

# Oxygen and Carbon Dioxide Transport Through High Barrier Polyester Blends

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The transport of oxygen and carbon dioxide through a set of random copolymer films based on poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN) were explored. Diffusivity and permeability of both gases decreased with increasing PEN content. The oxygen and carbon dioxide diffusion coefficients decreased 74 and 82% from pure PET to pure PEN, respectively. The presence of stiffer PEN moieties had an effect on the glass transition temperature ( $T_g$ ) of PET/PEN blends and gas barrier. In the complete range of tested blends, the differential scanner calorimeter analysis displayed a single value of thermal glass transition temperature. As the PEN content was increased, the fractional free volume (FFV) and the diffusion coefficients of the blends were decreased. The Doolittle equation provided the best fit for diffusivity and FFV and showed that the gas transport behavior was better understood when it was taken into consideration the cohesive energy of blends. As the PEN content in films was increased, their rigidity and the glass/rubber transition temperature were increased, and their capacity to be penetrated by small molecules like O<sub>2</sub> and CO<sub>2</sub> was decreased. POLYM. ENG. SCI., 49:1635–1641, 2009. © 2009 Society of Plastics Engineers

## INTRODUCTION

The plastic bottles and containers market is constantly growing. Poly(ethylene terephthalate) (PET) is a widely used polymer in packaging applications. Currently, it is

common to find a large variety of consumer products packed in a great diversity of shapes and sizes. For this application, the most important characteristics of a polymer are its barrier properties and the glass transition temperature ( $T_g$ ). These properties can be drastically modified by blending them with other polymers [1–5], by functionalizing the main chain [6, 7] or by chain orientation [4, 8–10]. Oxygen transport through copolymers of PET has been reported [11]. Some studies have found that for a family of polymers, the main chain structure has a strong effect on thermal and gas transport properties [12, 13]. In spite of the wide acceptance of PET in various industries, there is a continuous need for an improved polymer that can surpass PET product shelf life and its capacity for specialized applications like the hot-fill container market. Poly(ethylene 2, 6-naphthalate) (PEN), is a polymer that has proved to be a promising candidate to fulfill these specialized applications. The PEN double ring aromatic structure is responsible for its observed superior properties when compared with PET. PEN offers an improved performance over conventional PET in critical areas such as thermal stability, gas and vapor barrier properties, mechanical properties, dimensional stability [10, 12], and higher capability of absorbing UV radiation [14]. In spite of these advantages, a generalized use of PEN as packaging material has been limited. The main disadvantage is its high price when compared with the PET price [15]. The significant commercial interest of PEN is not as homopolymer but as a blend or copolymer with other materials, particularly with PET, to improve its thermal, mechanical, and gas barrier properties. By combining a small amount of PEN with PET, it is possible to obtain an accessible cost blended material with improved performance. This research objective was to evaluate the

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transport of O<sub>2</sub> and CO<sub>2</sub> through membranes made from different PET/PEN blends. The results could be used to improve the knowledge on gas transport behavior through glassy polymers.

## EXPERIMENTAL

PET/PEN blends with various compositions were prepared by inert atmosphere melt transesterification from commercial PET and PEN homopolymers (kindly provided by Eastman). PET and PEN pellets were dried in vacuum at 70°C for 24 h before being processed. Their molecular weights were determined by viscosimetry at 25°C using a 60/40 (w/w) phenol/tetrachloroethane solution. Films were prepared by hot pressing at a constant temperature of 290°C. A sample of blended material was sandwiched between two Teflon-coated aluminum foils (McMaster) and put in a preheated hydraulic press. After pressing the melted material, the samples were immediately soaked in a cool water bath to prevent crystallization. Glass transition temperature of the film samples was accomplished from a TA Instruments DSC 2920 with a heating rate of 10°C min<sup>-1</sup>, N<sub>2</sub> atmosphere, and a temperature scan interval of 40 to 300°C. X-ray diffraction was obtained using a SIEMENS D-5000 and Cu K $\alpha$  radiation. Film density was measured at 25°C with a density gradient column prepared from two aqueous solutions of calcium carbonate of different concentrations. The column covered the range of densities from 1.30 to 1.40 g cm<sup>-3</sup> and was calibrated with a set of glass beads of known densities. The samples for density measurements were cut from the area of the samples used for the gas transport experiments. Each reported value was obtained from the mean of three measurements. Permeation experiments were carried out in a laboratory-made permeator. This equipment has been described in many compositions [4–6]. The polymer samples were circular disks of 2.01 cm<sup>2</sup> area and the average thickness was obtained by measuring on 20 points of the sample using a Mitutoyo digital micrometer with a resolution of 1 mm. To perform the permeation experiments, flat film samples were clamped into the diffusion cell and a vacuum was kept on for 18 h to remove residual gases from the system and to desorb the O<sub>2</sub> and CO<sub>2</sub> from the sample. Measurements were performed in duplicate. The purity of O<sub>2</sub> was at least 99% and an absolute pressure of two atmospheres was maintained in the upstream side. All measurements were carried out at a controlled temperature of 25°C. After finishing the oxygen permeation, the film sample and the permeator apparatus were degassed again for 18 h before CO<sub>2</sub> measurements. Pressure and temperature of CO<sub>2</sub> measurements were the same as that for O<sub>2</sub>. The permeability,  $P$ , was calculated using Eq. 1 [5].

