

## **GAS SORPTION IN POLY(LACTIC ACID) AND PACKAGING MATERIALS**

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## **Abstract**

The solubility of nitrogen, oxygen, carbon dioxide, and water in the vapour phase in PolyLactic Acid (PLA) were measured, using a Quartz Crystal Microbalance (QCM). For that purpose a new apparatus based on Quartz Crystal Microbalance technique was built. This apparatus was calibrated with the system carbon dioxide in atactic polystyrene and the determined precision was of 1.5 %. Measurements were performed up to atmospheric pressure and in the temperature region from 293 to 313 K.

A study of the solubility of carbon dioxide in PLA over a temperature range from 283 to 313 K and at pressures below the atmospheric will be presented. The experimental results obtained were compared with the Flory-Huggins model.

**Keywords:** sorption; biodegradable polymer; quartz crystal microbalance; PolyLactic 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 the eco 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 between 20 - 40% of municipal waste. Consumption of plastic material in the EU was approximately 40 million tones in 2000 [1]. 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 therefore of interest in the wider war against environmental pollution and replacing non-degradable polymers by environmentally friendly degradable plastics is of major interest to both policy-makers and the plastics industry.

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 future widespread availability of PLA raises interesting and important questions regarding its application. Since the packaging industry, more precisely the food packaging, plays a dominant role in the short term use of cheap plastic materials, its replacement for 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, to prevent the food degradation, atmospheric gases, to prevent the oxidation, and volatile organic compounds, VOC, to preserve the aromas and the flavours. It is a common fact that there is mass transfer both from the food to the polymer and vice-versa, and it is this mass transfer that is responsible for the contamination of food and for the degradation of the packaging material. The food contamination issue can be neglected 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 of PLA in the food packaging industry.

Inverse gas chromatography [2] differential vapour pressure [4], light scattering [5], gravimetric techniques [6] and quartz crystal piezoelectric technique [7], [8] are some of the techniques used for sorption measurements. Usually the sorption measurements of gas in polymer are done by gravimetric techniques, like the sorption balance with an electronic or a quartz spring balance [9] or by inverse gas chromatography [2], [3]. The gravimetric techniques are very accurate and can also be used for pure gas diffusion measurements [10]. The main disadvantage of this method is the long equilibration times, which can be as long as weeks, depending on the system. The time to reach equilibrium can be minimized using a smaller microbalance. In this work, a new apparatus of Quartz Crystal Microbalance [7], based on quartz crystal piezoelectric technique, was built to evaluate the amount of gas sorbed in the polymer. The major advantage of this method is the short time to reach equilibrium, which ranges from three to thirty minutes, depending on the system, while retaining a good accuracy.

The QCM is based on the piezoelectric effect observed in AT-cut quartz crystal. The flat plate of quartz crystal has golden plates as electrodes in both sides. These electrodes create a perpendicular electrical field between them. The quartz crystal with electrodes is represented in the Figure 1.

At fixed potential, the effect of the electrical field produces a mechanical oscillation, a stationary wave. By changing the mass of the crystal, the frequency of the oscillation change. Sauerbrey [7], [11][13][14] concludes that the frequency change,  $\Delta F$ , is proportional to the mass change,  $\Delta m$ , according to:

$$\Delta F = -\frac{2F_0^2}{A\sqrt{\mu_q\rho_q}}\Delta m \quad (1)$$

where  $F_0$  is the fundamental crystal frequency,  $A$  is the electrode area,  $\mu_q$  is the shear modulus of quartz and  $\rho_q$  is the quartz density. Assuming that the coated mass on crystal electrode vibrates synchronously with quartz crystal, the mass increase on the crystal electrode is proportional to frequency change:

$$\Delta F = k \cdot m_s \quad (2)$$

where  $k$  is the proportionality constant and  $m_s$  is the coated mass on crystal electrode.

In sorption measurements, the crystal is coated with a thin polymer layer. The presence of gas sorbed in polymer will be measured by the frequency change,  $\Delta F_E$ . This frequency change is considered to be a sum of three terms, hydrostatic  $\Delta F_P$ , impedance  $\Delta F_V$ , and sorption  $\Delta F_S$  [12]:

$$\Delta F_E = \Delta F_S + \Delta F_P + \Delta F_V \quad (3)$$

For each crystal, the  $\Delta F_P$  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 (frequency, thickness and density). In this work,  $\Delta F_P$  and  $\Delta F_V$  were measured together using an uncoated crystal ( $\Delta F_S=0$ ), the reference crystal, at different gas pressures,  $p$ :

$$\Delta F_P + \Delta F_V = \Delta F_{P,V} = m \cdot p + b \quad (4)$$

A correlation for  $m$  and  $b$  with pressure at different temperatures was done for each gas. It was found that the calibration curves are very similar for carbon dioxide and oxygen which leads to the conclusion that the pressure term is dominant. For water that is not the case, since the pressure range is much smaller (the vapour pressure of water at 308 K is 57 mbar ) and the  $\Delta F_{P,V}$  term is larger.

