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# Positron annihilation and differential scanning calorimetry studies of plasticized poly(ethylene oxide)

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## Abstract

Positron annihilation spectroscopy (PALS) and differential scanning calorimetry (DSC) measurements were performed in pure and plasticized poly(ethylene oxide) (PEO)–dioctyl phthalate (DOP) and (PEO)–ethylene carbonate (EC) systems. The plasticized PEO samples were prepared by co-dissolution and melting methods in the concentration range of 0–25 wt% of plasticizer. The mean free volume hole size ($V_f$) values were calculated from the positron lifetime data. For the PEO–DOP it was observed an increase of the $V_f$ values with increasing DOP concentration, while for PEO–EC system the $V_f$ values remained constant. The relative concentration of vacancies showed to be not dependent on DOP concentration and for PEO–EC system it was observed a small decrease with the increase of EC concentration. The thermal behaviour characterized by DSC measurements showed variations of transition and melting temperatures as well as on the degree of crystallinity of PEO with plasticizer concentration. The PALS and DSC results clearly showed the presence of plasticization effect with DOP in opposite to the antiplasticization with EC. The compatibility limit of DOP in PEO was about 15 wt% in the preparation conditions of these samples. The efficiency of plasticization was estimated from the slope of $V_f$ curves for PEO–DOP systems. © 2001 Published by Elsevier Science Ltd.

*Keywords*: Positron lifetime; Free volume; Plasticization effect

## 1. Introduction

A plasticizer is incorporated into a polymer to improve the material processability and flexibility [1,2]. On a molecular level the plasticizer induces the weakening of intermolecular interactions and the increase of the space among molecules. The physical and mechanical properties of the polymer change dramatically with the addition of the plasticizer, as can be observed by the decrease of the modulus and glass transition temperature ($T_g$) values.

Three theories have been proposed to explain the plasticization [2–5]: the gel, the lubricity, and the free volume theories. The lubricity theory considers that the plasticizer improves the movement of the macromolecules over each other. The gel theory proposes that the changes in the mechanical properties are associated to the presence of an entangled structure also called gel. The plasticizer acts by breaking the contact points of the gel increasing the flexibility of the material. The increase of the free volume is the basis of a mechanistic theory of plasticization. The free volume may be increased by the inclusion of a compatible compound of low molecular weight into a polymer, i.e. by external plasticization [2–5].

Variations of free volume have been successfully used to explain the effects of plasticization as well as the antiplasticization [6,7] in polymeric materials. In the last case the inclusion of small molecules into a polymer raises the rigidity of the material. In this work we present results of free volume variations due to the plasticization of PEO obtained from positron annihilation lifetime spectroscopy (PALS).

The PALS technique has been widely used in the study of polymeric systems at molecular level in the recent years [8–11]. Although an observed increase of the number of papers concerning PALS applications in the study of microstructure of polymers and polymeric blends, little attention has still been addressed to the effect of plasticization of polymers [4,6,12–18].

Positronium (Ps), the bound state between a positron and electron, can be formed by these two particles in two different spin states: *ortho*-positronium (*o*-Ps, triplet) and *para*-positronium (*p*-Ps, singlet), with intrinsic lifetimes of 142 and 0.125 ns, respectively, in vacuum. The positronium formation probability, $I_i$, and lifetime, $\tau_i$, however, are extremely sensitive to the physical and chemical properties

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of the surrounding molecules of the medium in which the Ps is formed. In polymeric systems the *o*-Ps relative intensities, $I_3$, and lifetimes, $\tau_3$, are found in the range of 0–40% and 1–3.5 ns, respectively. If positron and/or positronium chemical effects such as inhibition of Ps formation and *o*-Ps lifetime quenching [19,20] are not present, the $\tau_3$ and $I_3$ parameters are directly related to the mean free volume hole dimensions and relative concentration of these vacancies, respectively.

