

Gas Solubility of Carbon Dioxide in Poly(lactic acid) at High Pressures

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ABSTRACT: The sorption of carbon dioxide in poly(lactic acid) (PLA) was studied by quartz crystal microbalance at high pressures. To address the effect of the D isomer present in the polymer on the gas sorption, measurements were performed in PLA with two different L:D contents, 80:20 and 98:2. New data for the solubility of carbon dioxide in PLA 80:20 and PLA 98:2 over a temperature range from 303.2 to 323.2 K and up to 5 MPa are presented. The results obtained were correlated with the dual-mode sorption model and the Flory-Huggins equation. ©2006 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 44: 1010–1019, 2006

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INTRODUCTION

Up till now, petrochemical products have been the main driving force of the world's economy, playing a dominant role in world development as an energy source, polymer production, and many other products. However, they have a huge environmental impact. Among others, the use of petroleum-based nondegradable polymers for short-term applications, such as food packaging, led to the exhaustion of the municipal landfills. In the industrialized EU nations, they represent about 20–40% of the municipal waste.¹ In addition, their disposal by incineration produces toxic gases and contributes to the global warming. The replacement of nondegradable polymers in

short-term applications can provide a significant step toward a greener planet. As an alternative, biodegradable polymers made of renewable sources have been studied to replace the conventional polymers in food packaging. Polymeric foams based on conventional polymers are used in food packaging, and their substitution by biodegradable polymeric foams would cause an enormous impact in the biodegradability of food packaging. Since the production of CFC's has been prohibited, new environmentally benign alternative blowing agents such as carbon dioxide and nitrogen have been considered. To optimize the industrial foaming process it is important to study the solubility and diffusivity of these gases in the new biodegradable polymers.

In this work, we studied the solubility of carbon dioxide in PLA and evaluated the influence of the content of D isomer in the polymer on the gas solubility by performing measurements on samples with two different L:D content, 80:20

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and 98:2. The experiments were performed between 303.2 and 323.2 K and up to 5 MPa.

EXPERIMENTAL

Quartz crystal microbalance (QCM) is based on the piezoelectric effect observed in an AT-cut quartz crystal. The quartz crystal has golden electrode plates on both sides, creating a perpendicular electrical field between them. The effect of the electrical field produces a stationary wave. The frequency of the wave is a function of the crystal mass, and so a frequency change, ΔF , can be related to a mass change, Δm , according to the Sauerbrey equation²:

$$\Delta F = -k \Delta m \quad (1)$$

where k is a proportionality constant that includes physical and geometrical properties of the crystal. Two quartz crystals are usually used: a working crystal coated with a thin layer of the polymer under study, and an uncoated crystal used as the reference. It is assumed that this coated mass is uniformly spread and vibrates synchronously with the quartz crystal. When gas, or solvent, is injected into the system the frequencies of both crystals change. This frequency change, ΔF_E , is a sum of three independent terms, sorption ΔF_S , hydrostatic ΔF_P , and impedance ΔF_V ³:

$$\Delta F_E = \Delta F_S + \Delta F_P + \Delta F_V \quad (2)$$

ΔF_P is proportional to the pressure, while ΔF_V is a function of the properties of the gas (viscosity and density) and of the crystal (base frequency, thickness, and density). Each term can be represented by

$$\Delta F_P = F_0 \alpha P \quad (3)$$

$$\Delta F_V = - \left(\frac{F_0}{2\rho_q t_q} \right) \left(\frac{\rho\mu}{\pi F_0} \right)^{1/2} \quad (4)$$

$$\Delta F_S = -2.26 \times 10^{-7} F_0^2 \Delta m \quad (5)$$

where F_0 is the base frequency; α , the proportionality constant; ρ_q , and t_q , crystal density and thickness, respectively; ρ and μ , the medium density and viscosity, respectively; $2.26 \times 10^{-7} F_0^2$, the value of the proportionality constant, k ; and Δm is the sorbed mass.⁴ The terms, ΔF_P and

ΔF_V , were measured together using a reference crystal and ΔF_S was measured using a polymer coated crystal. The difference between the frequency change of the polymer coated crystal, ΔF_E , and the frequency change of the reference crystal, $\Delta F_{P,V}$, gives the frequency change of the gas sorption, ΔF_S . In this work, the gas solubility is expressed as the volume of gas at standard temperature and pressure (STP) per volume of polymer. As the gas molar volume at STP is $22,414 \text{ cm}^3 \text{ mol}^{-1}$ and considering the eq 1, the gas volume is given by

$$V_{\text{gas}}(\text{STP}) = \frac{-\Delta F_S/k}{M_{\text{gas}}} \quad (6)$$

where M_{gas} is the gas molecular weight. Using again eq 1, the volume of polymer can be calculated by

$$V_{\text{pol}} = \frac{-\Delta F_C/k}{\rho_{\text{pol}}} \quad (7)$$

where ρ_{pol} is the polymer density and ΔF_C is the difference between the resonance frequency (base frequency) of the uncoated and coated with polymer crystal in vacuum. Assuming that the differences in the properties of the crystal are negligible before and after sorption, the proportionality constants, k , in eqs 6 and 7 are the same and the gas solubility in polymer, C , can be calculated by

$$C = \frac{\Delta F_S \rho_{\text{pol}}}{\Delta F_C M_{\text{gas}}} \times 22.414 \quad (8)$$

