

Gas Transport and Thermal Characterization of Mono- and Di-Polyethylene Films Used for Food Packaging

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ABSTRACT: The permeability of carbon dioxide, oxygen, nitrogen, and air through commercial monolayer and multilayer films, based on polyethylene (PE), biaxially oriented polypropylene (BOPP), and polyamide (PA), used for food packaging is reported. The influence of temperature (from 10 to 60°C) on permeability and DSC characteristics changes was also analyzed. Literature data for gas permeability of the mentioned monofilms are quite variable due to differences in additives, thermal history, and crystallinity. In this work, the highest gas permeability is obtained for PE film at the higher temperature (50–60°C). Laminates exhibit different gas permeation behavior from that of monofilms. Generally, gas solubility coefficient increases at higher temperature (with an exception of PA/PE and BOPPcoex.met/PE),

being higher for monofilms in comparison with laminates, while diffusion coefficients are lower for monofilms in comparison with laminates. The temperature dependence of the permeability, diffusivity, and solubility of gases shows two different regions in PE, BOPPcoex/PE (10–40°C and 40–60°C), PA/PE, and BOPPcoex.met (10–30°C and 40–60°C) films. Correlation between activation energies for permeation and diffusion as well as heat of sorption and 17 gas properties is performed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1590–1599, 2006

Key words: DSC; gas permeability; laminates; monofilms; polyethylene

INTRODUCTION

A number of factors influence the barrier properties of polymers used for food packaging. A permeant present at high concentration can plasticize the polymer sufficiently to allow unexpectedly rapid diffusion of a trace permeant such as a flavor or odor molecule.^{1,2} The gas transport coefficients (permeability, the diffusion and the solubility coefficients) vary generally with parameters that can be intrinsic to the polymer, such as the degree of crystallinity, the nature of the polymer, or even the thermal and mechanical histories of samples.³

Previous studies have shown that the sorption and diffusion phenomena took place exclusively in the amorphous phase of a semicrystalline polymer and not in its crystalline zones.^{4,5} The crystalline portion increases the effective path length of gas diffusion, and they seem to reduce the polymer chains mobility in the amorphous phase (because chain ends are trapped in the neighboring crystalline lamellae).

The kind of gases used, characterized by its molecule size and nature as well as the conditions of temperature and pressure, are also factors influencing barrier properties.

Polyethylene (PE) is the first commodity plastic used for food packaging. PE films are often laminated with other polymers for applications in which PE is used for heat-sealing and/or as a barrier to water vapor.

Biaxially oriented polypropylene film (BOPP) is also a widely used transparent packaging material. Its advantageous properties include low density, no toxicity, good moisture resistance, good mechanical strength, and dimensional stability and printability. Commercial BOPP films have special inner structures obtained by the stretching of the thick, extruded sheets at high temperatures in the machine direction and in the transverse direction.⁶

To obtain high-performance films with superior properties, layering two or more different materials in a single structure is necessary. Polyamide (PA) has frequent use as a component in these multilayer film structures⁷ because of its unique combination of mechanical strength, puncture resistance, transparency, thermal stability, oxygen and aroma barrier, and thermoformability.

During the past two decades, the fast advances in extrusion technology has resulted in a rapid growth of

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TABLE I
Materials Used in the Experiments

Polymer	Abbreviation	Thickness (μm)
Polyethylene	PE	75
Polyamide	PA	15
Bioriented coextruded polypropylene	BOPPcoex.	20
Bioriented coextruded metalized polypropylene	BOPPcoex.met.	20
Polyamide/polyethylene	PA/PE	15/75
Polypropylene bioriented coextruded/polyethylene	BOPPcoex./PE	20/75
Polypropylene bioriented coextruded metalized/polyethylene	BOPPcoex.met./PE	20/75

coextrusion processes to manufacture multilayer films with specific end-use properties, which are superior to those of single-layer films.

Numerous studies²⁻¹⁷ were dedicated to the barrier properties of polymers. In previous works, we investigated gas permeability of several packaging materials.¹⁵⁻¹⁷

In this work, we focused our study on the transport of carbon dioxide, oxygen, nitrogen, and air through commercial monolayer and multilayer films, based on PE, BOPP, metalized BOPP and PA, used for food packaging.

EXPERIMENTAL

Investigated test films are listed and specified in Table I. Films are obtained, without graphics, directly from producer, Alufexpack d.o.o., Umag, Croatia.

Permeability measurement

Gas permeability determination is performed using manometric method, on permeability testing appliance, Type GDP-E (Brugger Feinmechanik GmbH), and was calculated according to following equation.¹⁸

Permeance unit calculation for the samples (monofilms) analyzed using the method A was determined from the eq. (1).

$$q = k_1 \frac{V}{T(29N - t_L)} \tag{1}$$

where $k_1 = 9.89 \times 10^8$, q is the permeance unit ($\text{cm}^3 \text{m}^{-2} \text{d}^{-1} \text{bar}^{-1}$), V is the measurement volume (mL), N is the slope of the measurement curve (s), T is the temperature (K), and t_L is the time-lag value (s). For the homogeneous plastic film (monofilm), the permeability, the diffusion and the solubility constants of the gas in film were calculated according to following equations.

Permeability constant:

$$P = k_2 ql \tag{2}$$

where $k_2 = 1.16 \times 10^{-9}$ and l is the polymer thickness (cm).