According to the free volume model, the lifetime of the *o*-Ps localized inside a rigid and spherical potential well of radius $R_0$, and free volume of radius $R$, below what no electron is found, is given by the following expression [21,22]:

$$\lambda_3 = (1/\tau_3) = 2[1 - R/R_0 + 1/2\pi \sin(2\pi R/R_0)] \quad (1)$$

where $(R_0 - R) = 1.656$ Å is the width of the electron layer at the internal surface of the potential well where the Ps annihilates at a constant rate ($\lambda_3$) of 2 $\text{ns}^{-1}$.

Due to the fact that *o*-Ps is preferentially localized in the free volume holes of polymer systems, the PALS parameters $\tau_3$ and $I_3$ have been widely used over the last years in the study of microstructural behaviour of this class of materials [8,9,11].

The mean free volume hole size may be estimated by using the simple equation:

$$V_f = (4\pi R^3)/3 \quad (2)$$

where $R$ is calculated by using the Eq. (1).

With the purpose to determine in a quantitative way the effect of the plasticization on the free volume of polymers, PALS measurements have been performed, in this work, in poly(ethylene oxide) PEO, using dioctyl phthalate (DOP) and ethylene carbonate (EC) as plasticizers.

High molecular weight PEO is a semicrystalline polymer which can easily attains 50% of degree of crystallinity without any special annealing treatment. Our group have studied the free volume features of PEO at various molecular weights and with temperature variations [11]. The polymer systems in which plasticizer effects on the free volume have been already studied are mainly amorphous as polystyrene [6], polymethyl methacrylate [4], or only slightly crystalline as polyvinyl chloride (with 5–10% crystallinity) [15–17]. The aim of this work is to study the effect of plasticizer in a truly semicrystalline polymer, from the PALS point of view, which can provide new insights related to the external plasticization mechanism. Different systems were prepared by varying the plasticizer type and the sample preparation method (codissolution and melting). The PALS results are analysed by comparison with the data obtained by DSC measurements as glass transition and melting temperatures and degree of crystallinity. Effects such as compatibility and changes in the degree of crystallinity are also evaluated.

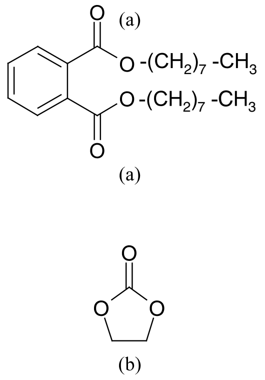

Fig. 1. Chemical formula of (a) DOP and (b) EC.

## 2. Experimental

### 2.1. Sample preparation

The dioctyl phthalate, ethylene carbonate, the PEO 1M, and the acetonitrile were purchased from Aldrich. The chemical formula of the plasticizers are given in Fig. 1.

The codissolution method was used to prepare PEO–DOP and PEO–EC samples. The two components were dissolved in 20 ml of acetonitrile at room temperature, being vigorously stirred for nearly 1 h until obtain an homogeneous system. After solvent free evaporation overnight, the plasticized PEO systems were dried under vacuum for 24 h. The same system was then prepared by a second method, melting. In this case the polymer was heated until melt (nearly 85°C), followed by the addition of the DOP. The mixture was stirred for 1 h at melting temperature and then cooled down at room temperature. The masses were selected in order to obtain pellets of about 1.5 mm thickness in both preparation methods.

### 2.2. PALS measurements

Positron annihilation lifetime measurements were carried out at 294 K using a conventional fast–fast coincidence system (Ortec), with time resolution of 280 ps, given by $^{60}$Co prompt curve. The $^{22}$Na positron source (Amersham), with activity of approximately $5.0 \times 10^2$ Bq, was sandwiched between two 3.5 μm thick foils of mylar with about 10% of source correction. The lifetime spectra were satisfactorily resolved into three components by the Positronfit-Extended program [23] leading to the intensities ($I_i$) and lifetimes ($\tau_i$). The subscripts "$i$" = 1, 2, and 3 refer to *p*-Ps, free positron and *o*-Ps, respectively. During the numerical calculations the shortest life component $\tau_1$, attributed to *p*-Ps annihilation, was fixed at 0.120 ns (below the time resolution limit of the equipment).