MODELING

Dual-Mode Sorption Model

The dual-mode sorption model assumes that two types of sorption mechanisms take place when a fluid interacts with a glassy polymer: one is described by a Henry's law type of sorption and the other by a Langmuir type of sorption, which accounts for the solute molecules trapped in microcavities. These two types of sorptions are typically assumed to occur in nonequilibrium glassy polymers consisting of two parts, a liquid state one, where sorption described by the Henry's law behavior takes place, and a solid state one, with the Langmuir type of sorption in

Table 1. Characteristics of the Polymers Used in This Work

Polymer	Trade Name	T_g (K)	Polydispersity	M_w
Polystyrene	Lacqrene Cristal 1450 N	378	2.7	190,000
PLA 80:20		324.6	1.46	102,800
PLA 98:2		332.7		871,31

T_g , glass transition temperature; M_w , weight-average molecular weight.

porous materials. The dual mode sorption model is described by

$$C = k_D p + C'_H \frac{bp}{1 + bp} \quad (9)$$

where C is the total concentration of the gas in the polymer film; k_D , the Henry's law coefficient; b represents the hole affinity parameter, which is a measure of the affinity between the solute molecules and the Langmuir sites; C'_H , the capacity parameter, characterizing the saturation of these cavities; and p is the pressure. This model has been extensively used to model the gas solubilities in polymers and the obtained results have been reviewed recently.⁵

Flory-Huggins Equation

The Flory-Huggins equation has been thoroughly described in the literature⁶⁻⁹ and widely used to correlate experimental data of solubility

of gases in polymers. This model considers that the activity coefficient results from entropic rather than enthalpic effects. The mixture entropy is calculated from the lattice theory, where each molecule occupies a number of sites proportional to its molecular volume. The mixture enthalpy is described by a binary interaction parameter, χ_{12} , which is used to correlate the experimental results. The Flory-Huggins equation can be written as

$$\ln(a_1) = \ln(\phi_1) + \left(1 - \frac{1}{r}\right) \phi_2 + \chi_{12} \phi_2^2 \quad (10)$$

$$r = \frac{v_2 M_2}{v_1 M_1} \quad (11)$$

$$\phi_1 = \frac{v_1 w_1}{v_1 w_1 + v_2 w_2} \quad \text{and} \quad \phi_2 = 1 - \phi_1 \quad (12)$$

where a_1 is the penetrant activity; w_i , the mass fraction of each component i ; r , the number of

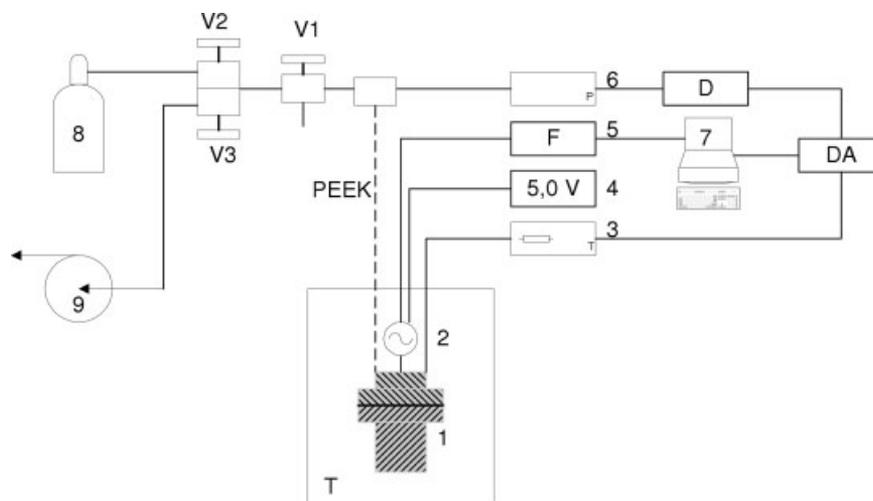


Figure 1. The high-pressure QCM apparatus: 1, solubility cell; 2, oscillator; 3, multimeter for Pt100; 4, power supply for oscillator; 5, frequency counter; 6, pressure transducer; 7, computer; 8, gas bottle; 9, vacuum pump; T, air bath (oven); D, digital display of the pressure transducer; DA, data acquisition system; V1, V2, and V3 are high pressure valves.

