

Gas Sorption in Semicrystalline Rubbery Polymers Revisited

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ABSTRACT: This work reports the solubility of carbon dioxide, ethylene and propylene in low density polyethylenes with densities lying in the range 0.870–0.940 g/cm³. The sorption behavior is studied as a function of the crystallinity in terms of the Flory–Huggins theory of polymer solutions. For each gas, both the Henry's solubility constant referred to the amorphous phase of the films and its temperature dependence do not change significantly with

the crystallinity of the LDPE films. The enthalpic polymer–gas interaction changes with the nature of the gases, but not with the crystallinity of the films. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 903–907, 2007

Key words: gas sorption; polyethylene films; semicrystalline rubbery polymers; Flory–Huggins theory

INTRODUCTION

Gas transport in polymer films under the driving force of a negative unidirectional chemical potential gradient involves solution of the gas in the polymer, diffusion of the gas molecules across the films, and desorption of the gas at the other side of the films.¹ In principle, the first step, or sorption process, can be predicted in amorphous rubbery films by making the activity a of the gas in the liquid form dissolved in the polymer equal to the ratio between the pressure p of the gas at equilibrium and that p_0 of the isolated gas in liquid form at the working temperature, T , i.e., $a = p/p_0$. The value of p_0 at T can be estimated from the boiling temperature of the gas at 1 atm using the Clausius–Clapeyron equation. Moreover, the activity of the gas can be made equal to the variation of free energy arising from the mixture of the gas in the liquid form with the polymer, which can be calculated from the Flory–Huggins theory of polymer solutions.² Utilizing this approach, and after some mathematical handling, the following expression for the gas concentration, C , is obtained as^{3,4}

$$C = \frac{22414}{76\bar{V}} p \exp \left\{ \left[- (1 + \chi) - \frac{\lambda}{RT_b} \left(1 - \frac{T_b}{T} \right) \right] + \frac{(1 + 2\chi)C\bar{V}}{22414} \right\} \quad (1)$$

where C is given in cm³ of gas (STP)/cm³ of polymer, p is the pressure at equilibrium in cm Hg, \bar{V} is the partial molar volume of the gas in the liquid state in cm³/mol, χ is the parameter that accounts for the gas–polymer enthalpic interaction, λ is the latent heat of vaporization at the boiling temperature T_b of the gas under one atmosphere of pressure, T is the working temperature, and R is the gas constant. The factor $\exp [(1 + 2\chi)C\bar{V}/22414]$ is practically equal to unity at low pressures and, as a consequence, eq. (1) suggests that in these conditions the concentration of gas in the polymer matrix is directly proportional to pressure. At high pressures, however, the exponential becomes important forcing the curve C versus p to be concave with respect to the ordinate axis. This behavior has been confirmed by sorption experiments of condensable gases in silicon elastomers,⁵ natural rubber, and natural rubber–cellulose composites.⁶

It is important to investigate the influence of the crystallinity degree on gas sorption processes in semicrystalline rubbery films. For this purpose, a thorough study was carried out focused on the variation of the measurements of the concentration of moderately condensable gases in low density polyethylene (LDPE) films with densities lying in the range 0.870–0.940 g/cm³. The solubility results are critical interpreted in terms of the Flory–Huggins theory of polymer concentrated solutions from which enthalpic parameters that account for polymer–gas interactions are obtained.

EXPERIMENTAL SECTION

Polyethylenes supplied by Dow (Tarragona, Spain), specifically, Dowlex 2740 E, Dowlex 2042 E, Dowlex

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2045 E, Attane SC-4106, Attane SC-4107, and Engage 8200, whose commercial densities are 0.940, 0.930, 0.920, 0.9115, 0.904, and 0.870 g/cm³, respectively, were used. LDPE films were prepared by compression molding between two heating plates at 200°C for 10 min. Then the films were cooled at room temperature. The acronyms for the films in decreasing order of crystallinity are, PE94, PE93, PE92, PE91, PE90, and PE87, respectively.