The frequency of the coated crystal was experimentally measured at a given temperature. The difference between the frequencies of the coated and the uncoated crystal,  $\Delta F_C$ , is proportional to the mass of polymer coating. Thus, the solubility at a given pressure,  $p$ , was calculated by using:

$$C = \frac{\Delta F_S \rho_{pol.}}{\Delta F_C M} \cdot 22416 \quad (5)$$

where  $\rho_{pol}$  is the polymer density and  $M$  is the gas molecular weight.

The wide variety of polymer applications, from paint/coatings to biotechnology and medical fields clearly depicts the enormous amount of data that is in need. The polymer thermodynamic modelling plays an important role since it provides a fast and

accurate description of the phase diagram of the systems under study. In this work the Flory-Huggins model was used to correlate the experimental results. This model has been described extensively in the literature [15] and it has the advantage of being able to correlate experimental results 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 on a lattice, where each molecule occupies a number of sites proportional to its molecular volume. For the sake of simplicity we do not use core volumes, but directly calculate the molecular sizes from specific volumes  $v_i$ , so that the Flory-Huggins equation can be written with volume fractions  $\phi_i$  that are based on the assumption of vanishing excess volumes. On the other hand, the enthalpy of mixing is calculated from a simple van Laar energetic term with the binary interaction parameter  $\chi_{12}$ , that is used to provide an accurate representation of the experimental data

$$\ln \gamma_1 = \ln \left( \frac{\phi_1}{w_1} \right) + \left( 1 - \frac{1}{r} \right) \phi_2 + \chi_{12} \phi_2^2 \quad \text{with} \quad r = \frac{v_2 M_2}{v_1 M_1} \quad (6)$$

$$\phi_1 = \frac{v_1 w_1}{v_1 w_1 + v_2 w_2} \quad \text{and} \quad \phi_2 = 1 - \phi_1 \quad (7)$$

where  $\gamma_i$  is the weight fraction activity coefficient of the solvent,  $w_i$  are the weight fractions,  $r$  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 polymer. The activity of the solvent  $a_1$ , in the polymer is calculated by:

$$a_1 = \gamma_1 w_1 \quad (8)$$

From Equation 2, the weight fraction of the solvent in polymer is:

$$w_1 = \frac{\Delta F_s}{\Delta F_s + \Delta F_c} \quad (9)$$

The solubility of carbon dioxide in PLA at 293, 303 and 313 K up to atmospheric pressure was also measured by SB and QCM.

## 2. Materials and Characterization Methods

Atactic polystyrene (Mw 197.000) was purchased from Polyscience, Inc. a polydispersity of 1.05. Poly(Lactic Acid) (Mw 102800) with L:D ratio of 80:20 was provided by Cargill-Dow Polymers. 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 were obtained from Riedel-deHaen 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.

The 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, England.

### **3. Experimental Method**

The scheme of the QCM apparatus is presented in Figure 2. This apparatus is all made of glass and was designed in a simple and versatile way, allowing the replacement of parts of the system depending on the systems under study. The solubility cell, which has a volume of 100 cm<sup>3</sup> approximately, as well as the gas/vapour 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. One AT-cut quartz crystal of 9 MHz was mounted in the electrical oscillator circuit, inside the solubility cell. A 10 digits frequency counter HP 53131A, from Hewlett Packard measures the signal of the quartz crystal frequency when the oscillator is powered by a stabilized potential of 5.0 V. The temperature of the water bath is controlled by a previously calibrated Pt100 thermometer placed inside the solubility cell, close to the crystal. The Pt100 thermometer is connected to a digital multimeter HP 974A from Hewlett Packard. A rotatory high vacuum pump RV3 from BOC Edwards RV3, capable of reaching a vacuum of 0.08 mbar, performs the vacuum and the AEP transducer Bit02 of 4 digits measures the pressure inside the system, p. A computer records and controls the AEP transducer and the frequency counter.

#### 4. Experimental Procedure

*Method for Polymer Coating.* The crystal of 9 MHz was thoroughly cleaned with dichloromethane until the frequency became constant. Afterward, the crystal was coated with a polymer solution. A 0.5 (w/v) % solution of polymer in dichloromethane was used for both PS and PLA. One drop of this solution was placed on each side of the clean crystal electrode, which was supported horizontally. The solvent was left to evaporate under ambient conditions. The amount of polymer on the crystal was adjusted by the addition of more drops or the removal of the coating until a desired frequency change was reached. The desired frequency change has to be between a minimum, related to the frequency meter resolution, and a maximum value, related to the application of the Sauerbrey equation where the mass/area can not exceed 2% of the mass/area of the crystal.

After the coating of the crystal, a temperature treatment is carried out. The quartz crystal coated with polymer is placed in an oven, five degrees above its glass transition temperature ( $T_g$ ) for two days. This temperature treatment relaxes the polymer chains, producing a more uniform coating with minimal surface defects. The quality of the coating can be checked doing some sorption measurements. Cycles of temperature treatments and experimental measurements are performed till the sorption values remain constant.