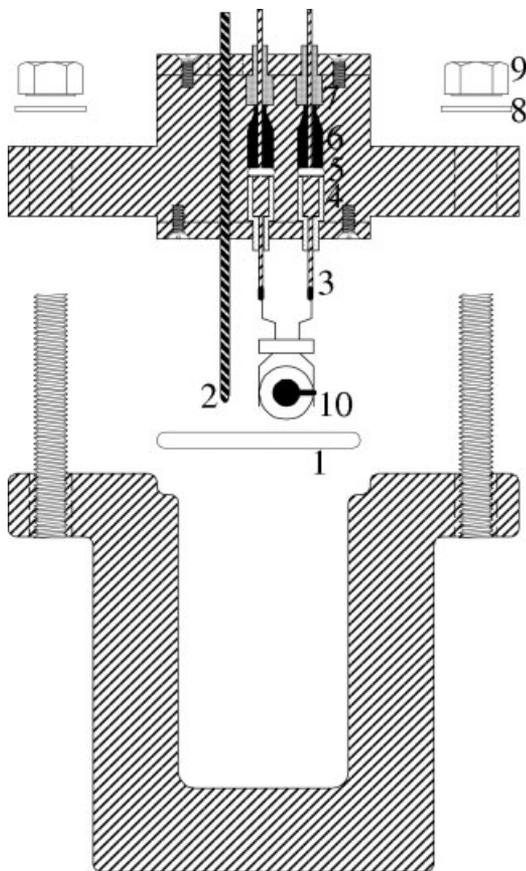


Figure 2. The solubility cell: 1, Teflon O'ring; 2, Stainless steel tube for Pt100 sensor; 3, connection system between crystal and oscillator; 4, sealing inferior part; 5, O'ring; 6, ceramic part; 7, sealing superior part; 8, back up ring; 9, Hex Nut; 10, quartz crystal.

segments in the polymer molecule; M_1 , molecular weight of penetrant; and M_2 is the average molecular weight of polymer. The measured penetrant activity is obtained from

$$a_1 = \frac{p}{p^{\text{sat}}} \frac{\varphi_1}{\varphi_1^{\text{sat}} FP} \quad (13)$$

where p is the system pressure; p^{sat} , the saturation pressure at system temperature; φ_1 , the fugacity coefficient of penetrant; φ_1^{sat} , the fugacity coefficient at saturation conditions; and FP is the Poynting factor.

Extended Flory-Huggins Equation

According to Qian et al.^{10,11} the binary interaction parameter in the classical Flory-Huggins equation can be considered temperature and concentration dependent, that is, $\chi_{12} = \chi_{12}(T, \phi_2)$.

The two effects can be separated and so the binary interaction parameter can be written as a product of a concentration function, $B(\phi_2)$, and a temperature function, $D(T)$:

$$\chi_{12}(T, \phi_2) = D(T)B(\phi_2) \quad (14)$$

where the following forms were proposed for $B(\phi_2)$ and $D(T)$

$$B(\phi_2) = 1 + b_1\phi_2 + b_2\phi_2^2 \quad (15)$$

$$D(T) = d_0 + \frac{d_1}{T} + d_2 \ln(T) \quad (16)$$

b_i and d_i are adjusted to the experimental data.

MATERIALS AND CHARACTERIZATION METHODS

The new high-pressure apparatus developed on this work was tested using atactic polystyrene from Atofina. The biodegradable polymer, poly(lactic acid) (PLA), was produced by Cargill-Dow Polymers with two different L:D contents, 80:20 and 98:2. The characteristics of PS and PLA were given by suppliers and they are reported in Table 1. Carbon dioxide was purchased from Messer (Germany) with a purity of 99.998%. Dichloromethane was obtained from Riedel-deHaan (Germany) with analytical reagent grade. Solvent and gases were used with no further purification. The quartz crystals were of 9 MHz base frequency with golden electrodes of 5 mm, and were supplied by ICM, USA.

A differential scanning calorimeter, DSC-50/DTA-50 from Shimadzu, was used to measure the glass transition temperature and the melting temperature of PLA. The crystallinity of the polymer films was estimated from the DSC results and X-Ray diffraction tests performed in a Philips X'Pert automatic X-ray diffractometer with 2θ from 6° and 33° .

Table 2. DSC Results of PLA Films with Different L:D Ratio

L:D	T_g (K)	T_c (K)	T_m (K)	χ (%)
98:2	323.5	369.4	435.3	20
80:20	323.4	—	—	0

T_g , glass transition temperature; T_c , crystallization temperature; T_m , melting temperature; χ , percentage crystallinity.