Sorption measurements were performed in an experimental device made up of two compartments, separated by a valve, immersed in a thermostat. One of the compartments, which acts as gas reservoir, is equipped with a pressure sensor of type Gometrics (0–35 bar), while the other compartment or sorption chamber contains a Ruska pressure sensor model 7230 (0–35 bar). Circular films 0.1 mm thick were placed in a perforated cylinder located inside the sorption chamber. To facilitate the sorption process each circular film was separated from the two neighbor ones by metallic grids. Both compartments were gas evacuated and then the pertinent gas at a given pressure was introduced into the reservoir. Once the gas reached the temperature of interest the valve separating the reservoir from the sorption chamber was suddenly opened and closed. The decrease of pressure in the sorption chamber by effect of the sorption process was recorded every second with a PC via the Ruska precision pressure indicator. After reaching the pressure a constant value, an additional amount of gas was introduced into the sorption chamber and then allowed to come again to equilibrium, and so on. The concentration of gas, in cm³ (STP)/cm³ of semicrystalline polymer, is given by

$$C = \frac{22414\rho V}{RTm} \left(\frac{p_i}{z_i} - \frac{p_e}{z_e} \right) \quad (2)$$

where m and ρ are, respectively, the mass and density of the polyethylene sample, V is the unoccupied volume of the sorption chamber, R and T are the gas constant and absolute temperature, and p and z are, respectively, the pressure and compressibility coefficient of the gas. The subscripts, i and e refer, respectively, to the initial and equilibrium conditions.

RESULTS AND DISCUSSION

The variation of the concentrations of carbon dioxide, ethylene and propylene with pressure in PE94, PE93, PE92, PE91, PE90, and PE87, at 303 K, is shown in Figures 1–3, respectively. The isotherms are straight lines at low pressures, but at moderate and high pressures the curves depart from linearity, clearly showing concavity towards the ordinates axis. It is worth noting that the higher the concavity, the lower the crystallinity. This behavior is in conso-

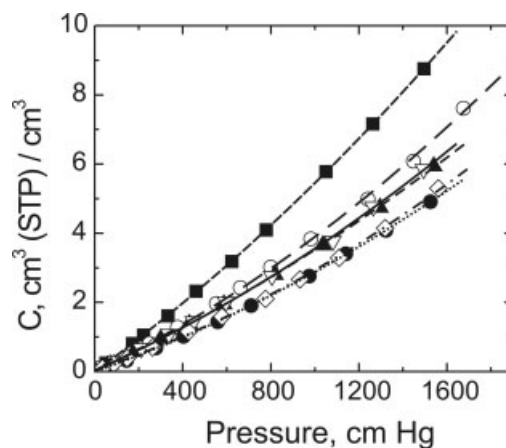


Figure 1 Changes in the concentration of carbon dioxide with pressure, at 30°C, in (■) PE87, (○) PE90, (▲) PE91, (▽) PE92, (●) PE93, and (◇) PE94 films.

nance with the insolubility of gases in crystalline entities. The concavity increases with increasing gas condensability so that the concentration isotherms for carbon dioxide and propylene only depart from Henry's behavior at high pressures. Departure from Henry's behavior is better detected if the concentrations of carbon dioxide and ethylene are plotted versus fugacity, instead of pressure (Fig. 4). If the sorption data are plotted in terms of the solubility coefficient, the resulting curves show a steady augment of the solubility coefficient S with pressure, even in the low pressure region. These results show that as far as gas solubility is concerned the behavior of semicrystalline rubbery films reminds that reported for rubbery polymers.

According to eq. (1), the solubility coefficient in rubbery polymers can be written as

$$S = \frac{22414}{76\bar{V}} \exp \left\{ \left[- (1 + \chi) - \frac{\lambda}{RT_b} \left(1 - \frac{T_b}{T} \right) \right] + \frac{(1 + 2\chi)C\bar{V}}{22414} \right\} \quad (3)$$

By taking into account that Henry's constant is given by

$$k_D = \lim_{p \rightarrow 0} S \quad (4)$$

Equations (3) and (4) lead to

$$k_D = \frac{22414}{76\bar{V}} \exp \left[- (1 + \chi) - \frac{\lambda}{RT_b} \left(1 - \frac{T_b}{T} \right) \right] \quad (5)$$

where k_D is given in cm³ of gas (STP)/(cm³ of amorphous polymer cm Hg) units. Values of the Henry's constant for different gases in different LDPE films are shown in the sixth column of Table I. However, taking into account that eq. (5) was deduced for

