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Crystallisation and miscibility of poly(ethylene oxide)/poly(vinyl chloride) blends

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Isothermal crystallisation of blends of Poly(ethylene oxide) and Poly(vinyl chloride), PEO/PVC, was analysed by differential scanning calorimetry (DSC). The influence of the amorphous polymer, PVC, on crystallisation rate of PEO was investigated using pure PEO as reference. Pure PEO and PEO/PVC blends were submitted to different crystallisation temperatures (from 40 to 58°C) and crystallisation times (from 1 to 72 h). Using the Hoffman-Weeks plot procedure, the equilibrium melting temperature, T_m°, was determined for pure PEO and for PEO/PVC blends with compositions (in wt%): 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70 and 20/80. The lamellar thickness factor of PEO crystals for pure PEO and for the blends showed a strong decrease when the PVC content was higher than 60 wt%. A small depression in T_m° was verified as the composition of PVC was increased. From the depression in T_m° the polymer-polymer interaction parameter, χ_{12}, was evaluated using the Nishi-Wang equation. The results indicate that the miscibility between PEO and PVC in the molten state depends on the blend composition. The crystallisation rate also depends on the blend composition: the richer in PVC is the blend, the slower the crystallisation process.

1. Introduction

The crystallisation process in a blend constituted of amorphous and semi-crystalline polymers is more complex when compared to the crystallisation of pure components. The presence of amorphous polymer induces changes in the crystallisation, mainly in the morphology and in the crystallisation rate [1]. In this sense, interesting effects may be observed, such as a depression in equilibrium melting temperature, decrease of crystallinity and changes in structure and morphology of the spherulites [1–5].

Due to the low entropy of mixing, $\Delta_m S$, the miscibility between the components of a polymer blend is driven mainly by the enthalpy of mixing, $\Delta_m H$ [1, 2]. Thus, effects decreasing $\Delta_m H$ will decrease the Gibbs energy of mixing, $\Delta_m G$, favouring the miscibility [1, 6]. Usually, interactions among side groups or polymer segments are responsible for the miscibility. Several techniques have been used to investigate the miscibility, for instance, the determination of glass transition temperature (T_g) [1–9], spectroscopy (FTIR, NMR, etc.) [5, 6, 10], microscopy (OM, SEM, TEM, AFM, etc.) [1, 6, 10] and simple techniques, such as viscometry [11]. When the components of the blend are semi-crystalline and amorphous polymers, the depression in the melting temperature is frequently used to investigate the miscibility [12].

It is well known that polymeric materials do not have a well-defined temperature of melting, T_m, as occurs in compounds of low molar mass. In fact, the T_m for a crystalline polymer has strong dependence to variables related to the polymer itself, such as molar mass, polydispersity, etc. and to parameters related to thermal treatment, such as thermal history, temperature of crystallisation, speed of quenching, ageing of the crystals, etc. To investigate the polymer-polymer miscibility by depressing in the melting temperature, it is important to measure the equilibrium melting point (T_m°) because this parameter is not time-dependent [12]. The Hoffman-Weeks plots procedure has been widely used to determine the T_m° of polymers [12]. According to this approach, the dependence of the observed melting point, T_m, to the crystallisation temperature, T_C, is given by Equation 1, where η is the lamellar thickness factor, i.e., the ratio of the lamellar thickness to the critical nucleus thickness, in the crystallisation process.

$$T_m = \frac{1}{\eta} T_C + T_m^\circ\left(1 - \frac{1}{\eta}\right) \qquad (1)$$

The Equation 1 shows that T_C may affect the T_m, mainly due to the dependence of mobility on the temperature [12].

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In a previous work, we investigated the miscibility of poly(ethylene oxide) with poly(vinyl chloride) by thermal analysis, viscometry and microscopy [13]. By viscometry and thermal analysis, it was observed that PEO/PVC blends are miscible in all range of compositions, but the presence of PVC rich phase were detected by SEM. We suggested that interactions among chlorine atoms in PVC and oxygen atoms in PEO are the responsible for the miscibility. Depression in melting temperature (T_m) of PEO spherulites in the PEO/PVC blends, related to the pure PEO, up to 7°C was observed. However, in that work the used melting temperatures were not in equilibrium.