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 with different annealing times. The sequence of Figures 3-5 show SEM images of the polymer film with different times, 0 h, 48 h and 109 h, respectively,

of annealing at 333 K in an air-vented oven. The Figure 6 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. The SEM images clearly show a more regular film in the last case and this was the procedure adopted for preparing the coating during this work.

A more thorough study of the surface topography and surface heterogeneity of the polymer on the crystal with nanometric resolution were performed using AFM, in the tapping mode. In Figures 7 and 8 a two dimension topographic images for a PLA coating that has been cyclic annealed, with a magnification of 100 and 10  $\mu\text{m}$  respectively, are shown. It can be observed that the surface is still rather irregular, with a maximum topographic 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 a value of 2.6  $\mu\text{m}$ . Nevertheless, the topography of the surface does not affect the neither the precision nor the accuracy of the solubility results measured in this work.

***Experimental Procedure.*** The QCM apparatus operates in the range from  $2 \times 10^{-6}$  to 1 bar and is shown in Figure 2. The crystal is connected to the oscillator and introduced in the solubility cell. The power supply of 5.0 V and the frequency counter are turned on. The vacuum pump and the transducer are turned on, by opening the valves V5, V3, V2 and V1, and for cleaning, all apparatus is under vacuum for 2 days. For a given temperature, by closing the valve V2 and opening valve V1, the gas is inserted inside the gas/vapour thermostat from the gas bottle. A computer program controls the frequency counter and the transducer and records the frequencies of the crystal and the pressure of the system. By opening valve V2 and closing valve V3, the gas is inserted into the solubility cell from the gas/vapor thermostat and the change in frequency of the

crystal was scanned and recorded as a function of time. This procedure is performed during the calibration, in order to obtain  $\Delta F_{P,V}$ , and with the crystal coated with polymer, in order to obtain  $\Delta F_E$ . When it reached a stable frequency, within an acceptable tolerance ( $\pm 2$  Hz), the reading was recorded as an equilibrium frequency. The Pt100 thermometer reads the temperature of gas inside the solubility cell. By closing valve V2 and opening valve V3, the gas in the solubility cell is evacuated and desorption process starts.

## 5. Results

In order to estimate the precision of the QCM, the sorption of carbon dioxide in PS at pressures below the atmospheric pressure and temperatures 303 to 313 K was measured. The solubility results obtained have a precision of  $\pm 0.02 \text{ cm}^3(\text{STP})\text{cm}^{-3}_{\text{polymer}}$  and are listed in Table 1. The carbon dioxide solubility in PS is compared with literature [17] in Figure 9. It can be observed that a good description is obtained for both temperatures, with an average absolute deviation (AAD) of 1.5 % for 303.15 K and 3.6 % for 313.15 K. For 313 K the available data in the literature depends strongly on the polymer weight average molecular weight and orientation (atactic/syndiotactic). The polymer weight average molecular weight can be related to polymer density. For the same orientation, same structure, the sorption decreases dramatically as the polymer densities increases. 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 [18]. In this work the PS weight average molecular weight is 200 000 and thus it agrees well with the literature results for similar weight average molecular weight and orientation.

The results sorption isotherms obtained for carbon dioxide, oxygen, nitrogen and water in PLA at different pressures are displayed in Tables 2 to 5 and Figures 10 to 13, respectively. Since there are no results available in the literature for this system, no comparisons could be made. Also in the Figures 10-13, the correlations of experimental results for each system using the Flory-Huggins model are presented, as well as the respective AAD. The Flory-Huggins interaction parameters, listed in Table 6, were correlated for each temperature, assuming no concentration dependency.

## **6. Conclusions**

The solubility carbon dioxide, oxygen, nitrogen and water in PLA at 293, 303 and 313 K, and pressures up to atmospheric pressure, were measured with a QCM. The results obtained during this work show that it is very sensitive 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, providing a fairly good description.

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## References

- [1] G. Piringer, A. L. Baner, "Plastic packaging materials for food: Barrier Function, Mass Transport, Quality Assurance, and Legislation", WILEY-VCH, Weinheim, Germany, 2000.
- [2] Enrique Morales and José Luis Acosta, *Polymer Journal*, 1996, 28, 127.
- [3] Rafael Gavara, Ramon Catalã, Susana Aucejo, Daniel Cabedo and Ruben Hernandez, *Polymer*, 1996, 34, 1907.
- [4] H. J. Lechermeier, J. R. Dorgan, J. D. Way, *Journal of Membrane Science*, 2001, 4922, 1.
- [5] F. Mantovani, M. Grassi, I. Colombo, R. Lapasin, *Fluid Phase Equilibria*, 2000, 167, 63.
- [6] Pilar Hernandez-Muñoz, Rafael Gavara, Ruben J. Hernandez, *Journal of Membrane Science*, 1999, 154, 195.
- [7] G. Sauerbrey, *Z. Phys.*, 1959, 155, 206-222D.
- [8] W. H. King, *Anal. Chem.*, 1964, 36, 1735.
- [9] W. J. Koros, "Sorptions and transport of gases in glassy polymers", The University of Texas at Austin, Austin, USA, 1977.
- [10] J. Crank, "The Mathematics of Diffusion", Oxford, Clarendon Press, 2<sup>nd</sup> ed, 1975.
- [11] H. C. Wong, S. W. Campbell, V. R. Bhethanabotla, *Fluid Phase Equilibria*, 1997, 139, 371.

