

## Gas sorption in poly(lactic acid) and packaging materials

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### Abstract

The solubility of nitrogen, oxygen, carbon dioxide and water in poly(lactic acid) (PLA) was measured using a quartz crystal microbalance (QCM). For that purpose an apparatus based on the quartz crystal microbalance technique was built. This apparatus was calibrated with the system carbon dioxide in atactic polystyrene and the determined precision was of 3%. Measurements were performed up to atmospheric pressure and in the temperature region from 293.2 to 313.2 K.

A study of the solubility of carbon dioxide in PLA over a temperature range from 283.2 to 313.2 K and at pressures below the atmospheric will be presented. The experimental results obtained were correlated with the Flory–Huggins model with an overall AAD of 6%.

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**Keywords:** Sorption; Biodegradable polymer; Quartz crystal microbalance; Poly(lactic acid) (PLA)

### 1. Introduction

Numerous scientists all over the world have been studying polymeric materials based on non-renewable fossil resources for the packaging industry. Due to the increasing concerns about the preservation of ecological systems, it is increasingly being recognized that the use of long-lasting polymers for short-lived applications is not entirely justified. Conventional plastics that persist in the environment due to improper disposal are a significant source of environmental pollution and a waste management problem. In industrialized EU nations, plastics represent approximately 20–40% of municipal waste. The time has therefore come to think of a cooperative approach for research and development of products and strategies for degradable. The elimination of conventional plastics is of interest in the wider war against environmental pollution and replacing non-degradable polymers with environmentally friendly degradable plastics is of major interest to both policy makers and the plastics industry [1].

The need for the development of polymeric materials based on renewable sources has led to the development of

new materials, such as the poly(lactic acid) (PLA), which is currently being produced from a feedstock of corn rather than petroleum. The lactide monomer from which PLA is made comes from lactic acid, that has two enantiomers, L and D. Control of the (L:D) ratio monomer content is a very important feature in PLA, since it has a large effect on material properties, including the degradation time. The future widespread availability of PLA raises interesting and important questions regarding its application. Since the packaging industry, more precisely food packaging, plays a dominant role in the short term use of cheap plastic materials, their replacement with PLA could provide a significant step towards a greener planet. In order to preserve adequately the quality of the food, the packaging materials have to provide efficient barriers against water vapor, atmospheric gases and volatile organic compounds (VOC), preventing food degradation and oxidation and preserving aromas and flavors. It is commonly known that there is mass transfer both from the food to the polymer and vice versa, and that it is responsible for contamination of food and degradation of the packaging material. The food contamination issue can be minimized with the use of PLA since the lactide monomer, from which PLA is made, comes from lactic acid, a non-toxic substance available in the human body. Thus, the determination of the permeability (solubility and diffusion) of gases, flavors and aromas in polymers is of vital importance in the application

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of PLA in the food packaging industry. This work is the first of a study of the solubility of atmospheric gases, aromas and flavors in PLA with an (L:D) ratio of 80:20, which exhibits especially favorable mechanical, optical and degradation properties for being use in the food packaging industry.

## 2. Experimental method

The solubility studies of sorbents in polymers are usually done by gravimetric techniques, like the electronic sorption balance [2] or a quartz spring balance [3] or by inverse gas chromatography [4,5], although other methods like vapor pressure [6] and light scattering [7] are also reported. Gravimetric techniques are very accurate and can also be used for pure gas diffusion measurements [8,9]. The main disadvantage of this type of method is the equilibration time, which can be as long as weeks, depending on the system. The time to reach equilibrium can be minimized using a smaller quartz crystal microbalance (QCM) [10–15], which is the technique adopted in this work. The major advantage of this method is the short equilibration time, which ranges from 3 to 30 min, depending on the system, while retaining good accuracy.