$$P = \frac{22415VL}{ARTp} \left( \frac{dp}{dt} \right) \quad (1)$$

where  $V$  is the downstream volume,  $L$  is the film thickness,  $dp/dt$  is the rate of pressure increase on the downstream side at its pseudo-steady-state value,  $A$  is the membrane area,  $R$  is the universal gas constant,  $T$  is the absolute temperature, and  $p$  is the absolute ingoing pressure. Diffusion coefficient,  $D$ , was calculated from Barrer relationship, Eq. 2, based on the steady state solution of Fick's second law of diffusion [16].

$$D = \frac{L^2}{6\theta} \quad (2)$$

where  $\theta$  is the time lag.

Once permeability and diffusivity coefficients have been calculated, the solubility,  $S$ , can be evaluated by Eq. 3.

$$P = DS \quad (3)$$

## RESULTS AND DISCUSSION

The calculated number-average molecular weights with intrinsic viscosity measurements and the parameters of Mark-Houwink-Sakurada equation [17] were  $\sim 22,000$  g/mol for PET and  $\sim 18,000$  g/mol for PEN. Figure 1 depicts PET/PEN blend densities as a function of PEN wt% content. The results contrast with those reported by McDowell et al. [3] for PET/PEN semicrystalline random copolymers, in which the amorphous phase density resulted higher than the amorphous density of either homopolymer. In the case of semicrystalline copolymers (less than 10 wt% of either homopolymer), this is possible because the most ordered crystalline regions have influence on neighboring amorphous regions. But it is not easy to understand why the amorphous regions of this kind of copolymers are denser than amorphous phase in semicrystalline PET. Yet, the observed tendency for density variation with PEN content in PET/PEN blends was in agree-

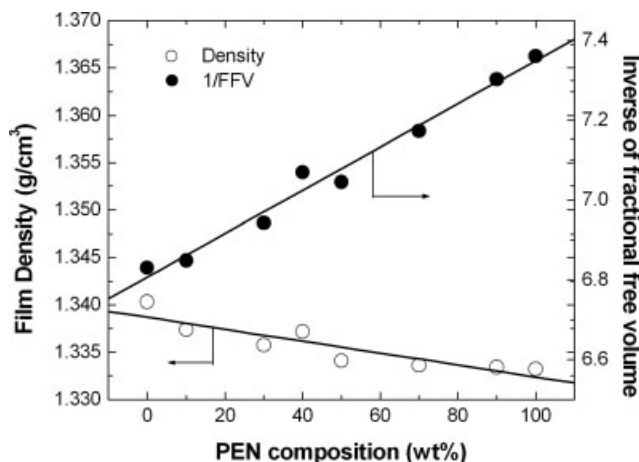


FIG. 1. Density and fractional free volume dependence with PEN concentration in PET/PEN blends.

ment with the reported values by Polyakova et al. [11] and by McGonigle et al. [4] for a set of PET/PEN copolymers. Other research [3] reported the same behavior but with completely amorphous copolymers. The reasons for these discrepancies must be in the previous thermal history and processing of the materials, as these factors have an effect on the degree of crystallinity as well as on the packing of the amorphous and crystalline regions. Figure 1 also shows the FFV, a characteristic intimately related to transport properties and calculated by Eq. 4 [18].