### 2.3. DSC measurements

The DSC measurements were performed with a Shimadzu DSC-50 in a set of three consecutive steps:

first, heating from room temperature to 100°C, and then isothermal annealing for 2 min, followed by cooling down from 100 to −100°C. After this second step, the samples were heated from −100 to 150°C. These scanning processes were performed at a heating rate of $10\ \mathrm{K\ min^{-1}}$ in a dynamic atmosphere of Helium ($70\ \mathrm{ml\ min^{-1}}$). The $T_g$ values were determined from the second heating run as the onset value. The $T_m$ values were determined at the peak and the PEO degree of crystallinity was calculated for each sample using the weight of PEO to correct the $\Delta H$ experimentally obtained and relating to the $\Delta H$ for 100% crystalline PEO ($213.7\ \mathrm{J\ g^{-1}}$).

## 3. Results and discussion

The PEO chains adopt, in the crystalline state, an helical conformation which contains seven chemical units and two or five turns in a fibre identity period of 19.3 Å [24] with a well defined Oxygen line cavity. The study of PEO–salt complexes have showed that similar short-range order is found in the amorphous phase [25].

For our work, PEO with molecular weight of 1 M was chosen to prepare the studied systems. In this case no chain-ends effects are expected to contribute to the plasticization mechanism [6]. Besides that, this molecular weight is quite large in relation to the entanglement molecular weight found for PEO(6800) by NMR analysis [26]. Therefore, the effects of the chain entanglements may participate on the plasticization mechanism.

DOP is an organic ester commonly used as plasticizer [2,4,16]. EC, on the other hand, is used in special cases with PEO, when electrochemical applications are pursued [13,27], since it presents a high dielectric constant (89.0). EC and DOP present both C=O and C–O bonds which introduce the possibility of Hydrogen bonds with PEO. However, they have very different dimensions, the EC has approximately a linear diameter of 3.3 Å considering C=O bound at one extremity of the chain [28]. DOP, in a roughly evaluation, presents an extension of 13.3 Å [29]. The aliphatic side of DOP $[-(CH_2)_7CH_3]$ can also contribute to a different behaviour. Therefore, the introduction of DOP and EC in PEO may produce changes in the transitions associated to the crystalline and amorphous phases as well as on the degree of crystallinity. The chemical formula of DOP and EC compounds are show in Fig. 1.

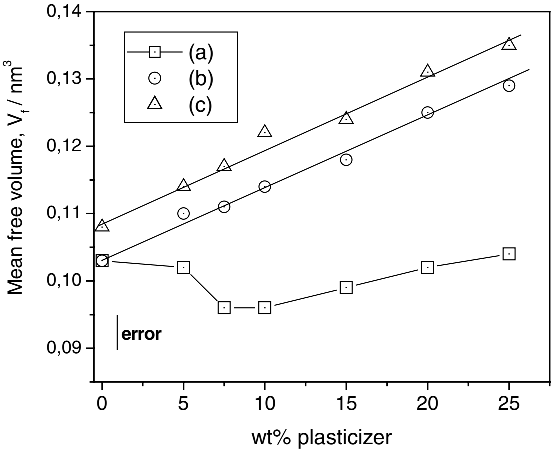

Fig. 2. Variation of $V_f$, as a function of the plasticizer concentration, for the systems: (a) PEO–EC/Codis.; (b) PEO–DOP/Codis.; and (c) PEO–DOP / melting.