QCM is based on the piezoelectric effect observed in an AT-cut quartz crystal. The quartz crystal wafer has golden electrode plates on both sides, creating a perpendicular electrical field between them. At fixed potential, the effect of the electrical field produces a stationary wave. The frequency of the wave is a function of the crystal mass so that a frequency change,  $\Delta F$ , can be related to a mass change,  $\Delta m$ , according to the Sauerbrey equation [10]:

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

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 is 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,  $\Delta F_E$ , is a sum of three independent terms, hydrostatic  $\Delta F_P$ , impedance  $\Delta F_V$ , and sorption  $\Delta F_S$  [16]:

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

$\Delta F_P$  is proportional to the pressure, while  $\Delta F_V$  is a function of the properties of the gas (viscosity and density) and of the crystal (base frequency, thickness and density). These two terms,  $\Delta F_P$  and  $\Delta F_V$ , were measured together using the reference crystal. For each temperature and pressure, the frequencies of the coated and the uncoated crystal were experimentally measured and their difference is proportional to mass of the coating, polymer and gas sorbed in it. Thus,

the solubility of the gas,  $C$ , in  $\text{cm}^3 \text{ gas (STP)/cm}^3 \text{ polymer}$  was calculated according to the following equation:

$$C = \frac{\Delta F_S \rho_{\text{pol}}}{\Delta F_C M} \times 22416 \quad (3)$$

where  $\rho_{\text{pol}}$  is the polymer density and  $M$  is the molecular weight of the gas and  $\Delta F_C$  is the difference between the frequencies of the coated and the uncoated crystals after the equilibrium was reached.

## 3. Thermodynamic modeling

The wide variety of polymer applications, from paints and coatings to biotechnology and medical fields, clearly depicts the enormous amount of data that is in need. On the other hand, reliable methods to estimate polymer phase equilibrium could be used in the decision of the polymer application. In this work the Flory–Huggins model was used to correlate the experimental results. This model has been described extensively in the literature [17–21] and it has the advantage of being able to correlate experimental results of solubility of gases in polymers.

The Flory–Huggins model considers that the main contribution for the activity coefficient comes from the entropic effects rather than enthalpic effects. The entropy of mixing is calculated from the lattice theory and it accounts for the number of ways of arranging polymer and solvent molecules in a lattice, where each molecule occupies a number of sites proportional to its molecular volume. On the other hand, the enthalpy of mixing is calculated from the van Laar energetic term with the binary interaction parameter,  $\chi_{12}$ , which is used to provide an accurate representation of the experimental data

$$\ln \gamma_1 = \ln \left( \frac{\phi_1}{w_1} \right) + \left( 1 - \frac{1}{r} \right) \phi_2 + \chi_{12} \phi_2^2$$

$$\text{with } r = \frac{v_2 M_2}{v_1 M_1} \quad (4)$$

$$\phi_1 = \frac{v_1 w_1}{v_1 w_1 + v_2 w_2} \quad \text{and} \quad \phi_2 = 1 - \phi_1 \quad (5)$$

where  $\gamma_1$  is the weight fraction activity coefficient of the solvent,  $w_i$  are the weight fractions of each  $i$  component,  $r$  is the number of segments in the polymer molecule, each segment having the same size as that of the solvent molecule,  $M_1$  is the solvent molecular weight and  $M_2$  is the weight average molecular weight of the polymer. The activity of the solvent  $a_1$ , in the polymer is calculated by

$$a_1 = \gamma_1 w_1 \quad (6)$$

From Eq. (1), the weight fraction of the solvent in polymer is given by

$$w_1 = \frac{\Delta F_S}{\Delta F_S + \Delta F_C} \quad (7)$$

Table 1  
Characteristics<sup>a</sup> of polymers

Polymer	$T_g$ (K)	$M_w$
Polystyrene	376.2	197000
Poly(lactic acid) 80:20	329.9	102800

<sup>a</sup>  $T_g$  = glass transition temperature,  $M_w$  = weight average molecular weight.

#### 4. Materials and characterization methods

Atactic polystyrene was purchased from Polyscience, Inc. and poly(lactic acid) was provided by Cargill–Dow polymers and their characteristics are shown in Table 1.

Carbon dioxide with 99.999% mol/mol minimum stated purity was purchased from Air Liquide. Nitrogen with 99.999% mol/mol minimum purity was used and it was obtained from Air Liquide. Dichloromethane was obtained from Riedel-deHaan with analytical reagent grade. Solvent and gases were used with no further purification.

A differential scanning calorimeter, DSC-50/DTA-50 from Shimadzu, was used to measure the glass transition temperature of PLA. A scanning electronic microscope, model S-4100 from Hitachi was used to study the polymer film surface with annealing time. The polymer surface topography was studied by atomic force microscopy, using a Multimode AFM with nanoscope IIIA controller from Digital Instruments.