$$\text{FFV} = \frac{V_T - V_0}{V_T} \quad (4)$$

where  $V_T$  is the specific molar volume of an amorphous polymer, in  $\text{cm}^3/\text{mol}$ , at temperature  $T(\text{K})$ . It is calculated from polymer density at 298.15 K and the molecular weight of the polymer structural unit.  $V_0$  is the zero point molar volume calculated by Eq. 5 [19].

$$V_0 = 1.30V_W \quad (5)$$

Being  $V_W$ , the van der Waals volume evaluated from the group contribution method [20]. Free volume ( $V_T - V_0$ ) increased when blend composition became richer in PEN. Consequently, based solely on the microstructure considerations,  $\text{CO}_2$  and  $\text{O}_2$  diffusivity, permeability, and solubility of the blends should rise with increasing PEN content because of the increment in free volume. However, results observed in Figs. 2 and 3 show that  $\text{O}_2$  and  $\text{CO}_2$  permeability and diffusivity decreased with PEN content. Only  $\text{O}_2$  and  $\text{CO}_2$  solubilities followed this established rule. Gas solubility is related to static free volume [11], whereas gas diffusion and permeability are related to dynamic free volume derived from accessible conformational changes and segmental motions of the macromolecules. The higher stiffness of naphthalate moieties reflected in a higher  $T_g$  of the blends, exceed the incre-

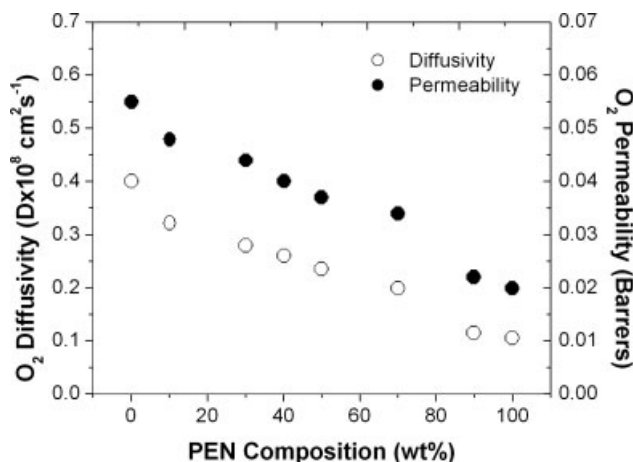


FIG. 2. Oxygen permeability and diffusivity through PET/PEN blends at 25°C.

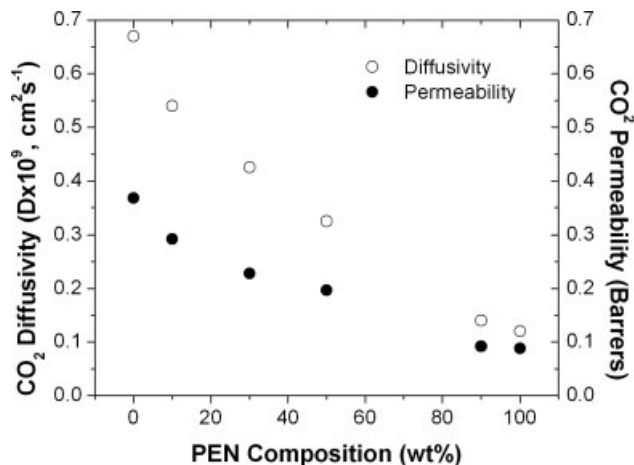


FIG. 3. Effect of PEN content on permeability and diffusivity of carbon dioxide in PET/PEN blends at 25°C.

ment of free volume. Figure 4 depicts a typical differential scanner calorimeter (DSC) thermogram in which three thermal signals can be seen: (a)  $T_g$ , (b) a cold crystallization peak,  $T_c$ , and (c) a melting peak,  $T_m$ . DSC measures show a single glass-rubber transition and this means that the materials are random copolymers.  $T_g$  rose with PEN content and its behavior was consistent with the predicted theoretical values calculated by the well known Fox equation, Eq. 6 [21].

$$\frac{1}{T_{gc}} = \frac{w_{PET}}{T_{g,PET}} + \frac{w_{PEN}}{T_{g,PEN}} \quad (6)$$

where  $w_{PET}$ ,  $w_{PEN}$ ,  $T_{g,PET}$ , and  $T_{g,PEN}$  stand for weight fractions and glass transition temperatures for pure PET and PEN, respectively, and  $T_{gc}$  is the predicted glass transition of the copolymer. As higher the  $T_g$  value, the more rigid the polymer backbone, and smaller the dynamic free volume available for diffusion. Transport parameters for  $\text{O}_2$  and  $\text{CO}_2$  ( $D$ ,  $P$ , and  $S$ ) are presented in Table 1 and