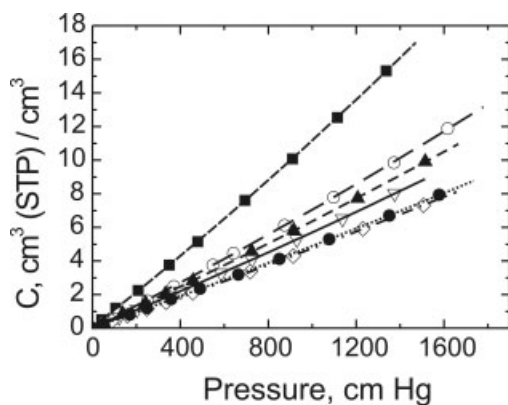


Figure 2 Variation of the concentration of ethylene with pressure, at 30°C, in LDPE films with different crystallinities. See Figure 1 for details.

totally amorphous polymers, the interpretation of the sorption processes in semicrystalline rubbery polymers requires to refer the values of k_D to 1 cm³ of amorphous polymer. To accomplish this goal, we have determined the fraction of the amorphous phase of polyethylene at 30°C from the following expressions given by Chiang and Flory⁹ for crystalline and amorphous polyethylene

$$v_l(T)_l = 1.152 + 8.8 \times 10^{-4}(T - 273.15) \quad (6)$$

and

$$v_c(T) = 0.993 + 3.0 \times 10^{-4}(T - 273.15) \quad (7)$$

where v is the specific volume and the subscripts l and c mean 100% amorphous and 100% crystalline polyethylene. By assuming additivity of volumes, the volume fraction of the amorphous phase of the samples ϕ_a can be obtained from the density in con-

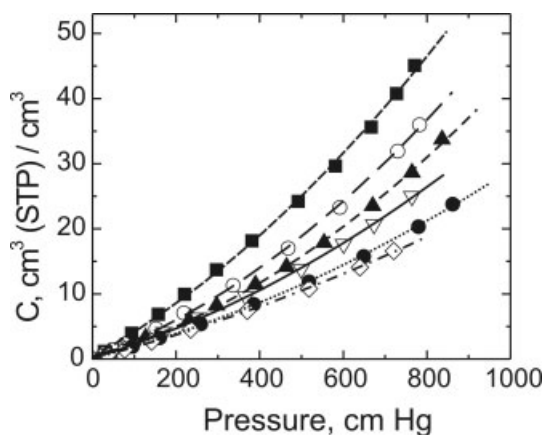


Figure 3 Pressure dependence of the concentration of propylene, at 30°C, in LDPE films with different crystallinities. See Figure 1 for details.

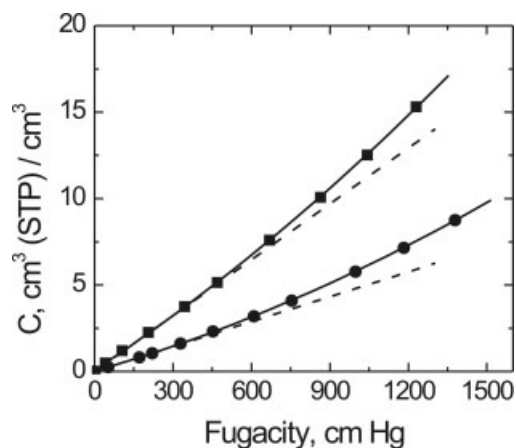


Figure 4 Variation of the concentration of ethylene (■) and carbon dioxide (●) in PE87 with fugacity.

junction with eqs. (6) and (7) by means of the following expression

$$\phi_a(T) = \frac{x(T)v_a(T)}{x(T)v_a(T) + [1 - x(T)]v_c(T)} \quad (8)$$

where

$$x(T) = \frac{v(T) - v_c(T)}{v_a(T) - v_c(T)} \quad (9)$$

The densities of PE94, PE93, PE92, PE91, PE90, and PE87 in g/cm³ units, obtained by picnometry at 30°C, are 0.941, 0.926, 0.920, 0.914, 0.902, and 0.879, respectively, while the expansion coefficients expressed in terms of $10^4 \times (1/v)(dv/dT)$ are 6.4, 5.9, 7.5, 9.1, 8.3, and 10.1 K⁻¹, respectively. The values of k_D/ϕ_a for propylene, ethylene and carbon dioxide are rather insensitive to the crystallinity of the samples. Actually, the average values of $10^3 \times k_D/\phi_a$ in the different films, at 30°C, are 49.4 ± 5.3 , 11.3 ± 1.3 , and 6.1 ± 0.9 cm³ (STP)/(cm³ amorphous polymer cm Hg), respectively, for propylene, ethylene, and carbon dioxide. Changes in crystallinity seem to have a negligible effect on the solubility of the gases in the amorphous phases of low density polyethylene and as a result crystalline-amorphous interfaces do not affect in the present case gas sorption processes.