- [12] M. T. S. R. Gomes, "Desenvolvimento de Sensores Baseados em Microbalanças de Cristais Piezoelétricos para a Determinação de CO<sub>2</sub> e SO<sub>2</sub>", Universidade de Aveiro, Aveiro, Portugal, 1996.
- [13] Siva P. V. N. Mikkilineni, D. Alan Tree, Martin S. High, *J. Chem. Eng. Data*, 1995, 40, 750.
- [14] S. Saeki, J. C. Holste, D. C. Bonner, *Journal of Polymer Science, Polymer Physics Edition*, 1981, 19, 307.
- [15] G. Kontogeorgis, "Polymer Thermodynamics", Chapter prepared for the Handbook of Colloid and Surface Chemistry (to be published by CRC Press, Editor: Birdi)
- [16] John M. Prausnitz, Rudiger N. Lichtenthaler, Edmundo Gomes de Azevedo, "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice Hall PTR, New Jersey, USA, 1999.
- [17] E. Sada, H. Kumazawa, H. Yakushji, Y. Bamba, K. Sakata and S-T. Wang, *Ind. Eng. Chem. Res.*, 1987, 26, 433.
- [18] C. Carfagna, L. Nicodemo, L. Nicolais and G. Campanile, *J. Polym. Sci. Part B: Polym. Phys.*, 1986, 24, 1805.
- [19] P.J. Flory, "Statistical Thermodynamics of Polymer Solutions", Chapter XII, Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, 1953.
- [20] Russell Paterson, Yuri Yampol'skii, *Journal of Physical and Chemical Reference Data*, 1999, 28, 1264-1449.
- [21] D. Raghavan, X. Gu, T. Nguyen, M. VanLandingham and A. Karim, *Macromolecules*, 2000, 33, 2573.

- [22] Marcel Mulder, "Basic Principles of Membrane Technology", Kluwer Academic Publishers, 2<sup>nd</sup> ed., 1996.
- [23] H. S. Elbro, A. Fredenslung and P. Rasmussen, *Macromolecules*, 1990, 23, 4707.

**Table 1:** Solubility of carbon dioxide in PS using QCM.

T/K	P/bar	Solubility/cm <sup>3</sup> (STP).cm <sup>-3</sup> <sub>polymer</sub>
		± 0.02 QCM
303.20	0.214	0.465
	0.360	0.824
	0.510	1.04
	0.655	1.50
	0.660	1.54
	0.668	1.29
	0.767	1.53
	0.824	1.63
	0.968	2.13
	0.983	1.95
	0.986	2.15
313.19	0.361	0.721
	0.665	1.30
	0.711	1.30
	0.769	1.42
	0.773	1.35
	0.968	1.73
	0.978	1.64

**Table 2:** Solubility of carbon dioxide in PLA using QCM.

Solubility/cm <sup>3</sup> (STP).cm <sup>-3</sup> <sub>polymer</sub> ± 0.02		
T/K	P/bar	QCM
293.15	0.142	0.784
	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
	303.15	0.226
0.512		1.65
0.645		2.15
0.677		1.94
0.805		2.28
0.857		2.39
0.960		2.63
0.961		2.66
313.15	0.197	0.456
	0.271	0.741
	0.334	0.847
	0.359	0.930
	0.487	1.13
	0.524	1.23
	0.634	1.50
	0.719	1.59
	0.949	1.68
	0.973	1.84

**Table 3:** Solubility of oxygen in PLA using QCM.

T/K	P/bar	Solubility/cm <sup>3</sup> (STP).cm <sup>-3</sup> <sub>polymer</sub>
		± 0.02 QCM
293.15	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
303.15	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
313.15	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 4:** Solubility of nitrogen in PLA using QCM.