Other researchers have observed miscibility in PEO/PVC blends, but some conflicting conclusions are found in the literature. For instance, Margarits and Kalfoglou [14] suggested that PEO and PVC are miscible when the blend is richer in PEO. Otherwise, Etxeberria and co-workers [15] pointed out that PEO/PVC blends are miscible when the PVC content is higher than 50 wt%.

In this paper, we investigated the influence of PVC on the isothermal crystallisation rate of PEO by using different temperatures and crystallisation times. In addition, results concerning the miscibility of the polymers, using equilibrium melting temperatures, are discussed and related to the crystallisation rate and lamellar thickness factor of PEO.

2. Experimental

2.1. Preparation of samples

Poly(ethylene oxide) [PEO, having average molar mass, M_n, 200 kg mol^{-1}, from Aldrich, 18.199-4] and Poly(vinyl chloride) [PVC, having average viscosimetric molar mass, M_v, 82.7 kg mol^{-1}, from Solvay do Brazil S.A.] were used as received. Tetrahydrofuran [THF, from Labsynth, Brazil] was purified by distillation.

Films of pure PEO and blends of PEO/PVC were prepared by casting solutions of the polymers in THF. The polymer concentration of solutions was fixed at 5.0 wt%, at the desired ratio to obtain blends with PVC content from 0 to 90 wt%. After dissolution with magnetic stirring, the solutions were dropped onto glass Petry dishes and evaporated under solvent saturated atmosphere conditions. Afterwards the films were detached and dried under vacuum at ambient temperature. The cast films were stored in a dissecator and in the absence of light.

2.2. Thermal analyses

Thermal analyses were carried out in a Shimadzu calorimeter, model DSC 50, with a heating program of 10°C/min under N_2 atmosphere. Temperature calibration was carried out using a pan with known quantities of indium. The samples were closed in an aluminium pan and the weights of the samples ranged from 6 to 8 mg. Thermograms were obtained from ambient temperature to 80°C.

2.3. Isothermal crystallisation process

2.3.1. Changing the crystallisation time

The samples prepared as described above were submitted to a previous heating up to 100°C for evaporation of remaining solvent and elimination of crystallisation effects during the blend preparation. After the heating, the samples were quickly cooled to a fixed crystallisation temperature, T_C, during times that varied from 0.5 to 72 hours, depending on the composition of the blend. The crystallisation was carried out in a homemade furnace, in which the temperature was controlled using a thermostatic bath with precision of ± 0.1°C. During the crystallisation, the samples were kept in vacuum and shielded from light. For each crystallisation time, the respective thermogram was obtained, from which the melting temperature and the melting enthalpy were determined.

2.3.2. Changing the crystallisation temperature

For pure PEO and each blend, the crystallisation temperature, T_C, was varied in steps of 2°C, from 40 to 58°C keeping the crystallisation time fixed in 1 hour. The value of T_m (the first inflection point calculated through the first derivative in the beginning of melting event) was determined for each run, using the Hoffman-Weeks plot procedure, based in Equation 1. The value of T_m° for pure PEO and blends were determined from the intersection of the respective T_m vs. T_C curve with the $T_m = T_C$ line.

3. Results and discussion

3.1. Crystallisation process and crystallisation rate

The crystallisation of polymers may occur in a range of temperatures limited by T_g and T_m. At temperatures below or near T_g, the chain mobility is slow and the probability of crystal formation tends to zero. This explains, for instance, the formation of amorphous material by rapid cooling crystalline polymer, from the molten state to temperatures below T_g. Otherwise, at temperatures near or above T_m the chain mobility is so high that crystallisation does not occur. Thus, the crystallisation rate has a maximum value between T_g and T_m [16].