Diffusion constant:

$$D = \frac{l^2}{6t_L} \tag{3}$$

Solubility constant:

$$S = k_3 \frac{qt_L}{l} \tag{4}$$

where $k_3 = 6.94 \times 10^{-9}$.

Permeation is a solution-diffusion process that can be described in terms of the sorption and transport coefficient for the individual polymer and gas.

$$P = DS \tag{5}$$

The temperature dependence of permeability, P ($\text{cm}^3 \text{cm}^{-1} \text{s}^{-1} \text{bar}^{-1}$), solubility, S ($\text{cm}^3 \text{cm}^{-3} \text{bar}^{-1}$), and diffusion, D ($\text{cm}^2 \text{s}^{-1}$), constants can be described by Arrhenius expressions and van't Hoff relationship, respectively.

Activation energy for permeation:

$$P = P_o \exp(-E_p/RT) \tag{6}$$

Activation energy for diffusion:

$$D = D_o \exp(-E_d/RT) \tag{7}$$

Heat of sorption:

$$S = S_o \exp(-H_s/RT) \tag{8}$$

where P_o , D_o , and S_o are pre-exponential factors, E_p and E_d are activation energies for permeation and diffusion, respectively (J mol^{-1}), H_s is heat of sorption (J mol^{-1}), R is gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), and T is temperature (K).

The permeability constant calculation for multilayered films is performed using the following relation:¹¹

$$P_T = \frac{l_T}{\left(\frac{l_1}{P_1}\right) + \left(\frac{l_2}{P_2}\right)} \tag{9}$$

where P_T is total permeability, l_T is total thickness, l_{1-n} is thickness of individual layer, and P_{1-n} is permeability of individual layer.

The eq. (9) is used to compare calculated and experimentally obtained transport coefficients data for laminates, to find out the possibility of using method A on the GDP-E instrument, which is proposed to be used for monofilms only.¹⁸

Gas permeation experiments were performed more than three times, and the reported values are the mean of three experiments.

Standard deviation, average values, and coefficients of variability (%) for P , D , and S values for analyzed polymers are

Polymers	Transport coefficients	Standard deviation	Average	Coefficient of variability (%)
PE	P	$2.3 (10^{-11})$	$2.2 (10^{-9})$	1
	D	$2.6 (10^{-9})$	$1.6 (10^{-7})$	2
	S	$2.8 (10^{-3})$	0.16664	2
PA	P	$6.1 (10^{-12})$	$2.8 (10^{-10})$	2
	D	$2.6 (10^{-11})$	$1.97 (10^{-9})$	1
	S	$4 (10^{-3})$	0.148	3
BOPPcoex	P	$4.83 (10^{-12})$	$6.98 (10^{-10})$	1
	D	$6.1 (10^{-11})$	$2.7 (10^{-9})$	2
	S	$1 (10^{-2})$	0.4696	2
BOPPcoex.met.	P	$6.14 (10^{-12})$	$3.7 (10^{-10})$	2
	D	$1.5 (10^{-10})$	$3.9 (10^{-9})$	4
	S	$2 (10^{-2})$	0.556	4
PA/PE	P	$3.4 (10^{-11})$	$2.1 (10^{-9})$	2
	D	$1.69 (10^{-7})$	$1.51 (10^{-6})$	11
	S	$1.96 (10^{-4})$	0.00204	10
BOPPcoex./PE	P	$2.8 (10^{-11})$	$2.8 (10^{-9})$	1
	D	$6.8 (10^{-8})$	$8.1 (10^{-7})$	8
	S	$8.8 (10^{-4})$	0.0107	8
BOPPcoex.met./PE	P	$1.8 (10^{-11})$	$2.64 (10^{-9})$	1
	D	$3.1 (10^{-7})$	$2.2 (10^{-6})$	14
	S	$1.8 (10^{-4})$	0.0013	14

DSC experiments

The DSC analysis was carried out on a Netzsch DSC 200 differential scanning calorimeter operating in the temperature range between -100°C and 500°C at a heating rate of $10^{\circ}\text{C min}^{-1}$ in a nitrogen atmosphere. Calibrations for both the temperature and the enthalpy were achieved from measurements of melting temperature and enthalpy of indium. From DSC thermograms, the heat of fusion was determined ΔH_f and the degree of crystallinity X_c was determined according to the following equation

$$X_c = \Delta H_f / \Delta H_{f,th} \quad (10)$$

The theoretical heat of fusion $\Delta H_{f,th}$ of 100% crystalline polymer was assumed to be 293 J g^{-1} for PE and 190 J g^{-1} for polypropylene and PA.¹⁹

RESULTS AND DISCUSSION

Thermal properties

Figure 1 shows the results of DSC measurements on as-received films. The curves exhibit one or two endo-