T/K	P/bar	Solubility/cm <sup>3</sup> (STP).cm <sup>-3</sup> <sub>polymer</sub>
		± 0.02 QCM
283.11	0.107	0.152
	0.138	0.235
	0.322	0.389
	0.591	0.859
	0.685	0.991
	0.863	1.18
	1.022	1.32
	1.258	1.54
292.95	0.116	0.079
	0.302	0.206
	0.478	0.318
	0.530	0.321
	0.755	0.462
	0.912	0.551
	1.046	0.637
303.08	0.077	0.062
	0.173	0.114
	0.302	0.145
	0.398	0.165
	0.501	0.203
	0.696	0.248
	0.904	0.317
313.08	1.026	0.360
	0.190	0.051
	0.273	0.065
	0.413	0.097
	0.605	0.141
	0.717	0.166
	0.810	0.190
1.022	0.230	

**Table 5:** Solubility of water in PLA using QCM.

T/K	P/bar	Solubility/cm <sup>3</sup> (STP).cm <sup>-3</sup> <sub>polymer</sub> ± 0.02
		QCM
293.15	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
303.15	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
313.15	0.032	11.85
	0.035	14.47
	0.004	0.67
	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	

**Table 6:** Flory-Huggins parameter for gases in PLA and AAD compared with experimental results.

Solute	T/K	$\chi_{12}$	AAD %
CO <sub>2</sub>	293.17	0.06	15
	303.19	0.09	12
	313.15	0.11	5
O <sub>2</sub>	293.15	1.40	12
	303.15	1.76	18
	313.15	2.10	18
N <sub>2</sub>	283.11	2.11	6
	292.95	2.90	5
	303.08	3.31	10
	313.08	3.84	4
H <sub>2</sub> O	293.15	3.52	7
	303.15	3.65	8
	313.15	3.67	6

## **FIGURE CAPTIONS:**

**Figure 1:** Representation of the quartz crystal with the golden plates.

**Figure 2:** The QCM apparatus. 1 – quartz crystals; 2 – solubility cell; 3 – oscillator; 4 – gas/vapor thermostat; 5 – power supply of 5.0 V. stabilized; 6 – computer to record pressure and frequency; 7 – transducer; 8 – vacuum pump; 9 – gas bottle; 10 – frequency counter. resolution of +/- 1 Hz; 11 – nitrogen trapp; 12 – bath; 13 – Pt100 thermometer; valves V1. V2. V3. V4 e V5.

**Figure 3:** SEM of the PLA sample coated on cover-glass with no temperature treatment.

**Figure 4:** SEM of the PLA sample coated on cover-glass that has been annealed at 60 °C in air for 48 h.

**Figure 5:** SEM of the PLA sample coated on cover-glass that has been annealed at 60 °C in air for 109 h.

**Figure 6:** SEM of the PLA sample coated on cover-glass that has been annealed cyclically. 38 h at 60 °C. 105 h at ambient temperature and 24 h at 60 °C.

**Figure 7:** Roughness analysis of PLA film coated on quartz crystal. by AFM tapping force mode.

**Figure 8:** Height images using tapping forces mode. Color contrast from black to white represents a total range of 1371.7 nm.

**Figure 9:** Representation of the solubility of carbon dioxide in PS using QCM and comparison with literature **Error! Reference source not found.. Error! Reference source not found..**

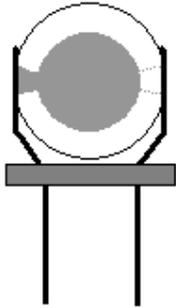
**Figure 10:** Representation of the solubility of carbon dioxide in PLA using QCM and the correlation with Flory-Huggins model.

**Figure 11:** Representation of the solubility of oxygen in PLA using QCM and the correlation with Flory-Huggins model.

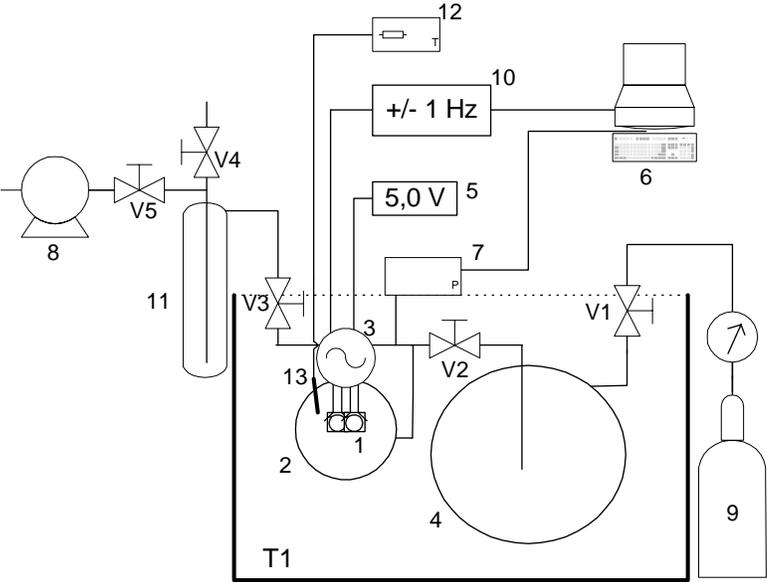
**Figure 12:** Representation of the solubility of water vapour in PLA using QCM and the correlation with Flory-Huggins model.

**Figure 13:** Representation of the solubility of nitrogen in PLA using QCM and the correlation with Flory-Huggins model.