The quartz crystals used were of 9 MHz base frequency, with golden electrodes of 3 mm and were supplied by Euroquartz, UK.

#### 5. Apparatus description

The scheme of the QCM apparatus used in this work is presented in Fig. 1. This apparatus operates in the pressure range from  $2 \times 10^{-6}$  to 1 bar and in the temperature range from 263 to 340 K. It was designed in a simple and versatile way, allowing the replacement of parts, according to the system under study. The solubility cell, which has a volume of 100 cm<sup>3</sup> approximately, as well as the gas/vapor thermostat, which has a volume of 500 cm<sup>3</sup> approximately, is placed inside of a large water bath, capable of maintaining the temperature to within 0.1 K. Two AT-cut quartz crystal of 9 MHz, the reference and the working crystals, were mounted in the electrical oscillator circuit, inside the solubility cell. The oscillator is powered by a stabilized potential of 5.0 V and both the quartz crystal frequencies were measured using a 10 digits frequency counter HP 53131A, from Hewlett Packard. The temperature inside of the solubility cell is controlled with a previously calibrated Pt100 thermometer connected to a digital multimeter HP 974A from Hewlett Packard. A rotatory high vacuum pump RV3 from BOC Edwards, capable of reaching a vacuum of 0.08 mbar

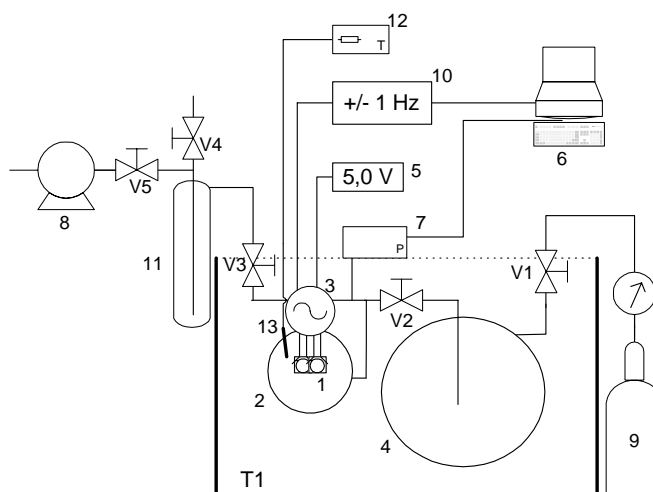


Fig. 1. The QCM apparatus: 1, quartz crystals; 2, solubility cell; 3, oscillator; 4, gas/vapor thermostat; 5, power supply; 6, computer; 7, pressure transducer; 8, vacuum pump; 9, gas bottle; 10, frequency counter; 11, nitrogen trap; 12, multimeter; 13, Pt100 thermometer; V1–V5, valves; T1, water bath.

was used while the system pressure was measured with an AEP transducer Bit02 of 4 digits.

The experiment starts by opening the valves V5, V3, V2 and V1 and the entire apparatus is kept in vacuum for 2 days.

After a given temperature is attained, valve V2 is closed and V1 is opened, inserting the gas from the gas bottle inside the gas/vapor thermostat. A computer program controls the frequency counter and the transducer and records the frequency of the crystals and the pressure of the system. By opening valve V2 and closing valve V3, the gas is inserted into the solubility cell, promoting a change in the frequency, which is recorded as a function of time. When a stable frequency is reached, within an acceptable tolerance ( $\pm 2$  Hz), the reading is accepted and recorded as the equilibrium frequency. By closing valve V2 and opening valve V3, the gas in the solubility cell is evacuated and desorption process takes place.

#### 6. Quartz crystal coating

The 9 MHz crystals were thoroughly cleaned with dichloromethane until the base frequency became constant ( $\pm 2$  Hz). Both sides of the working crystal were then coated with a polymer solution of known concentration and the solvent was left to evaporate under ambient conditions.

The quartz crystal coated with polymer was placed in an oven, 5° above its glass transition temperature for 2 days. This temperature treatment relaxed the polymer chains, producing a more uniform coating, and further dried it, eliminating contaminants. Cycles of temperature coupled with sorption measurements were performed until the sorption remained constant.