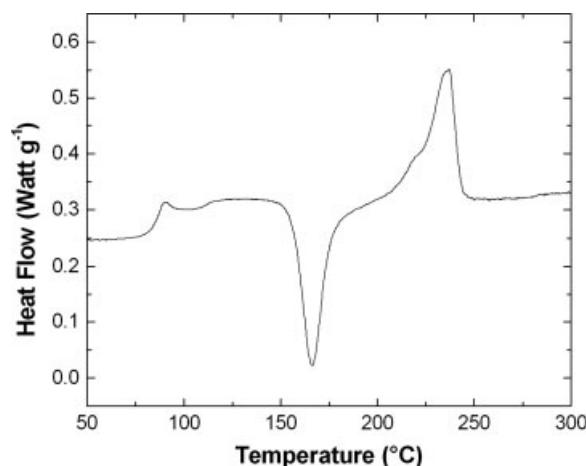


FIG. 4. Typical DSC curve for PET/PEN blend. A single glass transition region can be easily seen for 60/40 PET/PEN blend.

Figs. 2 and 3. The Doolittle equation, Eq. 7, has been successfully used to link polymer free volume and its diffusion coefficient [22].

$$D = A \exp(-B/FFV) \quad (7)$$

where  $A$  and  $B$  are empirical and characteristic constants of a polymer-penetrant system and FFV was defined by Eq. 3. Nonetheless, a better interpretation is possible taking into account that diffusivity not only is a static free volume function, calculated from bulk density but also of cohesive energy. This is the energy required to

separate the surrounding medium to give a space of sufficient cross section for the diffusing molecule to pass. From this approach the Doolittle equation can be written as Eq. 8.

$$\ln D = \ln A - \frac{B}{FFV} + C \left( \frac{e_{\text{coh}}}{RT} \right) \quad (8)$$

where  $C$  is an adjustable parameter,  $e_{\text{coh}}$  is the cohesive energy,  $T$  and  $R$  as defined above. Taking into account the amorphous density,  $\rho$ , and the molecular weight of the polymer structural units (MW), Eq. 3 can be written as a function of PEN content, Eq. 9.

$$FFV = \frac{(1 - w_{\text{PEN}})MW_{\text{PET}} + w_{\text{PEN}}MW_{\text{PEN}} - 1.30\rho[(1 - w_{\text{PEN}})V_{\text{W,PET}} + w_{\text{PEN}}V_{\text{W,PEN}}]}{(1 - w_{\text{PET}})MW_{\text{PET}} + w_{\text{PEN}}MW_{\text{PEN}}} \quad (9)$$

where,  $MW_{\text{PET}}$ ,  $MW_{\text{PEN}}$ ,  $V_{\text{W,PET}}$  and  $V_{\text{W,PEN}}$  denote molecular weight and van der Waals volume of the structural

unit of PET and PEN, respectively. After combining Eqs. 8 and 9, the relationship obtained is Eq. 10.

$$\ln D = \ln A - \frac{B[(1 - w_2)MW_{\text{PET}} + w_{\text{PEN}}MW_{\text{PEN}}]}{(1 - w_{\text{PEN}})MW_{\text{PET}} + w_{\text{PEN}}MW_{\text{PEN}} - 1.30\rho[(1 - w_{\text{PEN}})V_{\text{W,PET}} + w_{\text{PEN}}V_{\text{W,PEN}}]} + C \left( \frac{e_{\text{coh}}}{RT} \right) \quad (10)$$

Figures 5 and 6 show a nonlinear least square fit of the experimental  $\text{O}_2$  and  $\text{CO}_2$  diffusivity to Eq. 10. The activation energy,  $E_D$ , is the energy needed to open a cylindrical cavity of cross section equivalent to  $(1/4)\pi d^2$ ; if the cavity length is  $\lambda$ , then its volume is  $(1/4)\pi d^2 \lambda$ . The energy required to produce a mol of such cavities, in a medium with cohesive energy density  $e_{\text{coh}}$ , may be considered equal to the activation energy for gas diffusion [23], Eq. 11.