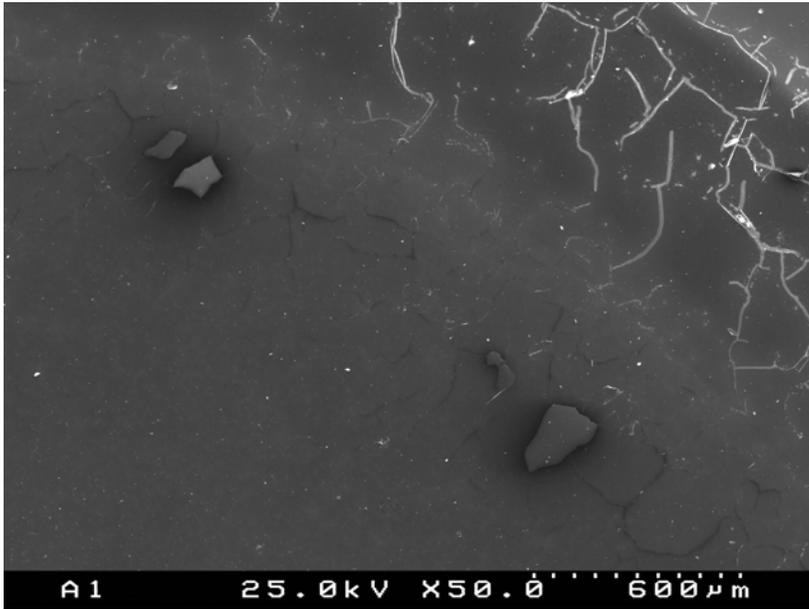
**Figure 1:**



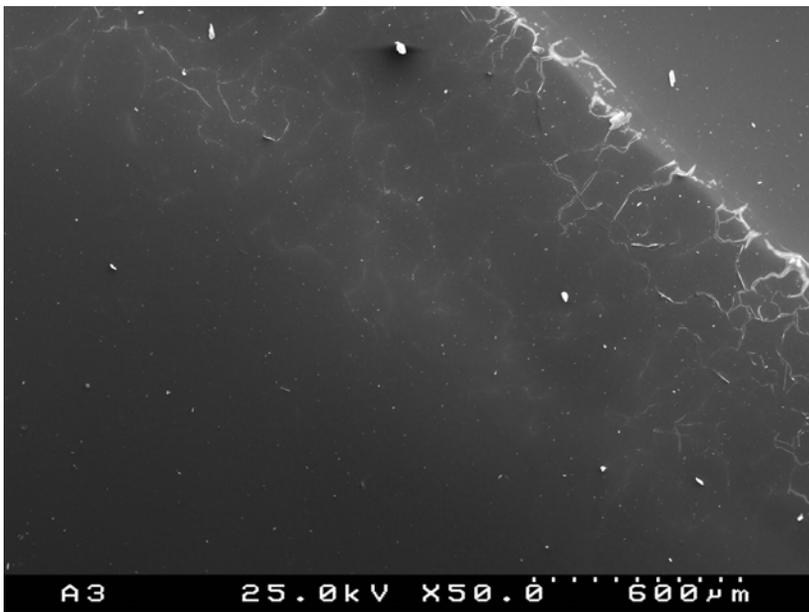
**Figure 2:**



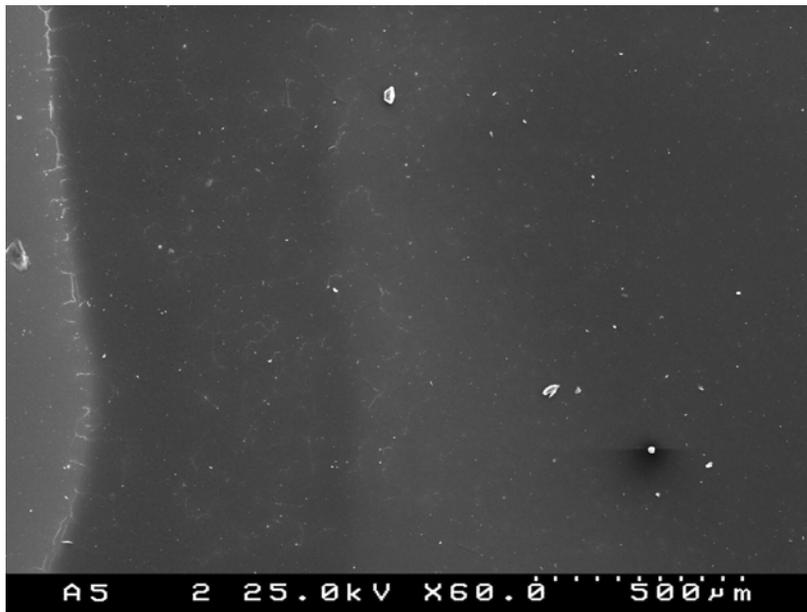
**Figure 3:**



**Figure 4**



**Figure 