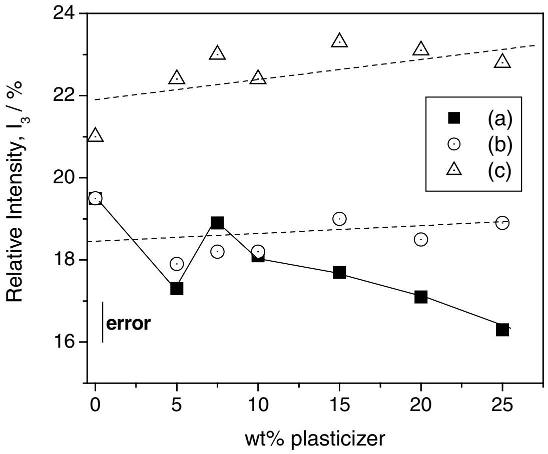

Fig. 3. Variation of the relative concentration of free volume cavities, $I_3$ %, as a function of the plasticizer concentration, for the system: (a) PEO–EC / Codis.; (b) PEO–DOP/Codis.; and (c) PEO–DOP/melting.

The positron annihilation results obtained for the PEO plasticized systems at 294 K are shown in Figs. 2 and 3. For PEO–EC system the results are presented only for samples prepared by codissolution and for PEO/DOP systems the results obtained for samples prepared by melting and codissolution are shown. The $\tau_3$ and $I_3$ values are an average over 10 different measurements, which guarantees the data error evaluation, shown in the figures. Fig. 2 displays the variation of the calculated mean free volume hole sizes, $V_f$, for the three polymer–plasticizer systems as a function of plasticizer concentration. Fig. 3 shows the variation of the *o*-Ps relative intensities, with the relative concentration of plasticizer. As can be observed in Figs. 2 and 3 the samples prepared by melting presented higher values of $V_f$ and $I_3$ compared with the ones prepared by codissolution.

In Table 1 the obtained DSC data: $T_g$, $T_m$ and the degree of crystallinity are given. As can be seen in Figs. 4 and 5 the polymer–plasticizer systems prepared with DOP exhibited a decrease of $T_g$ with the increase of plasticizer content, which indicates the presence of a plasticization effect. Otherwise, the increase of EC concentration raised the $T_g$ values of the system indicating the antiplasticization of the polymer.

### 3.1. PEO–EC systems

For the system PEO–EC, $T_g$ values and the degree of crystallinity increase with the increase of the plasticizer content (Table 1). In the other hand, the $T_m$ values are constant. As can be seen in Fig. 2a the $V_f$ values do not

Table 1
Glass transition temperature ($T_g$), melting temperature ($T_m$) and degree of crystallintity ($\chi$) values obtained for pure and plasticized PEO, by DSC technique

| System | Plasticizer concentration (wt%) | $T_g$ (°C) (onset)[a] | $T_m$ (°C) (peak) | $\chi$ (%) (PEO crystallinity) |
|---|---|---|---|---|
| PEO–EC (codissolution method) | 0 | −62 | 62 | 44 |
| | 5 | −56 | 64 | 49 |
| | 10 | −57 | 65 | 52 |
| | 15 | −45 | 65 | 47 |
| | 20 | −47 | 63 | 57 |
| | 25 | −44 | 65 | 55 |
| PEO–DOP (codissolution method) | 0 | −62 | 62 | 44 |
| | 5 | −78 | 66 | 46 |
| | 10 | −87 | 63 | 47 |
| | 15 | −87 | 63 | 43 |
| | 20 | −89 | 63 | 46 |
| | 25 | −89 | 62 | 40 |
| PEO–DOP (melting method) | 0 | −63 | 55 | 43 |
| | 5 | −68 | 57 | 49 |
| | 10 | −68 | 59 | 48 |
| | 15 | −68 | 57 | 52 |
| | 20 | −85 | 57 | 57 |
| | 25 | −85 | 57 | 59 |

[a] Two $T_g$ values were observed in some curves.

change significantly as a function of EC concentration, in the range 0–25 wt% EC, while the relative concentration of holes (Fig. 3a) slightly decreases with increasing EC concentration. This behaviour, associated to the increase of $T_g$ values (Fig. 5a) characterize an antiplasticization effect. The antiplasticization of EC in PEO at 294 K can be consequence from one or more of the following causes [6]:

(a) decrease in free volume associated with the increase of the degree of crystallinity (Table 1); in this case the polymer chains above $T_g$ have a degree of mobility which allows them to align in a more ordered densely packed state;