The melting enthalpy, ΔH, indicates the amount of crystallised material [16–18], because the higher is the crystallinity fraction (X_C), the higher the energy needed to melt the crystals. Thus, we used this parameter to evaluate the value of X_C in pure PEO and in the PEO/PVC blends. The values of ΔH, at the desired T_C, were calculated through the area in the thermogram assigned to the melting process. At fixed T_C, X_C was calculated as being the ratio between the melting enthalpy observed in a crystallisation time t, ΔH_t, and the melting enthalpy observed for the respective material crystallised during a long time ($t = 48$ hours), $\Delta H_{t=48\,\mathrm{h}}$. The dependence of $\Delta H_t/\Delta H_{t=48\,\mathrm{h}}$, or X_C, to the crystallisation time, at $T_C = 40$°C, is shown in Fig. 1 for the blends with 90, 40, 30 and 20 wt% of PEO. The initial slope of such curves may be related to the crystallisation rate at that temperature. From Fig. 1, it

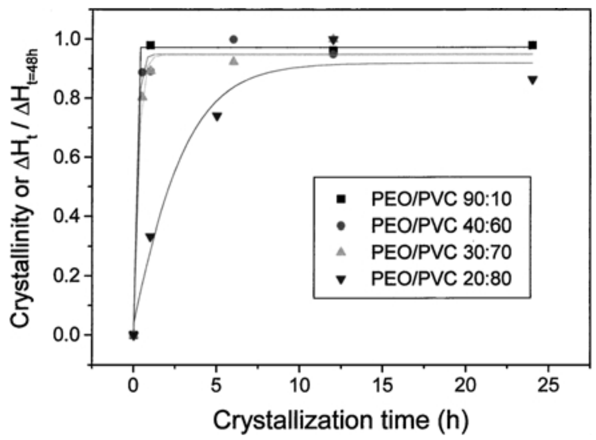

Figure 1 Crystallinity (X_C) as a function of crystallisation time. X_C was calculated as being the ratio of the melting enthalpy in a desired crystallisation time t, ΔH_t, to the melting enthalpy observed in crystallisation during long time (48 hours), $\Delta H_{t=48\,h}$.

may be verified that the initial crystallisation rate for the 20/80 PEO/PVC blend is lower than the blends richer in PEO. This fact suggests a decreasing mobility of the PEO chains at higher PVC content. The presence of PVC chains, in compositions above 60 wt%, reduces the diffusion of the molten material to be transferred to the growing PEO spherulites. The results presented in Fig. 1 show that, for the 20/80 PEO/PVC blend, a time equal to or greater than 12 hours is necessary to complete crystallisation and for blends richer in PEO the crystallisation reaches completion faster, less than one hour, at 40°C.

As aforementioned, a typical curve of crystallisation rate as a function of T_C possesses a maximum value between T_g and T_m [16]. Since the crystallisation of the 20/80 PEO/PVC blend is relatively slow compared to the blends richer in PEO investigated in this work, its dependence on T_C was determined. This was done by taking into account that the initial slope of the curves, presented in Fig. 1, is directly connected to the crystallisation rate. The dependence of crystallisation rate on the T_C for the 20/80 PEO/PVC blend is shown in Fig. 2. We observed that the blend shows a maximum when T_C is near to 40°C. This value lies between the T_g (−60°C)[13-14] and the T_m of PEO. From Fig. 2 it is observed that the crystallisation rate increases about 4 fold when the crystallisation temperature is lowered from 60°C to 40°C.

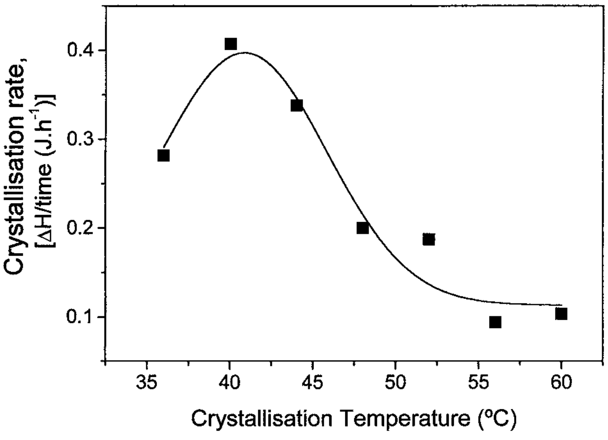

Figure 2 Crystallisation rate as a function of crystallisation temperature. Crystallisation rate was determined by taking into account the initial slope of the curves presented in Fig. 1.