5:**



**Figure 6:**

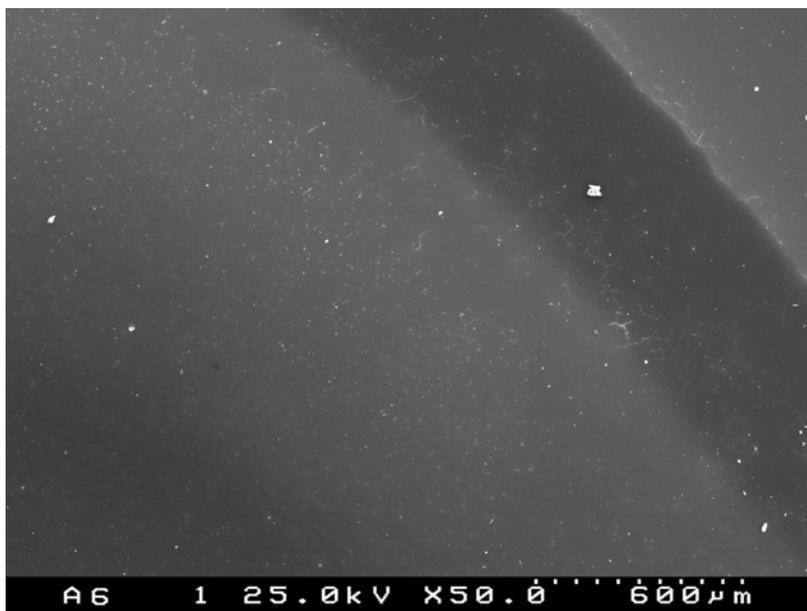


Figure 7:

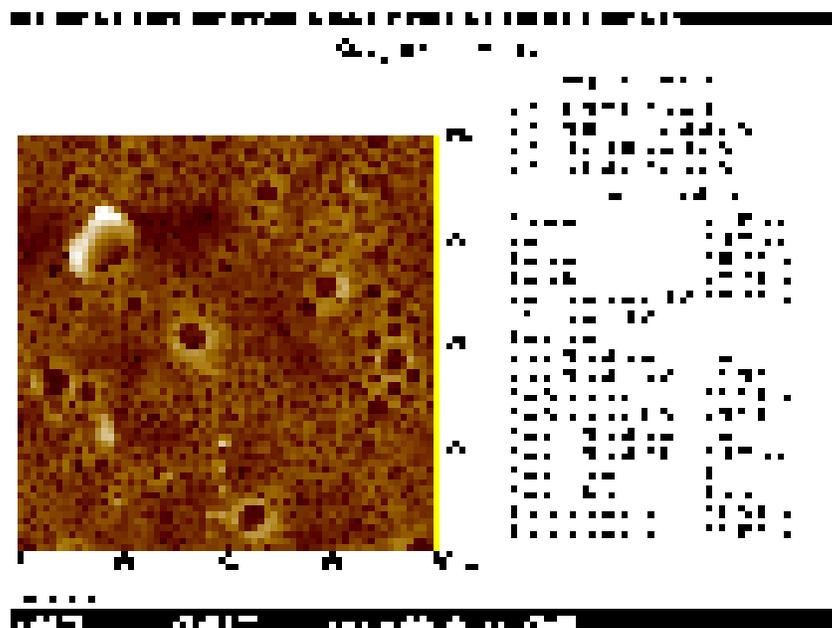
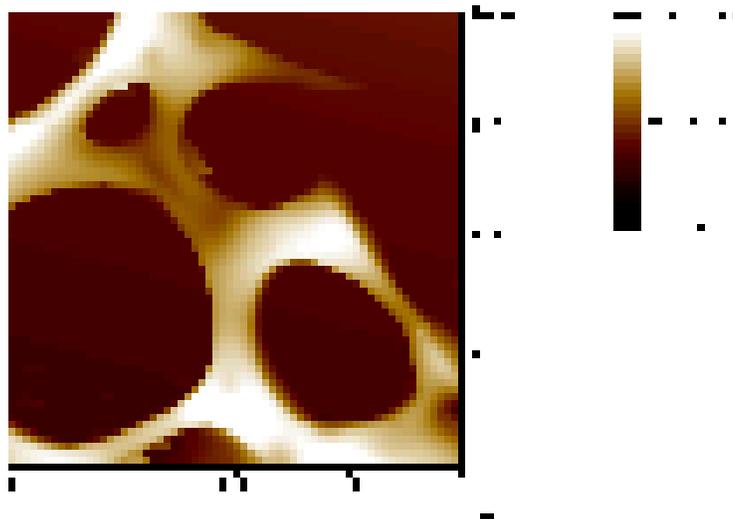
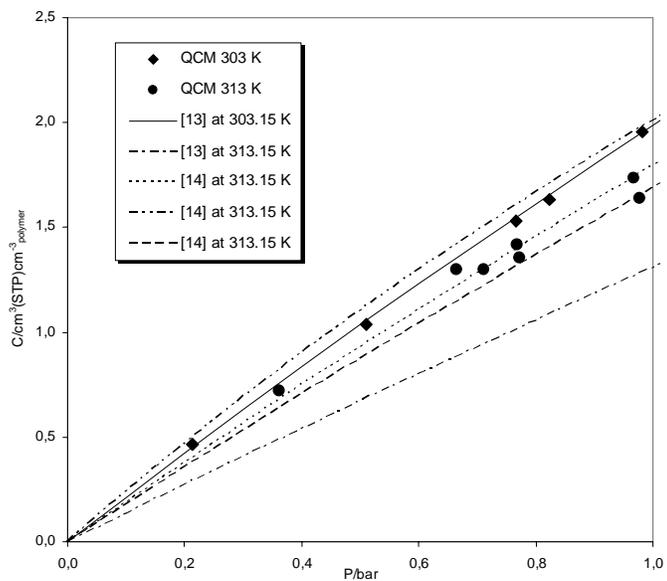


