a function of T_c for pure PEO and for the blends. For blend 1, blend 2 and blend 3 an increase of $\tau_{1/2}$ at a given T_c is observed. For blend 4 and blend 5, at a given T_c, $\tau_{1/2}$ and hence the overall crystallization are independent of the presence of copolymer in the blend.

For blend 1, blend 2 and blend 3 the increase of $\tau_{1/2}$ can be mainly attributed to the diluent effect that the copolymer seems to have on the PEO, in agreement with the spherulite growth rate data.

For blend 4 and blend 5 the constancy of $\tau_{1/2}$ with composition could be due to the influence of copolymer on the nucleation of PEO spherulites. In fact, taking into account that the overall bulk crystallization comprises the nucleation rate plus the spherulitic crystallization rate, and that G decreases with composition, in order to explain the constancy of $\tau_{1/2}$ we have to invoke a positive influence of the copolymer on the nucleation process of the PEO, in accordance with the values of the nucleation density of the spherulites in the blends.

The nucleation density N was obtained from the overall crystallization rate constant $K_n = l_n/\tau_{1/2}^3$ and the spherulite growth rate G, using the following relation[13]:

$$K_n = \tfrac{4}{3}\pi N G^3 \frac{\rho_c}{\rho_a} \frac{1}{1-\Lambda_\infty} \qquad (2)$$

where ρ_c and ρ_a are the densities of the crystalline and amorphous phases, and Λ_∞ is the crystallinity at infinite time. The values of N for $T_c = 50$°C are reported in *Table 2*. It can be seen that for the blends N is higher than that for the pure PEO, probably indicating a nucleating effect of the copolymer on the PEO crystallization.

CONCLUSIONS

This paper indicates that for the PEO/EVAc 80/20 (wt/wt) blends the copolymer composition as well as the crystallization temperature play an important role in the definition of the morphological and kinetic parameters related to the isothermal crystallization from the melt. For all the blends studied a depression in the spherulite growth is always observed, with the amount of the depression dependent on copolymer composition. The kinetic results together with the morphological evidence and the d.s.c. data lead to the hypothesis that at crystallization temperatures the copolymers EVAc-1, EVAc-2 and EVAc-3 are miscible with PEO, and the blends 4 and blend 5 are phase separated. For the latter blends the composition of the copolymer in the PEO-rich phase involved in the crystallization is lower than the nominal one. In order to find the composition of the PEO-rich phase in blend 4 and blend 5 an empirical relation was introduced based on the supposition that the diluent effect only is responsible for the decrease in G. Through this relation it is found that the PEO-rich phase contains about 9% of the copolymer.

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