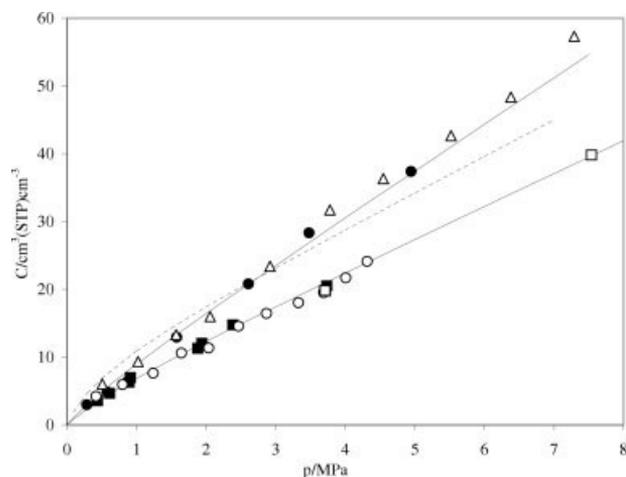


Figure 3. Solubility of carbon dioxide in atactic polystyrene at 337.8 (■) and 307.5 K (●) measured with QCM at high pressures and comparison with literature: Wissinger and Paulaitis¹⁴ at 308 K (△) and 338 K (○); Paterson and Yampol'skii¹⁵ at 308 K (----); Hilic et al.¹⁶ at 338 K (□). The solid lines are the correlation of the dual-mode sorption model to the experimental results.

Apparatus Description

A simplified scheme of the experimental arrangement used to measure the sorption isotherms of CO₂ in PLA is shown in Figure 1. The apparatus consists mainly of a high-pressure cell schematically presented in Figure 2. This cell is a cylindrical autoclave made of nonmagnetic stainless steel. It is closed by a plug in which five holes have been made for the electric connections to the quartz crystal to pass through. The electrical connections under pressure were set up according to the method recommended by Bridgman.¹² A sixth hole was made to allow the passage of a temperature probe housed in a metal finger, to isolate it from pressure stress. Finally a seventh hole was machined in the plug for the gas inlet and for the pressure measurement. A viton O-ring was used to seal the plug to the body of the cell. The plug

Table 3. Dual-Mode Sorption Model Parameters for Carbon Dioxide in Polystyrene

T (K)	k_D (cm ³ (STP) cm ⁻³ bar ⁻¹)	C'_H (cm ³ (STP) cm ⁻³)	b (bar ⁻¹)	AAD (%)
307.4	0.681	3.953	0.122	4
337.8	0.481	3.835	0.118	3.6

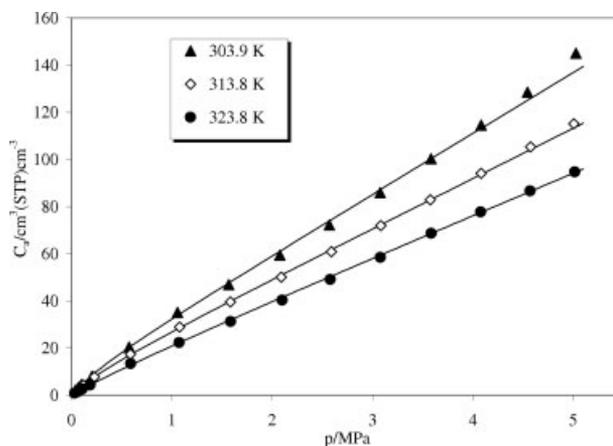


Figure 4. Solubility of carbon dioxide in Poly(lactic acid) with L:D content of 98:2 correlated with dual-mode Sorption Model.

was also used to hold two piezoelectric quartz crystals. One of them acted as a reference and the other as a working crystal. These elements consist of two similar AT-cut quartz crystals of circular section with golden electrodes on both sides. The crystals are excited by pulse trains of duration 2.0 ± 0.2 ns, pulse repetition frequency of 2.0 MHz by means of a Motorola chip, model MC12061, incorporated in home-made oscillators fixed on the outside of the plug. The resonant frequencies around the nominal frequency of 9.0 MHz were measured for both quartz crystals using a 10 digits frequency counter (Agilent 53131A) connected to a computer for recording. The geometric characteristics chosen for this cell offer a useful internal volume of 36.58 cm³ and

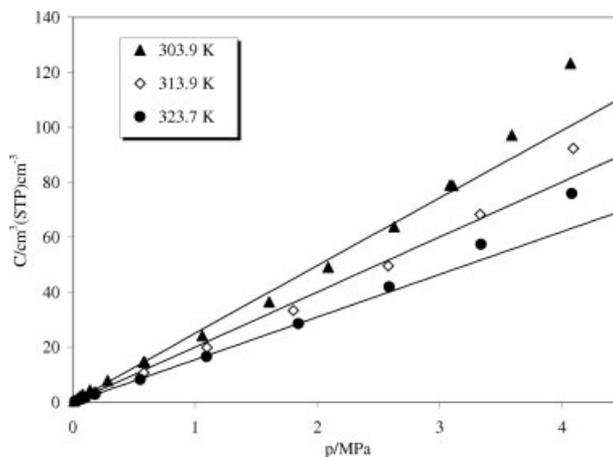


Figure 5. Solubility of carbon dioxide in poly(lactic acid) with L:D content of 80:20 correlated with dual-mode Sorption Model.