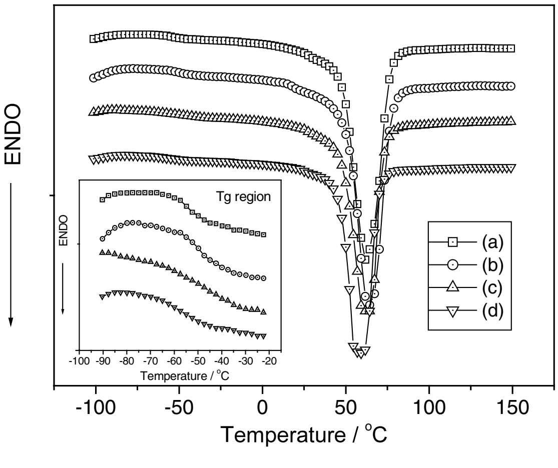

Fig. 4. DSC typical curves for: (a) PEO; (b) PEO–EC; (c) PEO–DOP/codis.; and (d) PEO–DOP/melting at 10 wt% of plasticizer. Magnification of $T_g$ region is shown.

(b) the plasticizer fill the free volume (hole-filling) of the polymer, which slightly decrease the concentration of free-volume, as observed by the decrease of $I_3$ (Fig. 3); in this case the average diameter of the plasticizer domains is less than the average size of free volume voids. The EC molecule presents the larger diameter of approximately 0.3 nm, while the diameter of the cavities observed are approximately of 0.6 nm (considering spherical free volumes), which demonstrates the possibility of EC to fill the free volumes. For the EC plasticizer, the possibility of molecules being placed inside the helical structure of PEO should also be considered, since this filling was observed in many electrolytes systems studied in the literature [25,26];

(c) or the last possible cause, the polymer–plasticizer interactions decrease the segmental mobility of the polymer, which is indicated by the increase of $T_g$ (Table 1). The filling in the PEO helical structure may also favours these interactions.

### 3.2. PEO–DOP systems

The DSC data obtained for the PEO–DOP materials prepared by codissolution and melting processes can be compared in Table 1. The melting temperatures are approximately constant with the plasticizer concentration and are smaller for samples prepared by melting. However, the degree of crystallinity is not significantly different for both DOP materials, showing even a tendency to increase

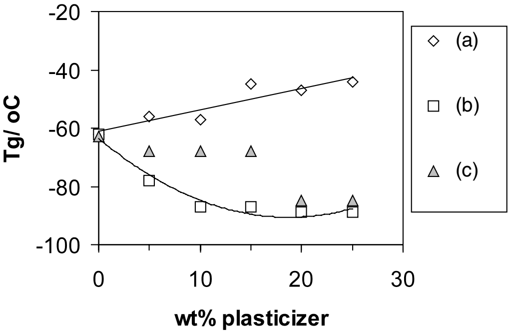

Fig. 5. $T_g$ values as a function of plasticizer concentration for: (a) PEO–EC / Codis.; (b) PEO–DOP/Codis.; and (c) PEO–DOP/melting systems. The errors in the $T_g$ values are ±2°C.

in the case of samples prepared by melting. It must be mentioned that there was not a widening of the melting peak, all samples showed approximately a range of 20°C between onset and endset of melting peak as can be seen in Fig. 4, which shows DSC curves for the three studied PEO–plasticizer systems. These results indicate that some breakdown of the macromolecular chains may occurred but the mainly process is probably a crystalline reorganization after the melting treatment, producing a decrease of melting temperature but a slightly increase of degree of crystallinity. The $T_m$ values near to 57°C are obtained for the melted blended samples in relation to approximately 63°C determined for the ones prepared by codissolution.