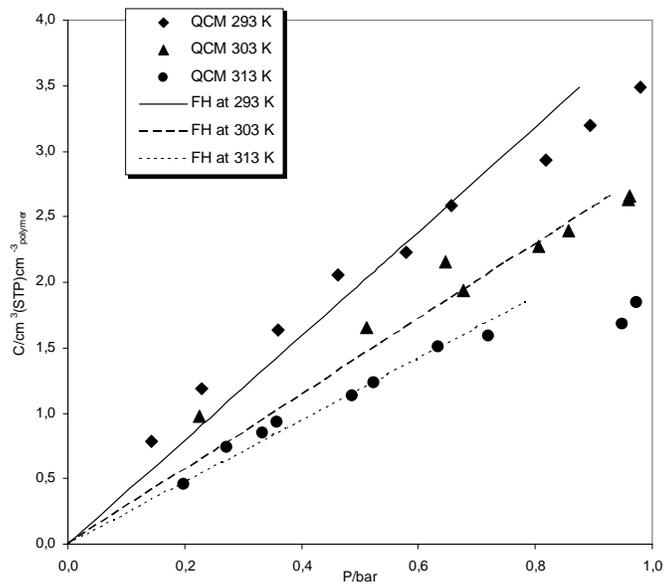
Figure 8:



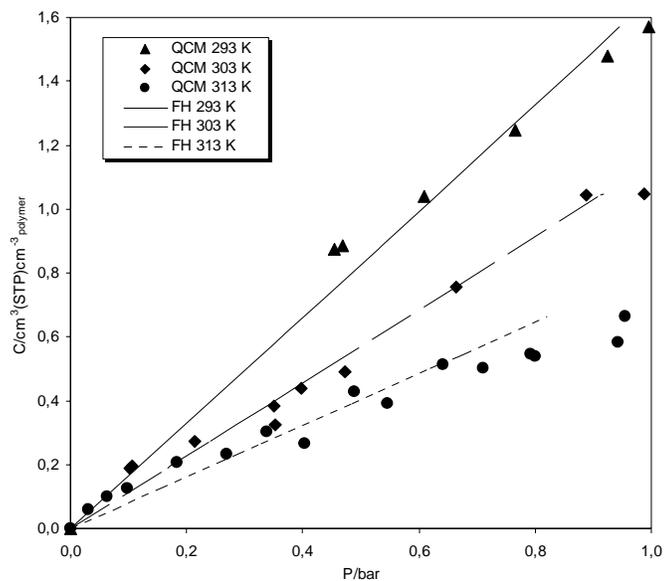
**Figure 9:**



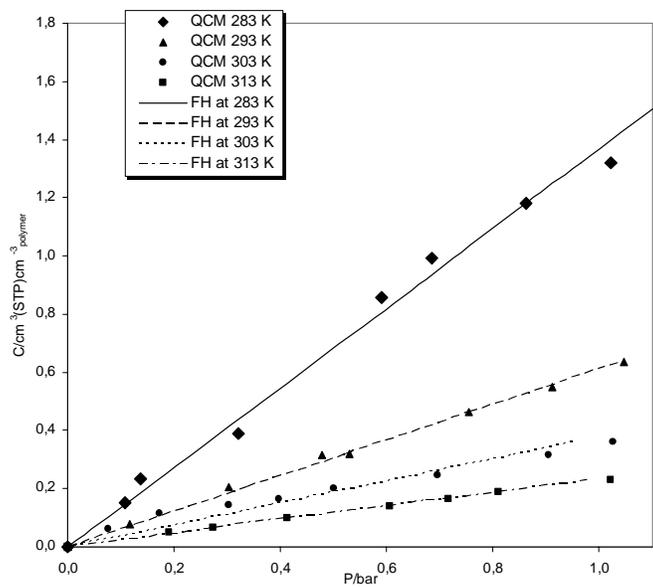
**Figure 10:**



**Figure 11:**



**Figure 12:**



**Figure 13:**