Table 4. Experimental Results for Carbon Dioxide Solubility in PLA 98:2

T (K)	P (MPa)	C (cm ³ (STP) cm ⁻³)	C_a (cm ³ (STP) cm ⁻³)	
303.9	0.038	1.39	1.74	
	0.042	1.70	2.12	
	0.065	2.33	2.92	
	0.066	2.38	2.97	
	0.068	2.19	2.74	
	0.080	2.93	3.66	
	0.103	3.65	4.56	
	0.207	6.45	8.06	
	0.576	16.40	20.50	
	1.057	28.07	35.09	
	1.566	37.55	46.94	
	2.076	47.50	59.38	
	2.572	57.73	72.16	
	3.076	68.75	85.94	
	3.584	80.23	100.29	
	4.082	91.60	114.50	
	4.544	102.75	128.44	
	5.029	115.98	144.97	
	313.8	0.036	1.19	1.49
		0.065	2.03	2.54
0.081		2.50	3.13	
0.120		3.48	4.35	
0.230		6.19	7.74	
0.588		13.88	17.35	
1.077		23.14	28.93	
1.584		31.70	39.62	
2.091		40.07	50.09	
2.591		48.75	60.93	
3.083		57.52	71.90	
3.578		66.29	82.87	
4.083		75.27	94.08	
4.576		84.30	105.37	
5.007		92.05	115.06	
323.8	0.035	0.65	0.81	
	0.070	1.31	1.63	
	0.087	1.62	2.02	
	0.111	2.05	2.57	
	0.187	3.48	4.35	
	0.592	10.72	13.40	
	1.074	17.90	22.37	
	1.589	24.97	31.21	
	2.100	32.27	40.34	
	2.582	39.29	49.11	
	3.080	46.74	58.43	
	3.587	54.89	68.61	
	4.080	62.16	77.70	
	4.572	69.32	86.64	
	5.016	75.72	94.64	

make it possible to carry out measurements at pressures up to 50 MPa over a temperature range of between 303 and 373 K. This temperature

range was chosen according to the operating limits of the transducers.

To avoid any electric interference during measurements, the vessel was thermoregulated by air instead of liquid. For this purpose, the cell was placed into a temperature-controlled air oven that controls and maintains the desired temperature within ± 0.1 K. The temperature was measured through a platinum probe (Pt100) placed inside the cell at 1 cm of both quartz crystals and connected to an Agilent 34401A multimeter. This platinum resistance is care-

Table 5. Experimental Results for Carbon Dioxide Solubility in PLA 80:20

T (K)	P (MPa)	C (cm ³ (STP) cm ⁻³)
303.9	0.01	0.44
	0.039	1.51
	0.061	2.22
	0.081	2.83
	0.14	4.45
	0.286	7.97
	0.579	14.59
	0.588	14.72
	1.058	24.3
	1.606	36.51
	2.088	49.13
	2.628	63.86
	3.085	78.98
	3.106	78.81
	3.588	97.16
4.069	123.35	
313.9	0.022	0.53
	0.049	1.13
	0.07	1.57
	0.097	2.09
	0.182	3.78
	0.582	11.07
	1.098	20.57
	1.802	34.52
	2.579	51.2
	3.328	70.54
4.092	95.31	
323.7	0.021	0.34
	0.047	0.78
	0.072	1.16
	0.104	1.67
	0.183	2.94
	0.553	8.65
	1.095	17.19
	1.845	29.78
	2.586	43.59
	3.337	59.67
4.08	78.91	

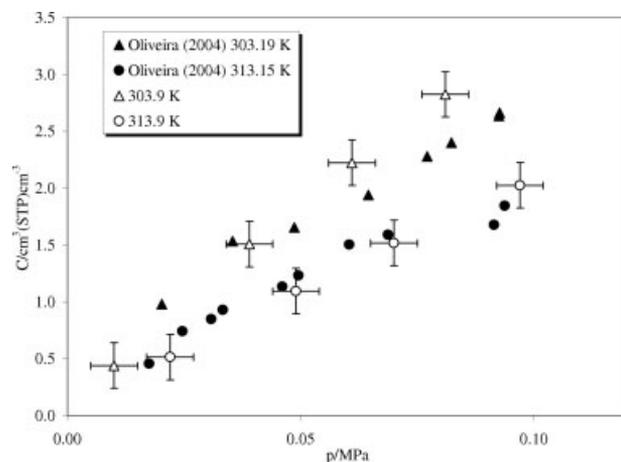


Figure 6. Comparison of low-pressure carbon dioxide solubility results in PLA 80:20 obtained in this work with literature results by Oliveira et al.¹⁸

fully and periodically calibrated against a precision thermometer accurate to 0.1 K.