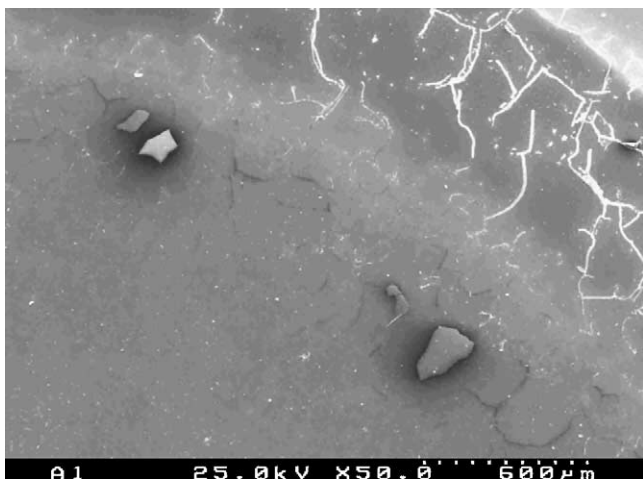


Fig. 2. SEM of the PLA sample coated on cover-glass with no temperature treatment.

In order to understand the effect of the temperature treatment on the polymer coating, scanning electronic microscopy (SEM) was performed on several PLA coatings on glass. The sequence of Figs. 2–4 shows SEM images of the polymer film with different annealing time periods, 0, 48 and 109 h, respectively, at 333 K in an air-vented oven. Fig. 5 shows the SEM image of the polymer film when a cyclic annealing (38 h at 333 K, 105 h at ambient temperature and 24 h more at 333 K) is done. These figures clearly show a more regular film (without cracks) in the last case and therefore this was the procedure adopted for preparing the quartz crystal coating during this work.

A more thorough study of the surface topography of the polymer on the crystal was performed using AFM, in the tapping mode [22]. Fig. 6 shows two dimension topographic images for a PLA coating that has been cyclically annealed, with a resolution of 100  $\mu\text{m}$ . It can be observed that, at this magnitude, the surface is still rather irregular, with a maximum

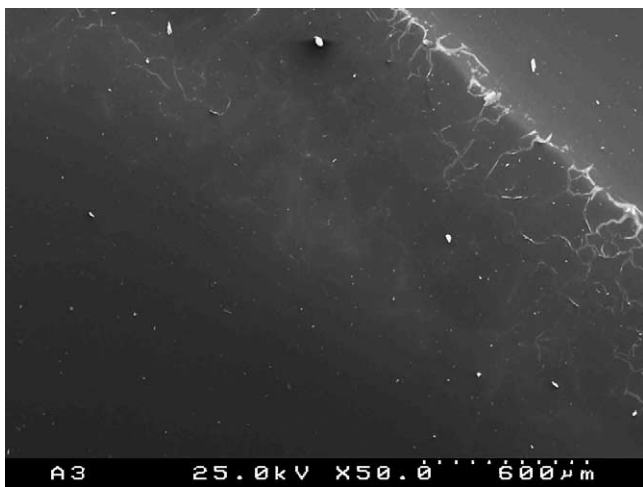


Fig. 3. SEM of the PLA sample coated on cover-glass that has been annealed at 333 K in air for 48 h.

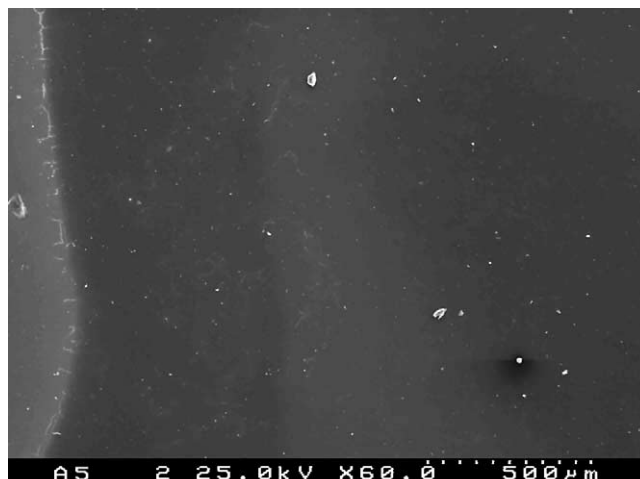


Fig. 4. SEM of the PLA sample coated on cover-glass that has been annealed at 333 K in air for 109 h.

topographical variation (height) of less than 1.2  $\mu\text{m}$  and an average roughness of 0.003  $\mu\text{m}$ . The thickness of the film was also measured and has an estimated value of 2.6  $\mu\text{m}$ .