The values of the Henry's constant referred to the totally amorphous polymers were used to determine the enthalpic polymer-gas interaction by means of eq. (5) At first glance, eq. (5) suggests that the higher the condensability of the gas, the higher k_D . However, $k_D(\text{ethylene}) > k_D(\text{CO}_2)$ in spite of $T_b(\text{CO}_2)$ being higher than $T_b(\text{C}_2\text{H}_4)$. By using the boiling temperature, latent heating of vaporization and the partial molar volume^{8,9} given for carbon dioxide, ethylene, and propylene in Table I, the values of the enthalpic parameter for these gases are 2.3, 1.1, and

TABLE I
Values of the Henry Constants Referred to λ cm³ of Semicrystalline Polymer, k_D , and to λ cm³ of the Amorphous Phase, k_D/ϕ

Gas	λ (kcal/mol) ^a	T_b (K) ^a	\bar{V} (cm ³ /mol) ^b	Polymer	$10^3 \times k_D$ (cm ³ /cm ³ cm Hg)	$10^3 \times k_D/\phi_a$ (cm ³ /cm ³ cm Hg)	χ
CO ₂	4.112	194.7	46	PE87	5.76	7.23	2.0
				PE90	3.34	5.18	2.3
				PE91	3.19	5.67	2.2
				PE92	3.22	6.16	2.2
				PE93	2.47	5.15	2.3
				PE94	2.69	6.93	2.0
C ₂ H ₄	3.23	169.5	49.3	PE87	10.81	13.56	0.9
				PE90	6.86	10.64	1.1
				PE91	6.16	10.94	1.1
				PE92	5.52	10.56	1.1
				PE93	4.81	10.02	1.2
				PE94	4.63	11.92	1.0
C ₃ H ₆	3.32	225.5	69.09	PE87	47.31	59.34	1.4
				PE90	31.69	49.16	1.6
				PE91	26.77	47.55	1.6
				PE92	24.48	46.82	1.6
				PE93	20.57	42.86	1.7
				PE94	19.64	50.58	1.5

λ , latent heat of vaporization of gases in the liquid state; T_b , boiling temperatures at 1 atm; \bar{V} , molar volume in the liquid state; χ , gas (in the liquid state)–polymer interaction enthalpic parameter.

^a Ref. 7.

^b Ref. 8.

1.6, respectively. Accordingly, propylene is less compatible with polyethylene than ethylene. Moreover carbon dioxide is less soluble in polyethylene than ethylene in spite of higher T_b presumably due to unfavorable carbon dioxide quadrupoles–polyethylene interactions.

The effect of temperature on gas sorption was investigated by measuring the concentration of carbon dioxide and propylene, as a function of pressure and at different temperatures, in the two LDPE films

with extreme densities: PE87 and PE94. The concavity of the sorption isotherms towards the ordinate axis decreases as temperature increases. Values of Henry's constant are given in Table II. The natural logarithm of the solubility Henry's constant of carbon dioxide and propylene in PE87 and PE94 films are plotted against the reciprocal of the absolute temperature in Figure 5. The good straight lines obtained indicate that the Henry's constant obeys Arrhenius behavior. The sorption heats associated with the Henry's solubility of propylene in PE87 and PE94 films are -4.0 and -4.6 kcal/mol, respectively.