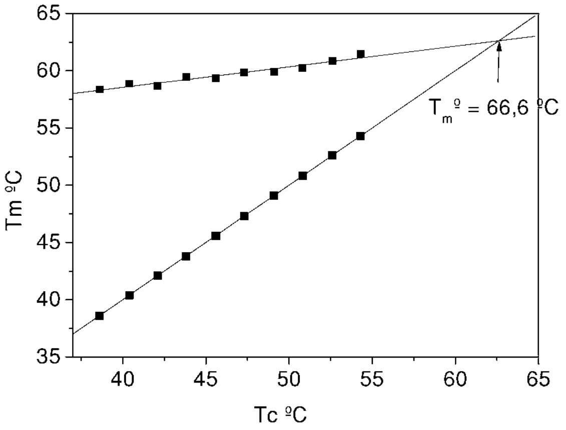

Figure 3 Hoffman-Weeks plot for the blend PEO/PVC 70/30.

3.2. Equilibrium melting temperature

The value of the T_m was determined at desired T_C, for the pure PEO and PEO/PVC blends, based upon the inflection point appearing in the thermogram during the melting process, by using the first derivative. From the value of T_m, obtained for the PEO and blends at several T_C values, it was possible to obtain the value of T_m° and the value of the lamellar thickness factor, η, through the Hoffman-Weeks plot procedure. Fig. 3 displays the dependence of T_m on the T_C for the PEO/PVC 70/30 blend. As expected from Equation 1, the dependence of T_m with T_C is linear. To determine the value of T_m°, for the pure PEO and blends, the respective curves of T_m vs. T_C, were projected up to intercept the curve for $T_m = T_C$, as presented in Fig. 3. The linear dependence of experimental data observed in Fig. 3 was also observed for the pure PEO and for the other blends investigated in this work. The value of η was determined from the slope of these curves. The values of T_m° and η for the pure PEO and PEO/PVC blends are presented in Table I. The lamellar thickness factor as a function of PVC content is presented in Fig. 4. A strong dependence of η on the PVC content is observed when it is higher than 60 wt%.

3.3. Miscibility of the system PEO/PVC

The use of depression in the melting point to investigate the blend miscibility has been often used [12, 19]. In these studies, the Nishi-Wang equation, in its complete version [20] (Equation 2) or in the simplified form

TABLE I Lamellar thickness factor, η and T_m° for pure PEO and PEO/PVC blends

PEO/PVC	η	T_m° (°C)
100/0	6.0	62.8
90/10	4.9	63.4
80/20	6.2	62.7
70/30	5.6	62.6
60/40	6.1	62.3
50/50	6.2	62.3
40/60	5.1	62.1
30/70	3.8	62.0
20/80	2.6	61.9

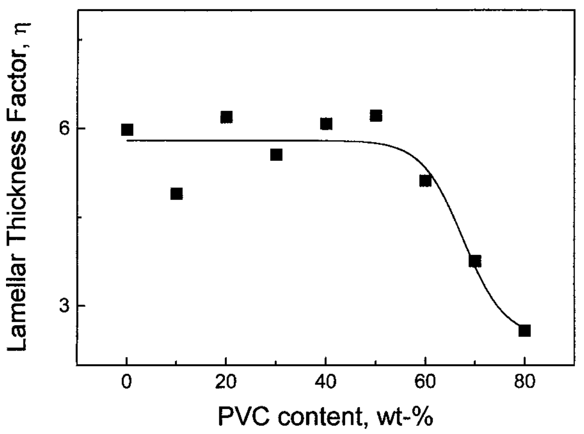

Figure 4 Lamellar thickness factor as a function of PVC content in the blend.