## 7. Results

In order to estimate the precision of the QCM, the sorption of carbon dioxide in polystyrene (PS) at pressures below the atmospheric pressure and at the temperatures of 303.2–313.2 K was measured. The solubility results listed in Table 2, have a precision of  $\pm 0.02 \text{ cm}^3 \text{ (STP) cm}^{-3}$  polymer and are compared with literature data [23–25] in Fig. 7. It can be observed that a good description is obtained for both temperatures, with an overall average absolute deviation (AAD) of 3%. At 313.2 K the literature data depends strongly on the

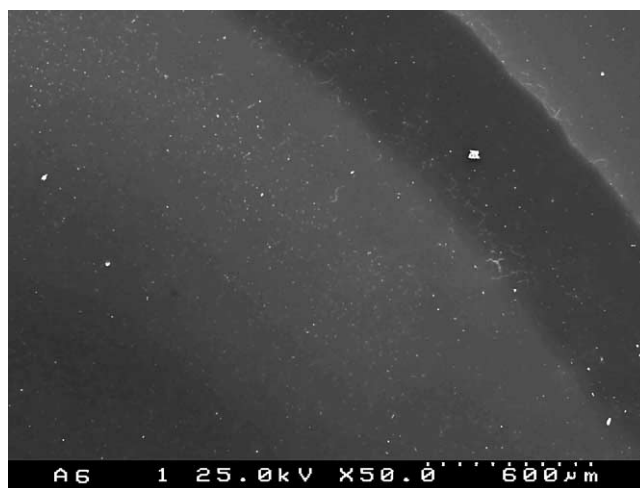


Fig. 5. SEM of the PLA sample coated on cover-glass that has been annealed cyclically 38 h at 333 K, 105 h at ambient temperature and 24 h at 333 K.



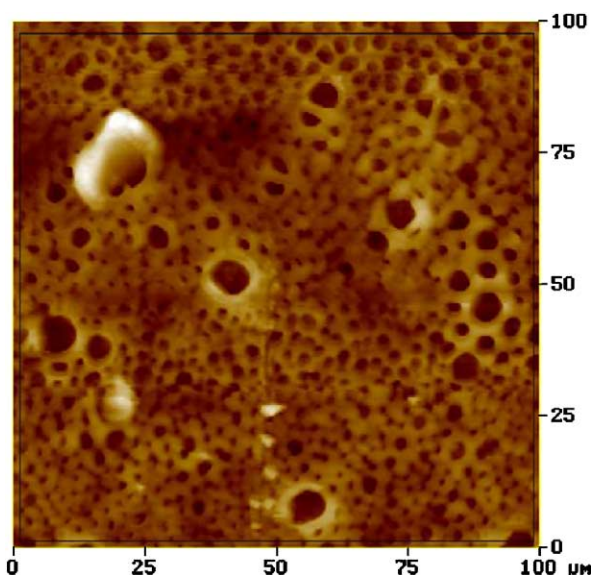


Fig. 6. Roughness analysis of PLA film coated on quartz crystal by AFM tapping force mode.

polymer weight average molecular weight ( $M_w$ ) and orientation (atactic/syndiotactic). The polymer  $M_w$  can be related to polymer density. For the same orientation, the sorption decreases dramatically as the polymer density increases [26]. Note that the polymer orientation does not change the nature of the sorption process; however, it changes its magnitude. For example, a decrease in the solubility can be correlated with the increase of density, due to orientation [24]. In this work, the PS weight average molecular weight is 197 000 and thus it agrees well with the literature results for similar weight average molecular weight and orientation.