TABLE II
Values of the Henry's Constants of Carbon Dioxide and Propylene in PE87 and PE94 as a Function of the Temperature in Sorption Processes

Polymer	Gas	T (K)	$k_D \times 10^3$ (cm ³ /cm ³ cm Hg)
PE87	CO ₂	303	5.76
		313	4.98
		323	4.33
	C ₃ H ₆	333	3.66
		303	47.31
		313	36.90
PE94	CO ₂	323	29.99
		333	26.23
		275	4.20
	C ₃ H ₆	293	2.87
		303	2.69
		313	2.23
PE94	C ₃ H ₆	275	42.01
		293	24.09
		303	19.64
		313	15.07

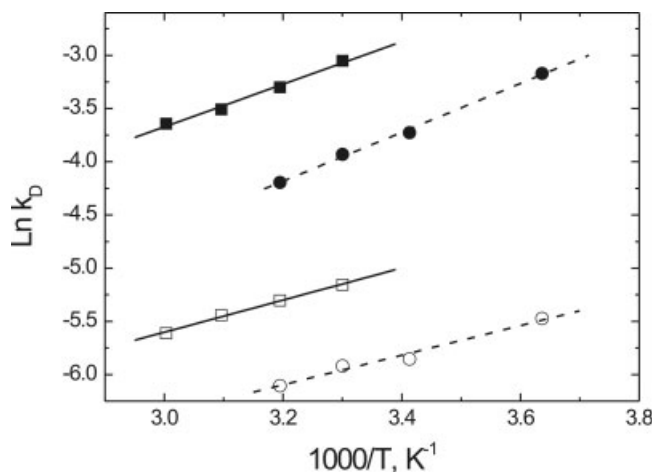


Figure 5 Arrhenius plots for the Henry's constant of propylene (filled symbols) and carbon dioxide (open symbols) in PE87 (squares) and PE94 (circles).

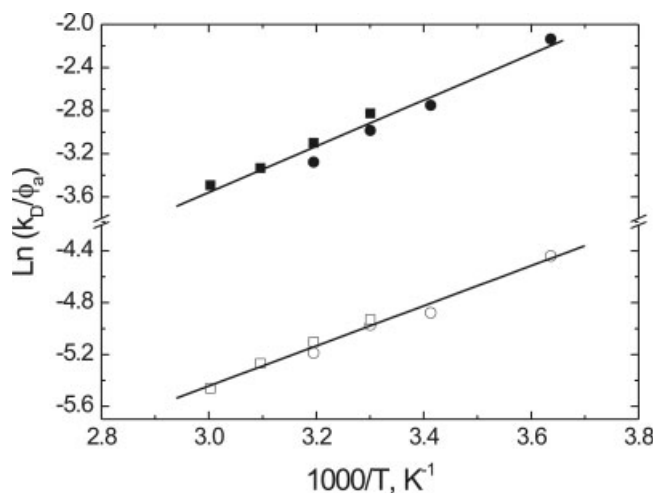


Figure 6 Arrhenius plots for k_D/ϕ_a of propylene (filled symbols) and carbon dioxide (open symbols) in PE87 (squares) and PE94 (circles).

For CO_2 these values amount to -3.0 and -2.8 kcal/mol, respectively. It is worth noting that the sorption heats are dependent on the chemical nature of the gases, but they are only slightly dependent on the crystallinity degree of the films. Therefore, the pre-factor of the Arrhenius equation, rather than the activation energy, is responsible for the differences observed for the Henry's constant of each gas in different films. By interpreting the results in terms of activated processes, the absolute value of the decrease of activated entropy associated with gas sorption increases with crystallinity. Arrhenius plots for $k_D(T)/\phi_a(T)$ of carbon dioxide and propylene in PE87 and PE94 are shown in Figure 6. As expected, the results for each gas in the two films lie nearly in the same straight line, as a consequence of the fact that the solubility of the gases in the amorphous regions is not affected by the crystallinity of the LDPE films. The values of the sorption heats obtained from the combined plots for carbon dioxide

and propylene are -3.10 and -4.28 kcal/mol, respectively, in good concordance with those obtained from k_D .

CONCLUSIONS

The Henry's solubility constant referred to 1 cm^3 of the amorphous phase of the semicrystalline polymer is independent on the degree of crystallinity of LDPE films. The pressure dependence of the solubility constant is concave with respect to the ordinate axis, as occurs for rubbery polymers.

Unfavorable polymer-carbon dioxide interactions presumably arising from the polar nature of this molecule are responsible for the fact that carbon dioxide is less soluble in polyethylene than ethylene in spite of having higher condensability.

The analysis of gas sorption in terms of the polymer-solutions Flory-Huggins theory gives reasonable values for gas-polymer enthalpic interactions.

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