The glass transition temperatures show similar tendencies for PEO–DOP materials prepared by the two methods. Fig. 5 shows that the decrease of $T_g$ is not linear, the values reached a minimum plateau above 20 wt% of plasticizer in both classes of PEO–DOP samples. An analysis of the DSC curves for the DOP plasticized samples indicated the presence of two $T_g$ values, which is associated with a limit of solubility of DOP in PEO. Fig. 6 shows typical DSC curves where the separation between the $T_g$ values can easily be observed. As DOP presents a significantly aliphatic character this behaviour is not unexpected. The compatibility limit is 15 wt% of DOP, after that the DSC curves presents anomalies characteristics of phase separation. Solubility limits for plasticizer content in polymeric materials are a matter discussed by several authors [2,4,17,30].

From the DSC analysis, the PEO–DOP/codissolution materials should be seen as semicrystalline samples in which the plasticizer did not produce changes in the $T_m$ or the degree of crystallinity. Besides that, the amorphous phase presents a decrease of $T_g$ and it is not also homogeneous with plasticizer concentration higher than 15 wt%. The PEO–DOP/fusion materials are different in relation to the crystallinity features: $T_m$ is lower than for the other systems and degree of crystallinity increases with plasticizer content.

The PALS analysis permit the observation of the microstructure using probes that do not distinguishes, in our kind of adjustment, between different amorphous or crystalline phases [31]. Therefore, the positron annihilation results are consequence of an average view of the free volume features. Fig. 2b shows that for the PEO–DOP system, prepared by codissolution, $V_f$ values increase linearly with increasing DOP concentration in the range 0–25 wt% DOP, while the relative concentration of vacancies remains constant within the experimental error (Fig. 3b).

The $V_f$ versus wt% DOP curve, in Fig. 2b, follows the equation:

$$V_f = (0.103 \times 10^{-2}\ \text{wt\% DOP} + 0.104)\ \text{nm}^3 \tag{3}$$

For the PEO–DOP system prepared by melting, the $V_f$ values increase linearly with DOP concentration (Fig. 2c), according to the equation:

$$V_f = (0.107 \times 10^{-2}\ \text{wt\% DOP} + 0.109)\ \text{nm}^3 \tag{4}$$

The behaviour of PALS parameters obtained for PEO–DOP systems in our work was equally observed for other systems in recent publications. Borek and Osoba have been studied plasticized polyvinyl chloride (PVC) using dibutyl phthalate, tricresyl phosphate and dioctyl phthalate as plasticizers [15–17], Okada et al. [12] and Nishijima et al. [18] have been studied epoxy resin bisphenol A plasticized with poly(propyleneglycol). These authors have found an increase of the $\tau_3$ values and a decrease of the $T_g$ values with the increase of the concentration of plasticizers. Concerning the $I_3$ parameter, Borek and Osoba [15–17] have observed an increase of these values, which changed from nearly 4–5% to about 8–9%, while Okada et al. [12] and Nishijima et al. [18] have observed that $I_3$ was invariant with plasticizer concentration, in agreement with ours results.

The decrease of $T_g$, per unity of the plasticizer concentration has been used as a measure of the plasticizer efficiency [32]. Our results show that this decrease is not linear since there was a compatibility limit. However, it was interesting to compare the plasticization efficiency for the PEO materials studied using PALS experiments. Taking the rate of $V_f$ increase per unity of plasticization concentration,

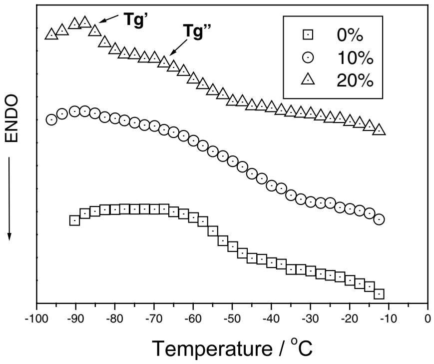

Fig. 6. DSC curves for pure PEO and PEO–DOP prepared by codissolution at 10 and 20 wt% of plasticizer.