To reduce electrostatic noise the solubility cell was connected to the pressure line without any electric contact by using a PEEK tube closed by a double valve. One outlet of this valve permits to control the vacuum, whereas the other is used for gas injection. The pressure is measured directly on the gas line with a pressure transducer from Setra, Model 204, with a precision of 0.005 MPa. Calibration of the probe certified per NIST traceable primary standards. Primary standard is DHI Model PPC3-2M No. 144, NIST# 821/265025-01 on 22 of June of 2004, with an accuracy in pressure better than 0.2%.

The pressure transducer and the multimeter for temperature recording are connected to a data acquisition Agilent 34970A with the multiplexer of 16 channels from Agilent, model 34902A. The data acquisition instrument, the multimeter and the frequency meter are connected to a computer for data recording.

Quartz Crystal Coating

The 9 MHz crystals were thoroughly cleaned with dichloromethane until the base frequency became constant (less than 1 Hz in 10 min). A thin polymer coating is prepared by dropping a dilute solution of polymer in dichloromethane, about 0.5% (w/w) on both sides of the quartz crystal electrode surface. The polymer coated on the crystal was subjected to a temperature treatment, placing it in an oven at 336.2 K (slightly above the glass transition temperature) for 2 days, cooled at ambient temperature for 1 day, and placed again in the oven at 336.2 K for one more day. The total mass of polymer coated on the quartz crystal can be determined by the difference in the oscillation frequency measured before and after coating.

RESULTS AND DISCUSSION

Film Characterization

The PLA films were characterized with DSC and X-ray diffraction. All the measurements in DSC were performed up to 473.2 K at 2 K/min with two complete scans. The first scan is used to measure the crystallization percentage, considering 93.6 J/g for 100% crystalline L-PLA,¹³ and the second scan is used to calculate the glass transition temperature without polymer stress. The DSC results for both PLA 80:20 and 98:2 films after the above described temperature treatment are presented in Table 2. It can be seen that the thermal treatment does not influence the T_g but the content of L and D isomers strongly influences the polymer crystallinity.

The results obtained by X-ray diffraction were performed at ambient temperature with 2θ between 5° and 30° , 3 s per step and 0.05° step width. The crystalline peaks were obtained at

Table 6. Dual-Mode Sorption Model Parameters for Carbon Dioxide in PLA

	Polymer					
	PLA 98:2			PLA 80:20		
T (K)	303.9	313.8	323.8	303.9	313.9	323.7
k_D (cm^3 (STP) cm^{-3} bar^{-1})	2.57	2.12	1.78	2.44	2.11	1.61
C'_H (cm^3 (STP) cm^{-3})	9.16	7.90	5.79	1.80	1.60	1.39
b (bar^{-1})	0.26	0.25	0.11	0.06	0.01	0.001
$C'_H b$ (cm^3 (STP) cm^{-3} bar^{-1})	2.355	1.956	0.623	0.110	0.020	0.001
AAD (%)	2.2	0.8	1.4	7.4	6.9	4.7

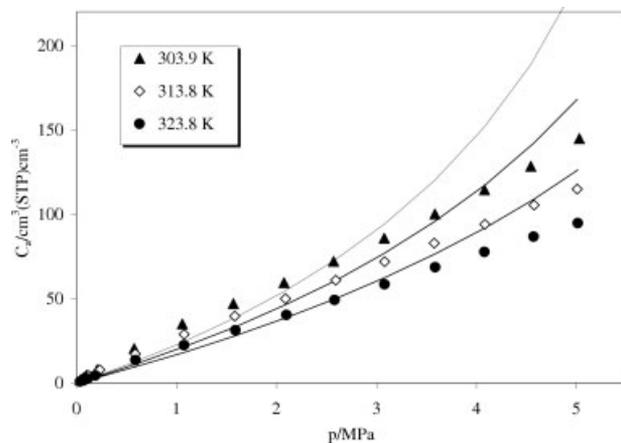


Figure 7. Correlation of the solubility of carbon dioxide in poly(lactic acid) with L:D content of 98:2 with Flory-Huggins Model.

16.6° and 18.7°. The results for PLA 98:2 films obtained by the X-ray diffraction confirm that the crystallization level is about 20% (v/v), confirming the results obtained by DSC.

Solubility Results

In Figure 3, the solubility results of carbon dioxide in atactic polystyrene at two temperatures, 307.5 and 337.8 K and pressures up to 5 MPa are presented and compared with literature. The results obtained are in good agreement with the literature showing an average absolute deviation (AAD) around 8% at 308 K^{14,15} and 3.3% at 338 K.^{14,16} The experimental data were correlated with dual-mode sorption model with an AAD of 4.0% at 307.5 K and 3.6% at 337.8 K.