$$\frac{1}{4RT} (\pi d^2 N \lambda) e_{\text{coh}} = E_D \quad (11)$$

where  $N$  is the Avogadro's number. According to Eq. 10, a nonlinear fit of  $\ln D$  against  $FFV^{-1}$  and  $e_{\text{coh}}$  gave the parameter  $C$  and by Eq. 11, this value was equated to  $0.25\lambda\pi d^2 N/RT$  and then the length step of gas diffusion,  $\lambda$ , could be calculated. The values obtained for the parameter  $C$  in the polyester blends were 0.0138 for  $\text{O}_2$  and 0.0130 for  $\text{CO}_2$ ; thus mean length steps of 6.04 Å for  $\text{O}_2$  and 6.24 Å for  $\text{CO}_2$  can be computed. These  $\lambda$  values are consistent with those reported by Meares [23], who estimated from experimental data, an average jump length equal to 9 Å for various gases in poly(vinyl acetate) below its  $T_g$ . Polyester blends studied here have higher  $T_g$  values than poly(vinyl acetate). The  $\text{O}_2$  and  $\text{CO}_2$  mean length steps, or unit diffusion steps, for PET/PEN blends are shorter than those of Meares, because of the blends stiffness. According to the literature [24, 25], the diffusion

coefficient and the average jump length are related to the average jump frequency ( $\nu$ ), Eq. 12.

$$D = (1/6)\lambda^2\nu. \quad (12)$$

$\nu$  can be interpreted as the frequency of chain openings that permit passage of the penetrant molecule. For  $\text{O}_2$  in PET and PEN, the  $\nu$  found values were  $6.6 \times 10^6 \text{ s}^{-1}$  and  $1.7 \times 10^6 \text{ s}^{-1}$ . For  $\text{CO}_2$  in the same polymers were  $1.0 \times 10^6 \text{ s}^{-1}$  and  $0.18 \times 10^6 \text{ s}^{-1}$ , respectively. Therefore, it can be noted that, independently of the penetrant gas,  $\nu$  is smaller for PEN than for PET. These values mirror the effect of the chain rigidity on the polymer transport properties.

TABLE 1. Effect of PEN composition on oxygen and carbon dioxide solubility in PET/PEN blends.

PEN composition (%)	Oxygen solubility ( $S \times 10^2$ , cc cm <sup>-3</sup> atm <sup>-1</sup> )	Carbon dioxide solubility ( $S \times 10^2$ , cc cm <sup>-3</sup> atm <sup>-1</sup> )
0	10.50	4.20
10	11.30	4.10
30	12.00	4.00
40	11.70	4.12
50	12.00	4.55
70	13.00	4.45
90	14.25	5.10
100	14.30	5.40



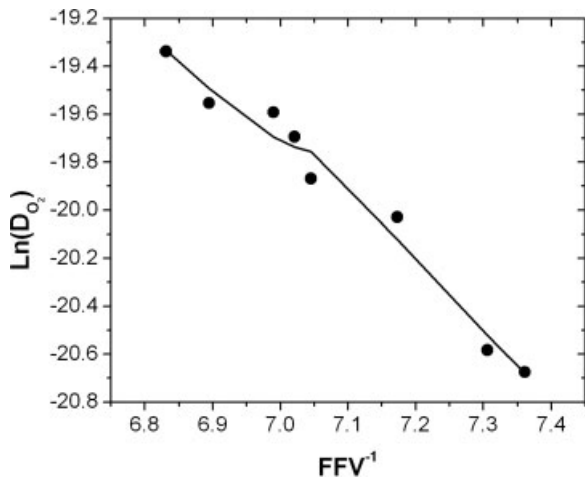


FIG. 5. Nonlinear fit of oxygen diffusivity data in PET/PEN blends at 25°C to Eq. 7. Filled circles are the experimental diffusivity data and the line is the fit of Eq. 7.