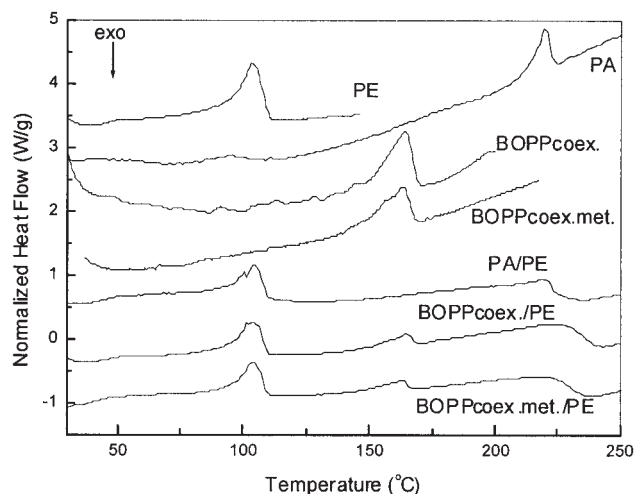


Figure 1 DSC thermograms of as-received films obtained at heating rate of $10^{\circ}\text{C min}^{-1}$.

thermic peaks that correspond to the melting of crystalline phases of semicrystalline polymers. All parameters of investigated specimens obtained from DSC measurements are summarized in Table II, where T_{onset} and T_{end} refers to the temperature of the onset and end of the melting process, and T_m is the melting temperature (DSC peak temperature).

For PA/PE laminate, it was difficult to estimate PA heat of fusion due to the overlapping of PA melting with the onset of PE oxidation. On the assumption that polymers in laminates have the same degree of crystallinity, the approximate content of polymers and tie-layers (or adhesive coatings) can be calculated. In PA/PE and BOPP/PE laminates, a minor peak appears in the DSC thermograms of about 101°C while the main peak is around 104°C . These findings indicate that the crystalline structure did change during the production of multilayer films probably because of the tempering at temperature of about 100°C . During tempering, crystal segregation occurs. Amorphous domains of highest order in molecular structure can form crystallites with melting points higher than the temperature at what the tempering was done. Complete melting deletes any thermal history as shown in Figure 2. The PA/PE laminate was heated from 30 to 150°C at $5^{\circ}\text{C min}^{-1}$, then cooled to -100°C at $5^{\circ}\text{C min}^{-1}$, and heated again to 150°C at $5^{\circ}\text{C min}^{-1}$.

To see the effect of the permeation test temperature on the crystallization behavior, DSC characterization of as-received PE film was made after tempering at 60°C for 35 min. The comparison between the DSC analysis of PE film performed at the initial state and after tempering is given in Figure 3. On the DSC curve obtained after the tempering, the small exothermal peak just before melting is observed indicating the so-called premelt crystallization. Integrating the melting peak, lower heat of fusion was obtained for pre-

TABLE II
Parameters of Investigated Films Obtained from DSC Measurements

Sample	T_{onset} (°C)	T_{end} (°C)	T_m (°C)	ΔH_f (J g ⁻¹)	X_c (%)
PE	42	110	103	92	31
PA	202	223	220	30	16
PP	128	168	165	72	38
BOPP coex.met	130	168	163	50	
PA/PE	40 (PE)	110 (PE)	104 (PA)	75 (PA)	
	–	226 (PA)	219 (PA)	–	
BOPPcoex./PE	41 (PE)	110 (PE)	104 (PE)	54 (PE)	
	145 (BOPP)	169 (BOPP)	165 (BOPP)	12 (BOPP)	
BOPPcoex.met./PE	41 (PE)	110 (PE)	104 (PE)	45 (PE)	
	145 (BOPP)	167 (BOPP)	163 (BOPP)	10 (BOPP)	

treated sample (79 J g⁻¹) in comparison to the as-received sample. It means a decrease of the degree of crystallinity of PE from 31 to 27%.

Permeability properties

The permeance values of PE, in the temperature range from 10 to 40°C, are between 245 and 310 cm³ m⁻² d⁻¹ bar⁻¹. The highest values (2100–7500 cm³ m⁻² d⁻¹ bar⁻¹), for all gases investigated, are obtained at higher temperatures (50–60°C). This can be attributed to the start of PE melting (at about 40°C), and consequently reduction in PE crystallinity.

For the PE and PA films, permeability values for N₂, CO₂, and O₂ (Fig. 4; oxygen is used as a representative) are within the same order of magnitude as already reported in the literature for the temperature of 20°C.^{12,16,17} At higher temperature (60°C) while P values show good agreement with literature data,¹² D -value is one order of magnitude lower and S -value is one order of magnitude higher for N₂ in PE film.

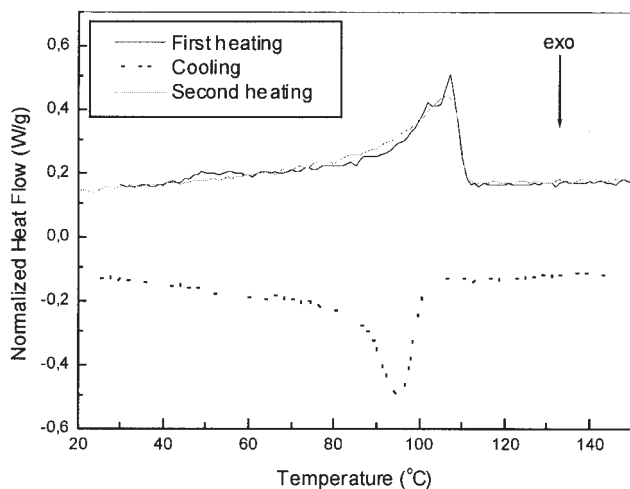


Figure 2 DSC thermograms of PA/PE film. First heating: from room temperature to 150°C at 5°C min⁻¹. Cooling: from 150°C to -100°C at 5°C min⁻¹. Second heating: from -100°C to 150°C at 5°C min⁻¹.