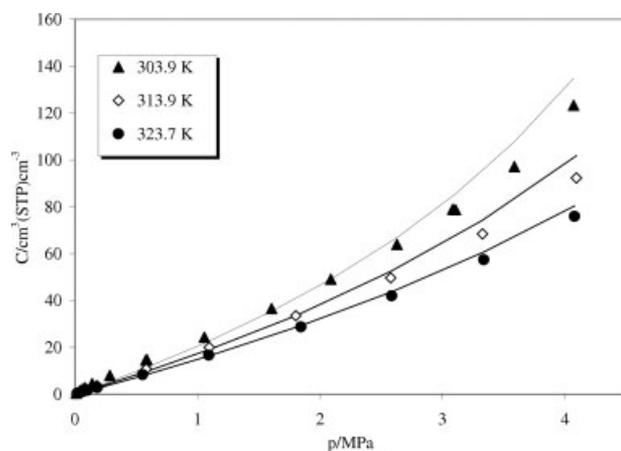


Figure 8. Correlation of the solubility of carbon dioxide in poly(lactic acid) with L:D content of 80:20 with Flory-Huggins Model.

Table 7. Flory–Huggins Parameters for Both Systems Studied in this Work

	Polymer					
	PLA 98:2		PLA 80:20			
T (K)	303.9	313.8	323.8	303.9	313.9	323.7
χ	0.06	0.00	-0.01	0.15	0.06	0.03
AAD (%)	31.1	25.7	18.5	14.6	10.1	7.1

The dual-mode sorption model parameters are presented in Table 3.

The solubility of carbon dioxide in PLA with L:D content of 80:20 and 98:2 was measured along three isotherms, 303, 313, and 323 K and up to 5 MPa. These results are represented in Figures 4 and 5 and tabulated in Tables 4 and 5, respectively. According to the DSC and the X-ray diffraction studies, PLA 80:20 does not crystallize while PLA 98:2 is semicrystalline, with around 20% of crystallinity. Considering that the crystalline regions do not accommodate any CO₂, the solubility of the CO₂ in the amorphous phase of PLA, C_a , can be calculated by

$$C_a = \frac{C}{\theta_a} \quad (17)$$

where C is the measured solubility in the semicrystalline polymer and θ_a is the amorphous volume fraction of the polymer.¹⁷ Thus, the solubility results for PLA 98:2 in amorphous phase were corrected for an amorphous volume fraction of polymer of 80%. The CO₂ solubility

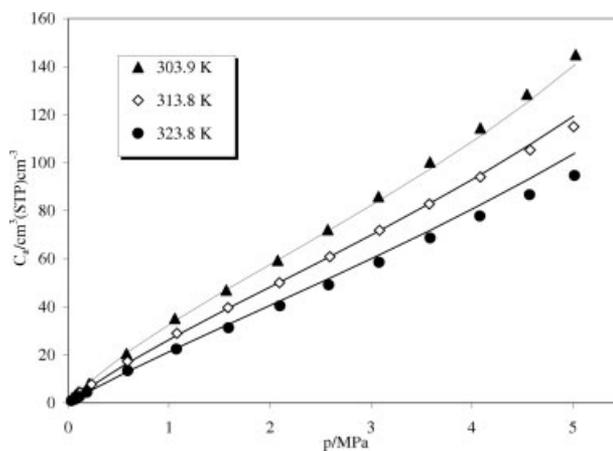


Figure 9. Solubility of carbon dioxide in poly(lactic acid) with L:D content of 98:2 correlated with an extended Flory-Huggins equation.

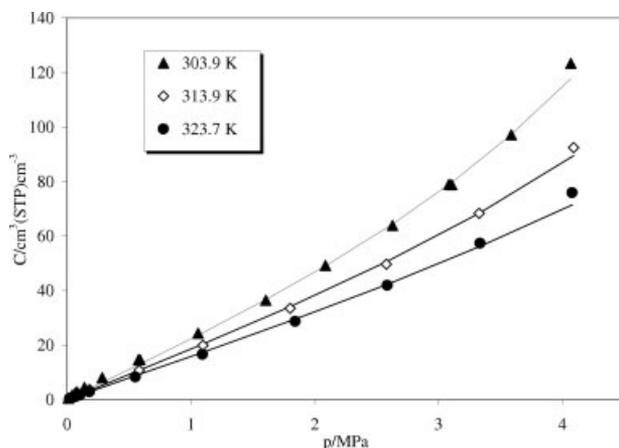


Figure 10. Solubility of carbon dioxide in poly(lactic acid) with L:D content of 80:20 correlated with an extended Flory-Huggins equation.