The sorption isotherms obtained for carbon dioxide, oxygen, nitrogen and water in PLA at different pressures are displayed in Tables 3–6 and Figs. 8–11, respectively. Analysis of the figures shows that water is the more soluble sorbent, even though the measurements could only be performed up to 90% of the water vapor pressure at that temperature. The atmospheric gases were measured up to atmospheric pressure and it was found that nitrogen and oxygen have ap-

Table 2  
Solubility of carbon dioxide in PS

$T$ (K)	$P$ (bar)	$C$ (cm <sup>3</sup> (STP) cm <sup>-3</sup> polymer)
303.2	0.214	0.46
	0.510	1.04
	0.767	1.53
	0.824	1.63
	0.983	1.95
313.2	0.361	0.72
	0.711	1.30
	0.769	1.42
	0.968	1.73

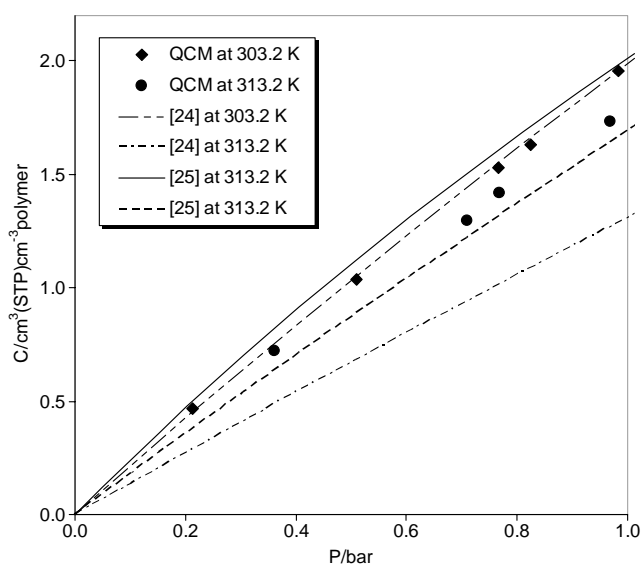


Fig. 7. Solubility of carbon dioxide in PS and comparison with literature [24,25]. The PS  $M_w$  used in [24] was 290 000 and no information was given in [25]. The dashed line and the solid lines represent biaxially oriented and unoriented PS, respectively, at 313.2 K.

proximate solubility values, which are half of that found for carbon dioxide. Since there are no results available in the literature for these systems, no comparisons could be made.

In Figs. 8–11, the correlation of experimental results for each system at each temperature using the Flory–Huggins

Table 3  
Solubility of carbon dioxide in PLA

$T$ (K)	$P$ (bar)	$C$ (cm <sup>3</sup> (STP) cm <sup>-3</sup> polymer)
293.2	0.142	0.78
	0.230	1.19
	0.361	1.63
	0.462	2.05
	0.578	2.23
	0.656	2.58
	0.818	2.93
	0.893	3.20
	0.980	3.49
303.2	0.226	0.98
	0.512	1.65
	0.677	1.94
	0.805	2.28
	0.857	2.39
	0.960	2.63
	0.961	2.66
313.2	0.197	0.46
	0.271	0.74
	0.334	0.85
	0.359	0.93
	0.487	1.13
	0.524	1.23
	0.634	1.50
	0.719	1.59
0.973	1.84	

Table 4  
Solubility of oxygen in PLA

$T$ (K)	$P$ (bar)	$C$ (cm <sup>3</sup> (STP) cm <sup>-3</sup> polymer)
293.2	0.110	0.50
	0.188	0.62
	0.188	0.58
	0.312	0.72
	0.454	0.88
	0.468	0.89
	0.610	1.04
	0.765	1.25
	0.925	1.48
	0.995	1.57
303.2	0.103	0.19
	0.106	0.20
	0.214	0.27
	0.351	0.38
	0.352	0.32
	0.396	0.44
	0.473	0.49
	0.663	0.76
	0.889	1.04
	0.987	1.05
313.2	0.030	0.06
	0.063	0.10
	0.098	0.12
	0.184	0.21
	0.270	0.23
	0.337	0.30
	0.404	0.26
	0.488	0.43
	0.547	0.39
	0.643	0.51
	0.711	0.50
	0.793	0.55
	0.799	0.54
	0.944	0.58
	0.955	0.66