According to Thran et al.,¹⁴ gas molecules should diffuse faster in stiffer polymers than in more flexible ones with the same fractional free-volume. The results of Doroudiani²⁰ showed that the diffusivity of CO₂ in the semicrystalline polymers is strong function of the crystallinity.

For all gases investigated, the diffusivity (Fig. 5) increase with increasing temperature, and are nearly the same, as also observed for PE films.²¹

Solubility values (Fig. 6) significantly increase at higher temperature (50–60°C). This is especially evident for PE; BOPPcoex, and BOPPcoex/PE films.

The effect of solubility could be due to the fact that the small crystals formed in the amorphous zone have less volume, consequently, the gas solubility in the polymer increases and so does the permeability. These changes, also observed by Villaluenga et al.,²² for LLDPE films, might be due to the melting of small and less perfect crystalline entities. This melting process might increase the solubility of the gases in the films and favor the ease of the gas diffusion due to the decrease of the obstruction of the diffusion paths. The time-lag values for PE film

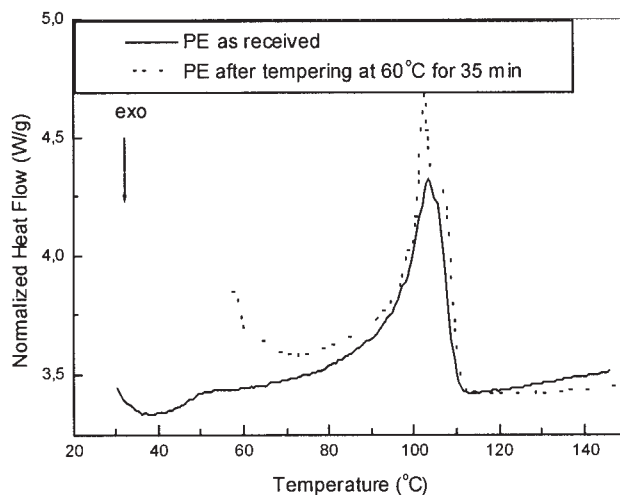


Figure 3 DSC thermograms of as-received and pretreated PE films obtained at heating rate of 10°C min⁻¹.

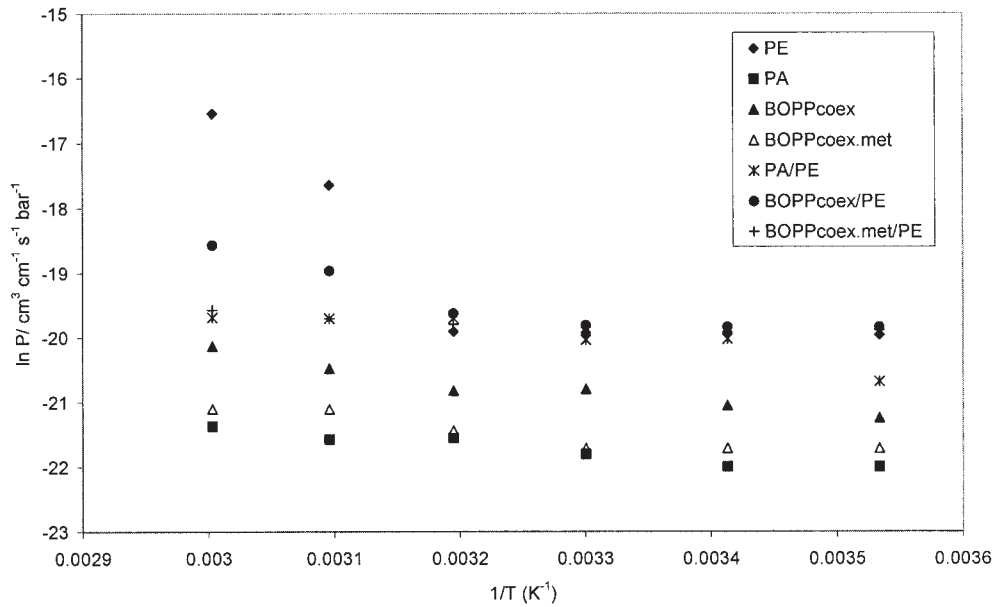


Figure 4 Arrhenius plots for the permeability coefficient of oxygen through polymers.

analyzed decreased with temperature (data not presented) increased, being the highest (360 s) at 10°C, for the most of the gases investigated (slightly higher value of 370 s is obtained for CO₂).

Permeability of PA is from one (in the temperature range from 10 to 40°C) to two orders of magnitude (in the temperature range from 50 to 60°C) lower than the permeability of PE (Fig. 4), due to lower D (Fig. 5) values. Solubility of gases in PA is not much affected with temperature increase (Fig. 6).

Better barrier properties of PA than those of PE was also reported by others.^{9,23}

It seems that the presence of polar amide groups and intermolecular hydrogen bonding in PA can barely allow the nonpolar gas molecules (i.e., O₂, CO₂, and N₂) to enter and permeate through amorphous regions of PA as compared to nonpolar PE molecules, although crystallinity of PE is higher than that of PA (Table II).