Table 2
Plasticization efficiency measured as the slope of the $V_f$ vs. $C$ and $T_g$ vs. $C$ curves for some plasticized polymer systems

| System | Plasticizer concentration range, in wt%, $C$ | Slope of the $V_f$ vs. $C$ curves, $nm^3/(wt\%)$ | Reference |
|---|---|---|---|
| PEO–dioctyl phthalate (prepared by heating method) | 0–25 | 0.0011 | This work |
| PEO–dioctyl phthalate (prepared by codissolution method) | 0–25 | 0.0010 | This work |
| PVC–tricresylphosphate (heating method, as prepared samples) | 0–35 | 0.0013 | [17] |
| PVC–tricresylphosphate (annealed samples) | 0–35 | 0.0011 | [17] |
| PVC–dibutyl phthalate | 0–35 | 0.0012 | [15] |
| Bis-phenol-A–poly-propylene | 18–33 | 0.0010[a] | [18] |
| Glycol | 18–33 | 0.0016[a] | [12] |

[a] These values were estimated from the data plotted in figures.

i.e. the slope of the curve $V_f$ vs. $C$ as a measure of the plasticization efficiency, the following results were obtained and collected in Table 2. The interesting result was that the plasticization efficiencies, as calculated from the $V_f$ vs. $C$ curves, are found in the range 0.0010–0.0013 $nm^3/wt\%$ for PEO–DOP (heterogeneous) materials in this work, the same observed for other systems [12,15,17,18]. DOP is one of the most common plasticizers used, particularly in PVC formulations [32]. From this work it is important to point out that the behaviour observed with the introduction of DOP in a truly semicrystalline polymer, i.e. PEO (crystallinity around 50%), and with the presence of amorphous heterogeneity after 15 wt% of plasticizer, is completely similar to other plasticized systems, from the PALS point of view (Table 2).

From the three different kind of PEO–plasticizer systems studied, the PEO–DOP/melt-blended materials present the higher values of $V_f$ (Fig. 2) and $I_3$ (Fig. 3) for all plasticizer contents. The DSC data can be correlated with this special behaviour, i.e. lower $T_m$ values were obtained for the samples prepared by melting. As can be noticed from Table 1 the $T_g$ values are not different between the two PEO–DOP systems either that prepared by codissolution or by melting and the degree of crystallinity even exhibited a slightly increase with plasticizer content when melting process was used. The decrease in $T_m$ values for the blends prepared by fusion may be attributed mainly to a reorganization of the crystalline structure after the thermal annealing. A change in the size and structure of crystallites and spherulites can be supposed. Therefore, the higher $V_f$ and $I_3$ for all melt-blended samples are probably due to an increase of the free-volume in the crystalline phase.

## 4. Conclusions

Plasticization of the semicrystalline PEO by DOP, which was introduced using codissolution and melting processes, in a range between 0 and 25 wt%, have been studied. There was an increase in free volume ($V_f$) and the relative concentration of vacancies remained approximately constant, as showed by PALS measurements. DSC results indicated that $T_m$ values are not variable with plasticizer content. The introduction of DOP in PEO through melting produced a decrease of $T_m$ from 63 to 57°C, in relation to the codissolution process. Meanwhile, the free volume parameters ($\tau_3$ and $I_3$) are increased between codissolution and melting prepared materials. These results lead to the conclusion that the melting prepared PEO–DOP systems show a crystalline reorganization and the increase in free volume is probably occurring mainly in the crystalline phase.

The antiplasticization of PEO by EC was observed in samples prepared by codissolution. $T_g$ values increase and $I_3$ values (related to free volume concentration) decrease with plasticizer content. These results probably indicate a hole-filling mechanism with additional interactions between plasticizer and polymer.

DOP and EC showed very different effects in the semicrystalline PEO. DOP was able to plasticize, increasing the free volume, but is limited in compatibility with PEO to 15 wt%, probably as a function of its aliphatic character. EC has a dimension capable to occupy the vacancies on the PEO polymer and, therefore, produced the antiplasticization. It was interesting to notice that none of them produced strong effects in the PEO crystalline phase, the degree of crystallinity was always higher than 43%.

## Acknowledgements

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