results obtained for PLA 80:20 with high pressure QCM were compared with results previously obtained with a low pressure QCM in Figure 6.¹⁸ The results show an agreement within the experimental uncertainty of the method at high pressure, about $0.2 \text{ cm}^3(\text{STP})\text{cm}^{-3}$ for gas solubility. The solubility of carbon dioxide in both polymers show the same trend, increasing with pressure and decreasing with temperature. However, for pressures higher than 2 MPa the solubility in PLA 80:20 is larger than in PLA 98:2, for the same pressure and temperature conditions. It was only possible to measure the solubility in PLA 80:20 up to 4 MPa, since after that the crystal stops vibrating. A probable explanation for this fact is the presence of swelling in PLA 80:20, which is also corroborated by the convex shape of the isotherms. For PLA 98:2, measurements were performed up to 5 MPa and the isotherms show a linear behavior. The possible explanation for this behavior is the presence

of crystallites in PLA 98:2 can restrict the chain mobility in the amorphous phase, acting as virtual crosslinks, thus reducing the volume that can be used for the penetrant to make a diffusional jump and also avoiding the swelling. The different behaviors of the solubility of CO_2 in PLA 80:20 and 98:2 are well illustrated by the correlation factors of the experimental data with the dual-mode sorption, where the overall AADs were of 1.5% for PLA 98:2 and 6.3% for PLA 80:20. The lines in Figures 4 and 5 represent the dual-mode sorption model and the respective parameters are in Table 6. As it was expected from the previous analysis of the experimental data the model performs extremely well for PLA 98:2, while large deviations are found for PLA 80:20 due to convex shape of the isotherms. Sensitivity analysis of the three parameters of the dual mode sorption mode clearly indicates the coupling of C_H and b terms. So $C'_H b$ product, which is often called the apparent Langmuir capacity, is also reported in Table 6. The apparent Langmuir capacity is very large in PLA 98:2 while in PLA 80:20 it is almost negligible. This is probably due to a more complex structure that is formed when crystallites are present, creating a larger free volume. Also, the apparent Langmuir capacity diminishes as temperature approaches the glass transition temperature. This observation is consistent with the fact that the Langmuir capacity is directly related to the effective free volume that tends to zero at T_g . These results show that the different content of L:D isomers in PLA does influence not only the solubility but also the solubility mechanism.

Since the dual mode sorption model cannot accurately describe the solubility of CO_2 in PLA 80:20, the Flory-Huggins equation was also used to correlate the experimental data. The correla-

Table 8. Extended Flory-Huggins Parameters

	Polymer					
	PLA 98:2			PLA 80:20		
T (K)	303.9	313.8	323.8	303.9	313.9	323.7
d_0	24.77			-3.81		
d_1	1.54			151.04		
d_2	-4.23			0.58		
b_1	3.69			-76.46		
b_2	-5.99			78.60		
AAD (%)	2.1	3.0	4.6	4.6	3.6	2.3

tion results are represented in Figures 7 and 8 for PLA 98:2 and PLA 80:20, respectively. Below the critical temperature of carbon dioxide, the specific volumes were calculated at experimental temperature and above the critical temperature the specific volumes were set equal to the one at 304 K. The binary interaction parameters for each temperature for both systems are tabulated in Table 7. The overall AAD is about 25% for PLA 98:2 and 11% for PLA 80:20, meaning that the Flory-Huggins model can not capture the behavior of these systems.

Qian et al.^{10,11} suggested a simple extension to the Flory-Huggins equation, assuming that the binary interaction is a function of temperature and concentration. The correlation results obtained using this method are represented in Figures 9 and 10 for PLA 98:2 and PLA 80:20, respectively, and the adjustable parameters are tabulated in Table 8. The overall AAD is about 3.3% for PLA 98:2 and 3.5% for PLA 80:20. The extended Flory-Huggins equation is in fact the model that correlates more satisfactorily the experimental CO₂ solubility data for PLA 80:20, especially at high pressures and temperatures. On the other hand, the dual mode sorption model is the most accurate model for the CO₂ solubility in PLA 98:2.

CONCLUSIONS

A QCM for measuring solubilities of gases at high pressure in polymers was constructed. The apparatus was tested with the carbon dioxide in PS system and a good agreement was obtained with literature data.

The solubility of carbon dioxide in both PLA 80:20 and 98:2 was measured between 303 and 323 K and pressures up to 5 MPa. The results obtained for pressures below 0.1 MPa are in excellent agreement with literature results for the same system using a low-pressure QCM. The results obtained for high pressures indicate that CO₂ is slightly more soluble in PLA 80:20 than in PLA 98:2. A possible swelling effect on PLA 80:20 and the crystallinity on PLA 98:2 produced different behaviors for the gas solubility results, where isotherms for PLA 80:20 are convex and for PLA 98:2 are linear with pressure.

Three models were used to correlate the experimental results, dual-mode sorption model, Flory-Huggins equation and an extended Flory-

Huggins equation. For the CO₂ in PLA 98:2 system the dual sorption model describes very closely the experimental data while for the CO₂ in PLA 80:20 system the extended Flory-Huggins equation shows the best agreement.

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