Table 5  
Solubility of nitrogen in PLA

$T$ (K)	$P$ (bar)	$C$ (cm <sup>3</sup> (STP) cm <sup>-3</sup> polymer)
283.1	0.107	0.15
	0.138	0.24
	0.322	0.39
	0.591	0.86
	0.685	0.99
	0.863	1.18
	1.022	1.32
	1.258	1.54
293.0	0.116	0.08
	0.302	0.21
	0.478	0.32
	0.530	0.32
	0.755	0.46
	0.912	0.55
303.1	1.046	0.68
	0.077	0.06
	0.173	0.11
	0.302	0.14
	0.398	0.16
	0.501	0.20
313.1	0.696	0.245
	0.904	0.32
	1.026	0.36
	0.190	0.05
	0.273	0.06
	0.413	0.10
313.1	0.605	0.14
	0.717	0.17
	0.810	0.19
	1.022	0.23

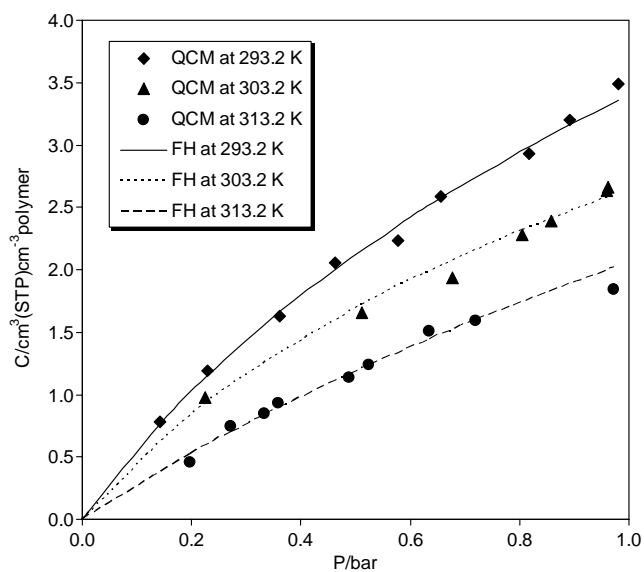


Fig. 8. Solubility of carbon dioxide in PLA and the correlation with Flory–Huggins model.

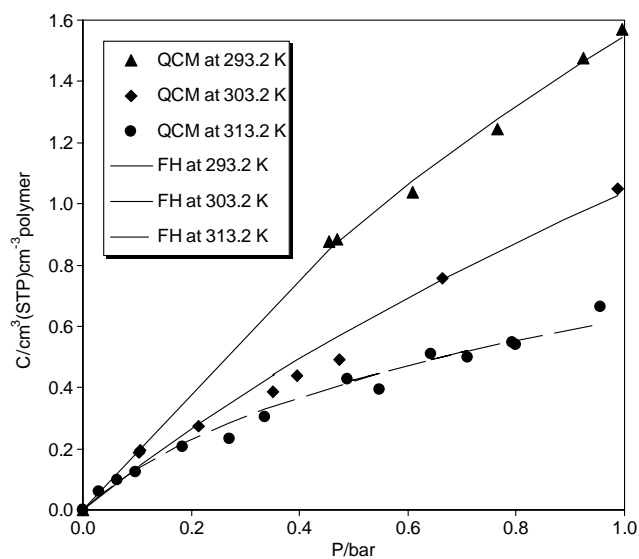


Fig. 9. Solubility of oxygen in PLA and the correlation with Flory–Huggins model.

Table 6  
Solubility of water in PLA

$T$ (K)	$P$ (bar)	$C$ ( $\text{cm}^3$ (STP) $\text{cm}^{-3}$ polymer)
293.2	0.003	2.18
	0.007	5.21
	0.007	4.80
	0.012	7.87
	0.015	10.30
	0.018	12.95
	0.020	15.96
	0.024	19.45
303.2	0.005	1.61
	0.011	3.10
	0.011	3.20
	0.012	4.00
	0.014	4.81
	0.020	6.50
	0.022	7.83
	0.026	9.67
	0.032	11.85
	0.035	14.47
	313.2	0.004
0.011		1.60
0.017		3.33
0.026		5.25
0.035		7.03
0.043		9.81
0.043		9.73
0.045		9.45
0.046	10.20	

model is depicted. The Flory–Huggins interaction parameters, listed in Table 7, were correlated for each temperature, assuming no concentration dependency. The analysis of the AAD shows that the deviations are larger for carbon dioxide and oxygen than for nitrogen and water. The figures also confirm that the experimental data obtained for the first two