(Equation 3), has been applied to quantify the polymer-polymer interaction parameter, χ_{12}. In Equation 2, V_i^u is the molar volume of the repeat unit of the polymer ($i = 1$ or 2), ΔH_{PEO} is the enthalpy of melting of fully crystalline PEO, ϕ_2 is the volume fraction of amorphous polymer in the blend, m_i is the molar mass of polymer and χ_{12} is the interaction parameter of polymer 1 to polymer 2. In this treatment, the polymer 1 is considered as the semi-crystalline and the polymer 2 the amorphous one.

$$\frac{1}{T^\circ_{m,1}} - \frac{1}{T^\circ_{m,\mathrm{blend}}} = \frac{RV_1^u}{V_2^u\Delta H_1^u}\left[\frac{\ln\phi_1}{m_1} + \left(\frac{1}{m_1} - \frac{1}{m_2}\right)\phi_2 + \chi_{12}\phi_2^2\right] \quad (2)$$

$$\frac{1}{T^\circ_{m,1}} - \frac{1}{T^\circ_{m,\mathrm{blend}}} = \left(\frac{RV_1^u}{V_2^u\Delta H_1^u}\right)\chi_{12}\phi_2^2 \quad (3)$$

when the molar mass of polymers is high, Equation 2 reduces to Equation 3. This approach has been critically reviewed [12]. It is important to notice that this approach has been developed at equilibrium conditions.

The dependence of $\frac{1}{T^\circ_{m,1}} - \frac{1}{T^\circ_{m,\mathrm{blend}}}$ versus ϕ^2_{PVC} is shown in Fig. 5. It is possible to observe the following behaviour: from 20 to 60 wt% in PVC content, the curve presents a negative slope while for PVC contents higher than 60 wt% the curve is positively sloped. According to the literature [12, 17, 19], or to the Equations 2 and 3, the slope of the curve presented in Fig. 5 is equivalent to $\left(\frac{RV^u_{\mathrm{PEO}}}{V^u_{\mathrm{PVC}}\Delta H^u_{\mathrm{PEO}}}\right)\chi_{\mathrm{PEO/PVC}}$, from which the polymer-polymer interaction parameter may be evaluated. Using the value for the slope of the curve between PVC content 20 and 60 wt%, the $\chi_{\mathrm{PEO/PVC}}$ was evaluated as being -0.02. The following parameters were used in the calculations [15, 21]: $R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $V^u_{\mathrm{PEO}} = 40.3 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}}$, $V^u_{\mathrm{PVC}} = 46.1 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}}$ and $\Delta H_{\mathrm{PEO}} = 7.6\ \mathrm{kJ\ mol^{-1}}$. This value of $\chi_{\mathrm{PEO/PVC}}$ suggests that in this composition range the blend would be miscible. In this sense, for blends having PVC content higher than 60 wt%, the positive slope indicates immiscibility. For the blend having 10 wt% PVC content, a different behaviour was observed: T°_{m} of the blend is higher than the T°_{m} observed for the pure PEO. This behaviour was also observed by Margarits and co-workers [14] for PEO/PVC blends lying in PVC content range up to 10 wt%. Despite this, the blends were considered miscible by those authors. If the blend having 10 wt% in PVC content is really miscible, it could be pointed out that the model proposed by Nishi and Wang would not be sufficient for the precise determination of miscibility of this blend. A possible explanation for this fact is that the equation proposed by Nishi and Wang does not consider the dependence of the interaction parameter χ_{12} to the composition [12]. It is known that the polymer-polymer interaction parameter may have linear or quadratic dependence on the composition [22–24]. In the model, Nishi and Wang [20] suggested that the curve should cross the origin due to the low entropy contributions when polymers having high molar mass are involved. The projection of the negative sloped part of the curve presented in Fig. 5 (from 20 to 60 wt% PVC content) crosses the origin. This indicates that, according to the Nishi-Wang approach, in spite of no high molar mass of PEO, no important entropic contributions were observed in the PEO/PVC blends investigated in this paper. Another fact observed in this work and that should be emphasised, is the small variation of the equilibrium melting temperature of PEO in the blends compared to pure PEO. As shown in Table I, the largest variation in T°_{m} is about 0.9°C, for the PVC content of 80 wt%. It has been suggested that to apply the Nishi-Wang equation accurately, larger variations in T°_{m} should be necessary [12]. According to the theory [1, 2], the highest value of the polymer-polymer interaction parameter for a miscible high polymeric blend is close to zero. Regarding that the Nishi-Wang theory supports small differences in T°_{m} between the pure semi-crystalline polymer and the blends [20], the study of the miscibility of polymer blends by the depression in melting temperature, considering small differences in T°_{m}, should be carefully interpreted.