Similar trend is observed between PE and BOPP films (Figs. 4–6). It is well-known that biaxial drawing of PP films decrease gas permeability, and the reduction of permeability is caused only by the reduction in gas diffusion.^{24,25} The changes of diffusion coefficient

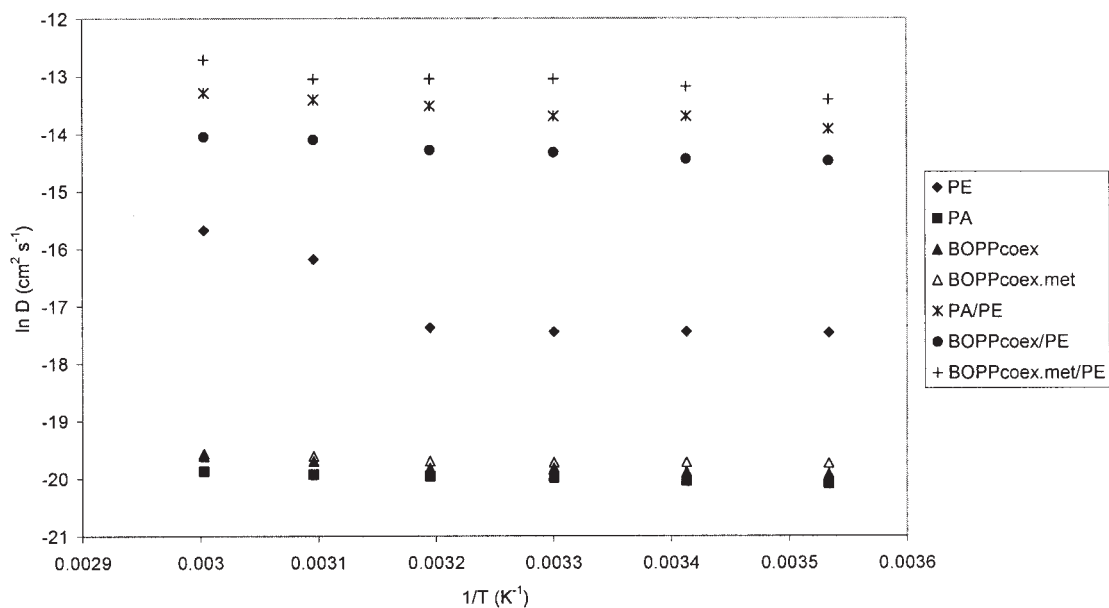


Figure 5 Arrhenius plots for the diffusion coefficient of oxygen through polymers.

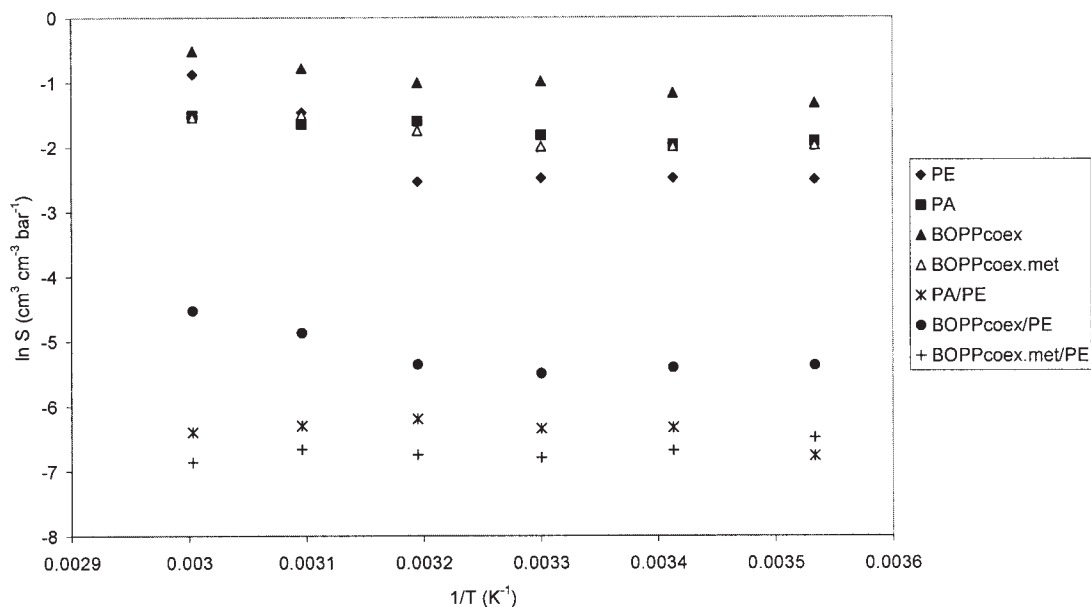


Figure 6 Arrhenius plots for the solubility coefficient of oxygen through polymers.

of O_2 for the drawn films, according to Wang and Porter,²⁴ are parallel with that of porosity. Authors also stated that the pores formed in the drawn PP films are well simulated by the integrated capillary model, and found out the ratio of permeability coefficient for O_2 and CO_2 to be 1.17. In our case, the closest value of O_2/CO_2 ratio of 1.14 is obtained for BOPPcoex film at 30°C.