The total volume of gas passing through a polymer film in the time unit is defined as the permeability coefficient. Permeability for O<sub>2</sub> and CO<sub>2</sub> in pure PEN resulted in 65 and 76%, respectively, lower than the obtained permeability for these gases in pure PET. It was ascertained that as more and more terephthalate linkages were replaced with naphthalate units, CO<sub>2</sub> and O<sub>2</sub> permeability of the blends became smaller. These effects are postulated to arise mainly from a decrease of segmental mobility of the blend chains because of the presence of more rigid naphthalate units. Indeed, a progressive reduction in *P* was observed as the naphthalate content increased, reflecting the presence of a more rigid structure in the polymer matrix. A research found a relationship between sub-*T<sub>g</sub>* molecular motions and the transport of gases in polyesters and copolyesters based on PET [12]. According to this report, naphthalate units restricted the molecular motions that occurred in the β-relaxation region and in turn decreased the O<sub>2</sub> and CO<sub>2</sub> permeability. According to the

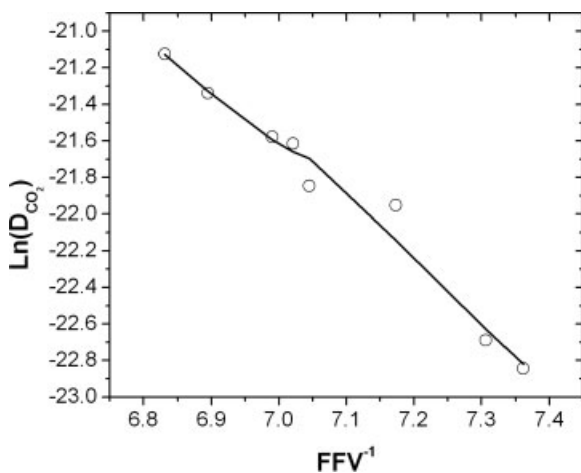


FIG. 6. Nonlinear fit of carbon dioxide diffusivity data in PET/PEN blends at 25°C to Eq. 7. Open circles stand for experimental diffusivity data and the line is the best fit of Eq. 7.

Lennard-Jones diameter, 3.94 Å for CO<sub>2</sub> and 3.47 Å for O<sub>2</sub> [26]; CO<sub>2</sub> should be less permeable than O<sub>2</sub>. On the contrary, the results show that CO<sub>2</sub> permeability resulted higher than O<sub>2</sub> permeability, as it is seen in Figs. 2 and 3. This observation could be explained from the point of view of gas solubility. Measurements of PET/CO<sub>2</sub> sorption isotherms at pressure greater than 1 atm were reported by Koros and Paul [27, 28]; they used a very crystalline commercially available 2-mil PET film and they reported that “X-ray peak areas indicated ~61 ± 5% crystallinity, in good agreement with the density measurements” [29]. The crystallinity degree, *X<sub>c</sub>*, was estimated according to the Hermans-Weidinger method [30]. *X<sub>c</sub>* was calculated by Eq. 13, where *A<sub>c</sub>* is the crystalline area and (*A<sub>c</sub>* + *A<sub>a</sub>*) is the total diffracted area.

$$X_c = \frac{A_c}{A_c + A_a} \quad (13)$$

The crystallinity degree values are shown in Fig. 7, alongside the O<sub>2</sub> diffusivity and permeability, as a function of PEN wt% in the blends. It is observed that the crystallinity change produced at about 50 wt% of PEN has not an effect in the calculated blend diffusivity and permeability. The same can be said for CO<sub>2</sub> diffusivity and permeability.

The morphology of the five PET/PEN film samples was studied by SEM and can be observed in Fig. 8. Clearly, it can be concluded that the PET/PEN films are amorphous and do not have porosity.

### Solubility

The results show that O<sub>2</sub> solubility increased with PEN concentration. This behavior was consistent with the observation of Polyakova et al. [11] for a set of PET/PEN

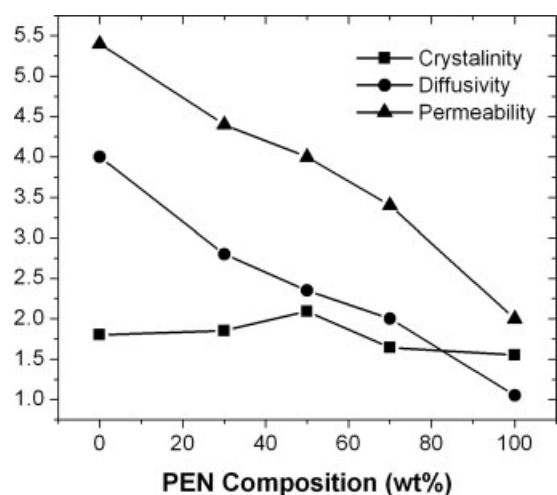


FIG. 7. Crystallinity, permeability at 25°C, and diffusivity of O<sub>2</sub> of PET, PEN, and PET/PEN blends films. (Note: Crystallinity values × 10<sup>-1</sup> [%], permeability values × 10<sup>9</sup> [Barriers], and diffusion × 10<sup>8</sup> [cm<sup>2</sup>/s]).