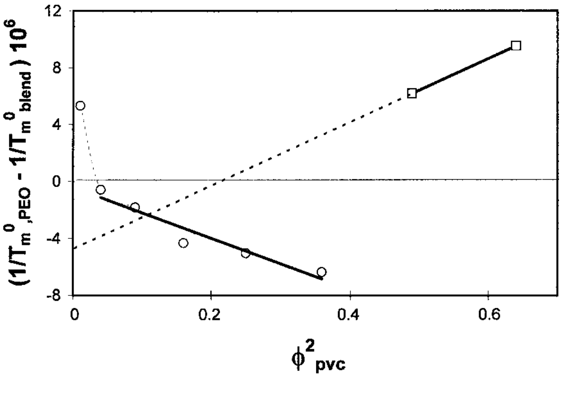

Figure 5 The dependence of $\frac{1}{T^\circ_{\mathrm{M,PED}}} - \frac{1}{T^\circ_{\mathrm{M,blend}}}$ versus ϕ^2_{PVC}, according to Equation 3.

The fact that PEO/PVC blends do not show large variations in the lamellar thickness of PEO spherulites, when the PVC content is changed from 0 to 60 wt% (Fig. 4), indicates that the PVC induces only little effects in the crystallisation of PEO. This suggests that such blends are not miscible in the molten state. In this case, richer PEO and richer PVC phases would be separated. Since the observation of small variations in

T_{m}° with the PVC content and the value of χ_{12} be close to zero, the critical value, the miscibility of PEO and PVC in blends richer in PEO, as observed in this paper by depression in T_{m}°, needs to be carefully considered. Otherwise, the lamellar thickness factor decreases in blends where the PVC content is higher than 60 wt%. In addition to the influence of PVC content in the lamellar thickness, the presence of PVC provides strong changes in the crystallisation rate (Figs 1 and 2). This is evidence that interactions between PEO and PVC occur in this composition range. Therefore, blends of PEO/PVC richer in PVC would be also miscible. This would be in agreement with the literature where it is reported that blends of PEO/PVC are miscible when richer in PVC content, as observed by Etxeberria and co-workers by inverse chromatography [15] and by C^{13}NMR in solid state [21].

4. Conclusions

From the melting depression data, blends of PEO/PVC having PVC content lying between 20 and 60 wt% possessed a polymer-polymer interaction parameter, $\chi_{\mathrm{PEO/PVC}}$, equal to -0.02. According to the theory, these blends should be considered miscible. But this miscibility should be carefully considered since a small depression in T_m° (when the PVC content was increased) was observed. In addition, even the value of χ_{12} being negative, is close to zero, the critical value. The PVC content in the blend changes the crystallisation rate: blends richer in PEO have a higher crystallisation rate. This was assigned to the decreasing mobility of PEO chains as the PVC content is increased. In fact, the presence of PVC alters, mainly, the mobility of melted PEO segments or chains to the interface of the growing crystals. In this sense, the presence of PVC could also decrease the nucleation process. Both factors tend to reduce the crystallisation rate. It was verified that the lamellar thickness of PEO in the blends has no influences when the PVC content is up to 60 wt%. Further increase in PVC content induces a sharp decrease in the lamellar thickness factor. At 40°C, the blends richer in PEO reach the maximum in crystallinity in periods shorter than 1 hour. At the same temperature the blend having 80 wt% in PVC reaches the maximum in crystallinity in ca. 12 hours. It was also verified that this blend reaches the maximum crystallisation rate at T_{C} close to 40°C.

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