The results of Hanika et al.²⁶ on BOPP films showed that complex interaction mechanism of film thickness, defects area, and defect spacing have an effect on gas permeability. Additionally, it was found that a higher permeability is caused by the presence of many small defects rather than a small number of large defects (above $0.5 \mu m^2$) of the same total area. Our results for BOPP films are one order of magnitude lower for oxygen permeability and diffusivity and one order of magnitude higher for O_2 solubility, at the temperature of 20°C, than those presented by Hanika et al.²⁶ The main reason for these differences in permeability is probably due to the restriction of diffusion (reduction of the tortuosity factor i.e., increasing of the average path of the diffusing molecule) in drawn polymer, caused by orientational and conformational changes of the polymer, which may block existing passages through the amorphous component.^{24,27}

Generally, higher barrier (Fig. 4) properties of BOPP films, among the investigated samples with the exception of PA film, is mainly due to kinetic effects, i.e., very low diffusion coefficients (Fig. 5).

In the case of laminates, the solubility (Fig. 6) is lower and diffusivity (Fig. 5) is higher in comparison with monofilms. Somewhat surprisingly, in the case of laminates, much lower time-lag values (min $t_L = 5$ s;

max $t_L = 30$ s) are obtained in comparison to monofilms (min $t_L = 60$ s; max $t_L = 370$ s).

Increased diffusivity in PA/PE, in comparison to PA and PE monofilms, could be due to increased amount of permeable region in laminate. The solubility of N_2 and CO_2 in PA/PE decreases with temperature, while O_2 solubility (Fig. 6) showed the highest value at 40°C. The obtained CO_2 , N_2 , and O_2 diffusivity and solubility values for PA/PE laminate agree with literature data.²⁸

The difference in the transport properties of gases in BOPP/PE laminates could be due to different crystallization behavior of the blends. In this case, it seems that the presence of PE reduced the crystallinity of PP, as observed also by Barra et al.²⁹ This effect, with regards to slightly increased diffusivity (Fig. 5), is probably not so pronounced.

BOPPcoex.met/PE shows decrease in nitrogen solubility values with temperature increase, while for other gases, slightly increase is observed in the temperature range 40–50°C (data presented only for oxygen in Fig. 6).

Permeability increase with temperature is mostly due to enhanced motion of the polymer segments³⁰ and increased energy level of permeating molecules.

A close analyses of the Arrhenius plots (Figs. 4–6) suggests that the temperature dependence of the transport coefficients could be divided in two intervals, which enable the fitting of the P , D , and S values to two straight lines with correlation coefficients close to or higher than 0.9. These breaks are the most significant for the BOPPcoex/PE and PE film (Fig. 4), as observed by others,^{22,31,32} with permeability plateau at $\sim 40^\circ C$ obtained for PE.³² This behavior is indepen-

TABLE III
Activation Energy for Gases Permeation (E_p) and Diffusion (E_D) and Heat of Sorption (H_s) Through Polymers

Films	Temp range (°C)	E_p (J mol ⁻¹)				E_D (J mol ⁻¹)				H_s (J mol ⁻¹)			
		O ₂	N ₂	Air	CO ₂	O ₂	N ₂	Air	CO ₂	O ₂	N ₂	Air	CO ₂
PE	10–40	1230	192	192	1758	1892	1044	1248	1758	-662	-852	466	-671
	40–60	14,6142	11,4045	11,4045	63,595	74,145	63,397	75,366	63,595	71,997	44,648	30,507	64,850
PA	10–60	10,427	3268	1113	1542	3310	2586	2490	1565	7117	682	-1377	-24
	10–60	16,187	13,330	10,903	7471	4695	5967	6153	2752	11493	7363	4750	4719
BOPPcoex.	10–30	-	2758	312	15,679	869	3946	1516	5217	-1090	-1188	-1205	10,462
	40–60	14,721	608	3353	26,758	5802	1033	3069	7013	8919	-425	284	19,745
PA/PE	10–30	23,143	2568	2366	1104	8042	-	-	-	15,102	-9481	-8740	-6873
	40–60	801	2824	1681	1681	9660	5154	5049	4517	-8858	-2330	-3367	-2835
BOPPcoex./PE	10–40	4597	2665	3006	1278	5009	2583	2918	5525	-411	81	88	-4247
	40–60	46,071	38,447	44,451	27,464	10,177	10,956	11,282	10,134	35,894	27,491	33,170	17,330
BOPPcoex.met/PE	10–60	4545	877	2675	326	8650	7719	9427	4813	-4106	-6842	-6751	-4487

dent of the gas employed, and similar behavior is noticed for the diffusivity (Fig. 5) and solubility (Fig. 6) coefficients. This effect is less pronounced in gas diffusivity for BOPPcoex/PE film (Fig. 5). According to literature data,³² the breaks observed in PE films may be caused by a α -relaxation process, produced by motions of the chain folds at the crystal surface.