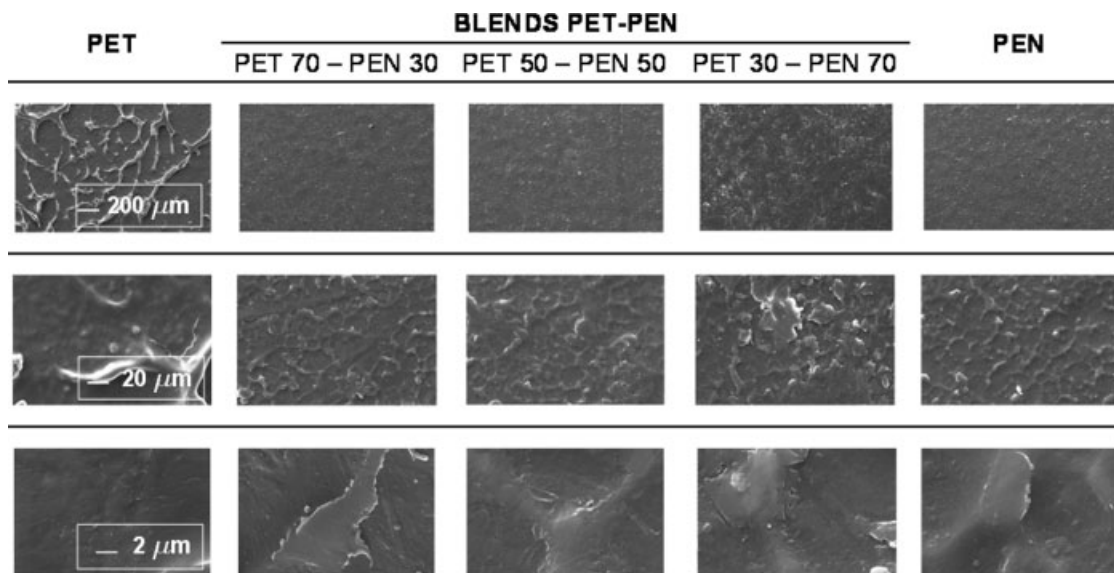


FIG. 8. PET, PEN, and PET-PEN blends SEM micrographs to different magnifications (the scale is the same for each photo along a row). Throughout the observation of all of them, it can be deduced the samples are amorphous and without porosity.

copolymers with different composition. In general, oxygen solubility increased with increasing PEN content and in pure PEN resulted  $\sim 36\%$  higher than in pure PET. The observed linear trend in this research and in Polyakova's report was compatible with a simple model, Eq. 14, which has been applied with certain success to describe penetrant solubility in heterogeneous copolymers and polymer blends [31].

$$S = w_{\text{PEN}}(S_{\text{PEN}} - S_{\text{PET}}) + S_{\text{PET}} \quad (14)$$

where  $w_{\text{PEN}}$  are the weight fraction of PEN in the copolymer or blend,  $S$  is the copolymer solubility, and  $S_{\text{PEN}}$  and  $S_{\text{PET}}$  are pure PEN and pure PET solubility. This empiri-

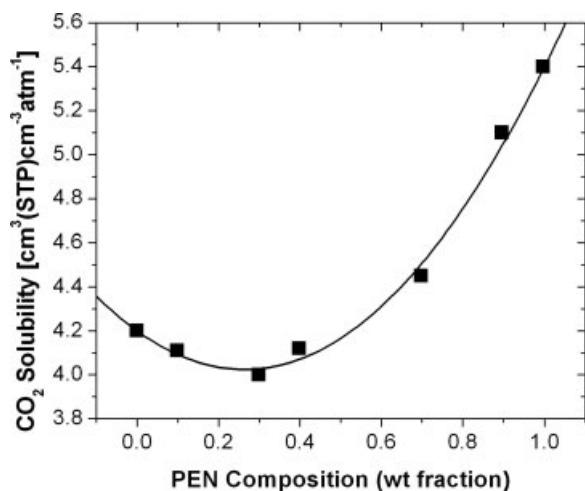


FIG. 9. Solubility of carbon dioxide in PET/PEN blends at 25°C, filled circles denote calculated solubility in the copolymers and the curve is a nonlinear least-square fit of Eq. 11, treating  $I$  as an adjustable parameter.