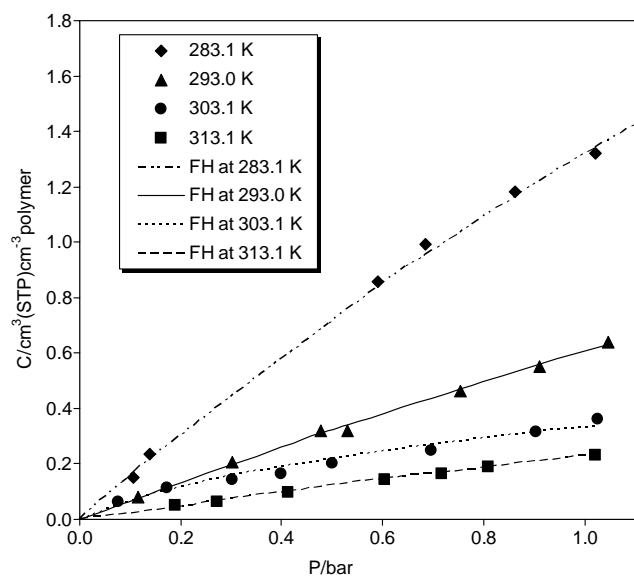


Fig. 10. Solubility of nitrogen in PLA and the correlation with Flory–Huggins model.

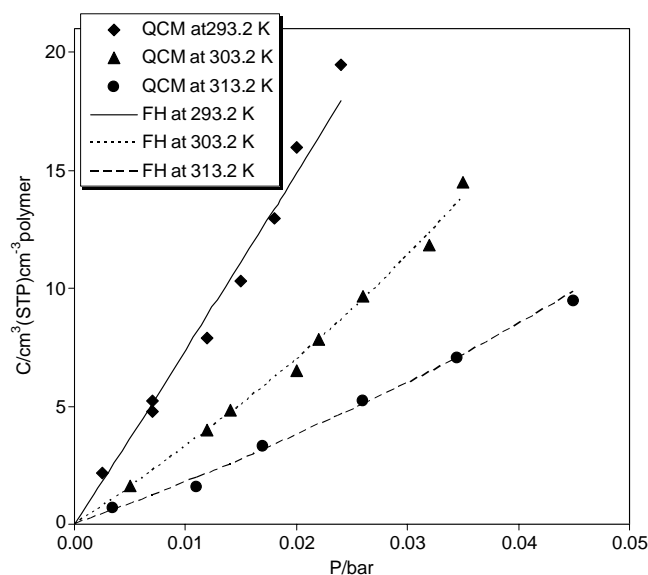


Fig. 11. Solubility of water vapor in PLA and the correlation with Flory–Huggins model.

Table 7  
Flory–Huggins parameter for gases in PLA and respective AAD

Solute	$T$ (K)	$\chi_{12}$	AAD (%)
$\text{CO}_2$	293.2	0.06	2
	303.2	0.09	3
	313.2	0.11	5
$\text{O}_2$	293.2	1.40	2
	303.2	1.76	14
	313.2	2.10	8
$\text{N}_2$	283.1	2.11	4
	293.0	2.90	3
	303.1	3.31	9
	313.1	3.84	4
$\text{H}_2\text{O}$	293.2	3.52	8
	303.2	3.65	3
	313.2	3.67	8

sorbents is less precise than for the last two. This fact is due to the successive upgrades performed in the QCM during the course of this work, namely improvements in the temperature and pressure control.

For the carbon dioxide/PLA system, the Flory–Huggins interaction parameter values are one order of magnitude smaller than for other systems. From a qualitative point of view, the  $\chi_{12}$  is a measure of the solvent/polymer affinity, where low values of  $\chi_{12}$  describe the highest sorption, and thus the highest affinity.

## 8. Conclusions

The solubility carbon dioxide, oxygen, nitrogen and water in PLA at 293.2, 303.2 and 313.2 K, and pressures up to atmospheric pressure, were measured with a QCM. The results obtained during this work show that it is very sensi-

tive method, useful method to study gas–polymer sorption. Conventional methods such as gravimetric or pressure decay have less sensitivity, require relatively larger samples and longer equilibrium times, usually hours or even days, depending on the system. QCM proved to be a reliable, precise, accurate and fast method for studying the solubility of gases in polymers. The experimental results were correlated using Flory–Huggins model.

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