Activation energies for permeation and diffusion (Table III) are higher in the higher temperature range (40–60°C) both for PE and BOPPcoex/PE films. Heat of sorption is exothermic (Table III) in the low temperature range (10–40°C) for O₂, N₂, and CO₂ in the case of PE, as also observed by others.³²

The heat of sorption, H_s , defines the effect of temperature on gas solubility coefficients in a given polymer. This value is governed primarily by the negative average enthalpy change associated with the gaseous permeates being sorbed into the polymer matrix, and the positive enthalpy required to create a site into which a permeate can sorb.³³

The values for diffusion activation energy (Table III), in the temperature range 10–40°C, are higher than that obtained for permeability activation energy in PE. Similar behavior is reported by Villaluenga et al.²²

Activation energy for gas permeability and diffusivity and heat of sorption in PE film decrease, at the lower temperature interval (10–40°C), in the order

Permeability: CO₂ > O₂ > N₂ = Air

Diffusivity: O₂ > CO₂ > Air > N₂

Solubility: Air > O₂ > CO₂ > N₂

Activation energy for gas permeability and diffusivity and heat of sorption in PE film decrease, at the higher temperature interval (40–60°C), in the order

Permeability: O₂ > N₂ = Air > CO₂

Diffusivity: Air > O₂ > CO₂ > N₂

Solubility: O₂ > CO₂ > N₂ > Air

The activation energy for gas permeation (Table III) is significantly higher, in PA (for O₂, N₂); BOPPcoex (for all gases); PE (for O₂, N₂, and air at temperature range 40–60°C); PA/PE (for all gases at temperature

range 10–30°C); and BOPPcoex/PE (for all gases at temperature range 40–60°C), than the activation energy for the gas diffusion. This suggests that gas diffusion through film may not be a single activated process as a consequence of the morphological changes caused by recrystallization process.

Physical characteristics of permeates (Table IV) are correlated with activation energy for permeation and diffusion as well as heat of sorption (Table III).

Excellent correlation is obtained between collision diameter with activation energy for gas diffusion for PA, BOPPcoex, BOPPcoex.met/PE, and BOPPcoex/PE (Fig. 7) in the whole temperature range investigated. Such a correlation is also obtained for PE, at lower temperature range and BOPPcoex.met at higher temperature range. According to literature data,³⁹ collision diameter is a widely accepted correlating parameter for diffusivities in relatively high mobility rubber or liquid media.

It was reported that the solubility increases as Lenard–Jones force constant (indication of molecular interaction) or critical temperature (measure of the ease of condensation for gaseous molecules) increases.^{35,40} In fact, excellent correlation between Lenard–Jones force constant, with heat of sorption was obtained for PA, BOPPcoex, and PE (Fig. 7) in the whole investigated temperature range. For the PE film, excellent correlation is also obtained between T-critical and heat of sorption.

Correlation between van der Waals constant a , which is a measure of the attraction force between the molecules, while the term b is due to the finite volume of the molecules and to their general incompressibility,^{34,35} and heat of sorption is obtained for PA, PE, and BOPPcoex.met./PE (Fig. 7).

Such a correlation between van der Waals constants and activation energy for permeation exists in the case of PE (at higher temperature interval), BOPPcoex, BOPPcoex.met.(at lower temperature interval), BOPPcoex/PE, and BOPPcoex.met/PE films.

TABLE IV
Properties of Gases Used in the Experiments

Properties	Nitrogen	Carbon dioxide	Oxygen	Air	Ref.
Molecular diameter (cm 10 ⁻⁸)	3.15	3.34	2.98		(34, 35)
Mean free path (cm 10 ⁻⁶)	9.29	6.15	9.93		
Average velocity (cm s ⁻¹ 10 ²)	471	376	440		
van der Waals constant <i>a</i> (L ² bar mol ⁻²)	1.390	3.592	1.36	1.372516	
van der Waals constant <i>b</i> (L mol ⁻¹)	0.03913	0.04267	0.03183	0.0372516	
Gas constant (kJ kg ⁻¹ K ⁻¹)	0.2968	0.1889	0.2598	0.2870	(36)
Molar mass (kg kmol ⁻¹)	28.013	44.01	31.999	28.97	
Critical temperature (K)	126.2	304.2	154.8	132.5	
Critical pressure (MPa)	3.39	7.39	5.08	3.77	
Critical volume (cm ³ mol ⁻¹)	88.9	94.3	78	88.3	
Effective diameter (cm 10 ⁻⁸)	3.66	3.63	3.44		(35)
Lennard-Jones force constant	91.5	190	113		
Collision diameter (cm 10 ⁻⁸)	3.68	4.00	3.43		
Kinetic diameter (cm 10 ⁻⁸)	3.64	3.30	3.46		
Diffusion coefficients of gases in water at 20°C (cm ² s ⁻¹ 10 ⁵)	1.64	1.77	1.8		(37)
Gas density (kg m ⁻³)	1.25055	1.9769	1.42895	1.2929	
Molecular volume (cm ³ mol ⁻¹)	31.2	34	25.6	20.1	
Viscosity (μP)	176	147	204	0	(38)

Correlation between the kinetic diameter is close to the molecular sieving dimension of a gas and is a sensitive measure of ability to move in highly restrictive environments,³⁶ and activation energy for diffusion is obtained for PA/PE and BOPPcoex.met./PE (in the whole temperature range), BOPPcoex.met. (in the temperature range 10–30°C), and PE (in the temperature range 40–60°C).

Since polymer films possess both solid and liquid properties, an effective molecule diameter for gases, (the square root of the product of gas collision diameter and kinetic diameter) which describes the relationship between diffusivity and gas molecule diameter, is correlated with activation energy for gas permeability and diffusivity. For all polymers

analyzed, with the exception of BOPPcoex.met./PE film, an excellent correlation is obtained between the activation energy for gas diffusion and effective volume (Fig. 7).