cal model predicts a linear variation of the solubility with the PEN composition in the blends and is a good theoretical approximation for our experimental data. Still, polar gases such as CO<sub>2</sub> are mostly more soluble in polyesters [22]. The  $-\text{COO}-$  concentration in PET is  $1.4 \times 10^{-2}$  and in PEN it is  $1.1 \times 10^{-2}$  mol cm<sup>-3</sup>. According to Koros et al. [29], increasing the concentration of  $-\text{COO}-$  or  $-\text{SOO}-$  groups in a polymer will increase the solubility of CO<sub>2</sub> because of the polar interactions. As such, CO<sub>2</sub> should be less soluble in PEN than in PET. However, the solubility data in PET/PEN blends did not follow this experimental observation. In the case of CO<sub>2</sub>, an interacting penetrant, the calculated solubility did not suggest a linear trend, and Eq. 14 did not describe its solubility in PET/PEN blends. The CO<sub>2</sub> solubility was then analyzed with the aid of a semiempirical relationship derived for a binary homogenous blend, in which a particular property,  $Y$ , can be quantified by Eq. 15 [32].

$$Y = Y_1\Phi_1 + Y_2\Phi_2 + I\Phi_1\Phi_2 \quad (15)$$

where  $Y_1$  and  $Y_2$  stand for the value of a property in homogenous polymers,  $\Phi_1$  and  $\Phi_2$  are the volume fraction of each pure polymer and  $I$  is a binary interacting and adjustable parameter which describes the mixing of the two polymers. Figure 9 shows the best application of Eq. 15 to the experimental CO<sub>2</sub> solubility. The parameter  $I$  was estimated to be  $-2.5357$  from a nonlinear fit of Eq. 15 to the experimental solubility data. A negative value of  $I$  denotes a nonsynergistic behavior of the blend in respect to the weighted average of the property in homopolymers [32]. This model predicts a minimum at  $S = 4.024$  and PEN fraction of 0.263 which was calculated from Eq. 11 and there is no experimental evidence in

this work because a blend with 0.20 PEN blend was not prepared.

## CONCLUSIONS

A series of PET/PEN copolymers was prepared by mixing them in molten state. They were characterized by X-rays, SEM, DSC, and density measurements and used to perform O<sub>2</sub> and CO<sub>2</sub> transport experiments. Measurements of DSC revealed that the glass transition temperatures of copolymers were nearest to the predicted values found by the Fox equation for compatible blends. Density of these copolymers rose monotonically with increasing PET content from 1.3332 g cm<sup>-3</sup> in PEN to 1.3403 g cm<sup>-3</sup> in PET. The free volume of the polymer blends then increased and a higher amount of free volume was available for gas permeation. Therefore, it is reasonable to expect higher O<sub>2</sub> and CO<sub>2</sub> diffusivities and permeabilities through pure PET film than through copolymers PET/PEN and pure PEN films, at least inside the 16–26% range of crystallinity that we worked in this research. With the O<sub>2</sub> and CO<sub>2</sub> diffusivity data, a nonlinear least-square fit to the Doolittle equation was performed and a better fit was achieved by considering the cohesive energy of polymers and blends. This approach provides a better understanding of permeation process because it was possible to calculate the length step of gas diffusion and the average jump frequency. The length steps for both gases were almost the same but the smaller average jump frequency for PEN reflects the higher stiffness of the polymer chain. This higher rigidity arises mainly from a decrease of segmental mobility of the polymer chains due to the existence of more rigid PEN sequences joined to less rigid PET segments. The increased stiffness resulted in higher activation energy of diffusion, decreased the frequency of chain opening and decreased diffusion coefficients. As CO<sub>2</sub> is an interacting gas with polar polymers, its solubility resulted higher than O<sub>2</sub> in this set of polymers. Interestingly, CO<sub>2</sub> solubility rises with PEN content and it performed a nonlinear least-square fit having an adjustable parameter. The concluded value of this parameter suggested that PET/PEN copolymers are nonsynergistic blends.

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