To find out the possibility of using method A on the GDP-E instrument, for transport coefficients determination in laminates, correlation between the experimentally obtained *P* values, according to eq. (9), and experimentally obtained gases permeability values through laminates are obtained.

Generally, the experimentally obtained permeability values of all laminates are slightly higher in comparison to calculated (Fig. 8; the results are presented only for the oxygen permeability, as a very similar trend is obtained with other gases). An excellent cor-

	10-60						10-30			40-60			10-30			40-60			10-40			40-60			10-40			40-60		
	PA		BOPPcoex		BOPPcoex.met/PE		BOPPcoex.met.			PA/PE			PE			BOPPcoex/PE														
	Ep	Ed	Hs	Ep	Ed	Hs	Ep	Ed	Hs	Ep	Ed	Hs	Ep	Ed	Hs	Ep	Ed	Hs	Ep	Ed	Hs	Ep	Ed	Hs	Ep	Ed	Hs	Ep	Ed	Hs
Effective dia.	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Lennard-Jones	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Kinetic dia.				•																										
Collision dia.	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
p-critical				•																										
T-critical				•																										
Molar mass				•																										
Diffusion coeff.		•					•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Molecular vol.				•																										
Gas density				•																										
Viscosity	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Critical vol.	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Van der Waals (b)	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Van der Waals (a)				•			•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Average velocity				•																										
Mean free path	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Molecular dia.	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•

Figure 7 Correlation between activation energy (J mol⁻¹), for permeation (*E_p*), diffusion (*E_D*), and heat of sorption (*H_S*) values, and gas properties, for the polymers showing Arrhenius behavior (*r* > 0.9) in the temperature range.

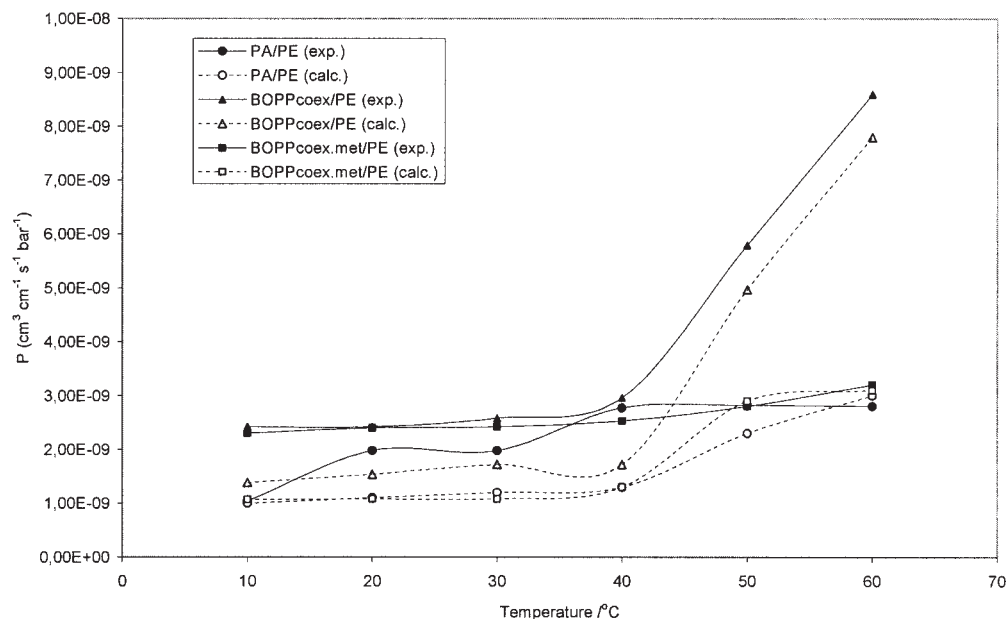


Figure 8 Comparison between experimentally obtained and calculated P -values for oxygen in di-laminates.

relation between calculated and experimentally obtained value is obtained for permeability of all gases investigated (Table V). Among the analyzed laminates BOPPcoex/PE showed the highest correlation for all gases.

CONCLUSIONS

Among the analyzed samples, PE film showed the highest gas permeability increase at higher temperatures (50–60°C) for all investigated gases. This is probably due to the decreased crystallinity (from 31 to 27%) as analyzed by DSC.

Solubility values significantly increase at higher temperature (50–60°C). This is especially evident for PE; BOPPcoex, and BOPPcoex/PE films.

In the case of laminates, the solubility is lower and diffusivity is higher in comparison with monofilms. Somewhat surprisingly, in the case of laminates, much lower time-lag values (min $t_L = 5$ s; max $t_L = 30$ s) are obtained in comparison to monofilms (min $t_L = 60$ s; max $t_L = 370$ s).

For all polymers analyzed, with the exception of BOPPcoex.met/PE film, an excellent correlation is ob-

tained between the activation energy for gas diffusion and effective volume (the square root of the product of gas collision diameter and kinetic diameter).

An excellent correlation between experimentally and calculated gas permeability value is obtained for the investigated laminates.

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TABLE V
Correlation Coefficient (r) Between Calculated and Experimentally Obtained P -Values

Laminates	O ₂	N ₂	Air	CO ₂
PA/PE	0.69627	0.875829	0.783148	0.818697
BOPPcoex./PE	0.99784	0.908878	0.886608	0.970994
BOPPcoex.met/PE	0.92684	0.787076	0.912606	0.614855

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