High-pressure gas sorption in polymers using a quartz crystal microbalance.

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Abstract
The sorption of atmospheric gases in poly(lactic acid) (PLA) at high pressures was studied using a quartz crystal microbalance (QCM). This apparatus was built to support pressure up to 50 MPa and it was tested with carbon dioxide in atactic polystyrene (PS). The overall absolute average deviation (AAD) of the solubility of carbon dioxide from the literature [1,2] is less than 5 %. The solubility of carbon dioxide in PLA with two different contents of isomer L and D, 80:20 and 98:2, was studied over a temperature range from 303.2 to 323.2 K and up to 5 MPa is presented. The results obtained were correlated with the Flory-Huggins model with an overall AAD of 3 %.

Introduction
Currently, most of the polymeric materials are based on non-renewable fossil resources. Their disposal by incineration produces toxic gases and contributes to the global warming. The need for the development of a green plastic based on renewable sources has led to the development of PLA. The recent implementation of low cost production of PLA has led to its widespread availability and rising important questions regarding its permeation properties [3]. Low pressure studies are already available in the literature [4]. However, no data exists for gas sorption in PLA at high pressures.

The study of sorption of fluids in polymers at high pressures is motivated by the importance of these phenomena in a wide range of applications, such as polymer foaming processes, addition of additives, membrane separation processes and packaging. Gas sorption at high pressures has typically been determined by a number of other experimental methods, like manometric, gravimetric and chromatographic. Bonner and Cheng [5] demonstrated that the quartz crystal microbalance (QCM) technique could be used to measure gas solubility in polymers at high pressures. In this work, this technique was set up to study the solubility of carbon dioxide in PLA between 298 and 323 K and up to 5 MPa. The apparatus was calibrated with CO₂ in polystyrene and the average deviations from the literature [1, 2] are within 2.2 % at 338 K. The polymer deposition technique is similar to the one developed by Oliveira et al [4] for low pressures.

Materials
Atactic polystyrene was purchased from Polyscience, Inc. and poly(lactic acid) was provided by Cargill-Dow Polymers with two different L:D percentage, 80:20 and 98:2.
Carbon dioxide was purchased from Messer with a percentage purity of 99.998%. Dichloromethane was obtained from Riedel-deHaan with analytical reagent grade. Solvent and gases were used with no further purification.

The quartz crystals used were of 9 MHz base frequency, with golden electrodes of 5 mm and were supplied by Euroquartz, England.

Experimental

The carbon dioxide sorption isotherms were determined with a high pressure QCM, presented in the Figure 1. This apparatus was built to operate in the temperature range between 303 and 373 K and pressures from 0.1 MPa up to 50 MPa. The solubility cell, made of stainless steel 316, is placed in an oven capable to maintain the temperature within ±0.1 K. Two AT-cut quartz crystals of 9 MHz, the reference and the working crystal, are placed inside the solubility cell and are connected to two oscillators installed outside the cell. The oscillators are powered by a stabilized potential of 5.0 V and both the quartz crystal frequencies were measured using a 10 digits frequency counter Agilent 53131A. The temperature inside the cell is measured with a previously calibrated Pt100 connected to an Agilent 34401A multimeter. The solubility cell is connected to a high-pressure valve by a PEEK tube, to isolate the cell from any electrostatics charges. This valve also connects to the pressure sensor. A second valve is used to control the quantity of gas to be injected and to vacuum.

![Figure 1: The High-Pressure QCM apparatus](image)

The quartz crystal coating was presented in a previous paper [4]. The coated quartz crystal with PLA was heated up to 523 K at 2 K/min and cooled down to ambient temperature at 10 K/min. This procedure melts the polymer film, lowering the crystallization percentage to around 15%. The working and reference quartz crystal were outgassed for 2 h till the frequencies becomes stable. The gas was then introduced in the system and allowed to equilibrate with the polymer sample coated in the working crystal. Pressure readings were made with a pressure transducer from Setra, model 204, with a precision of 0.004 MPa.
Results

In Figure 2, the solubility results of carbon dioxide in atactic polystyrene at two temperatures, 307.46 and 337.79 and pressures up to 5 MPa are presented and compared with literature. The results are in good agreement with the literature showing an average absolute average deviation (AAD) around 8% at 308 K [1,6] and 2.2% at 338 K [1,2].

The solubility of carbon dioxide in poly(lactic acid) with L:D content of 80:20 and 98:2 was measured at 303, 313 and 323 K up to 5 MPa. The results are presented in Figures 3 and 4. According to previous studies, PLA 80:20 does not crystallize and PLA 98:2 has around 15% of crystallinity. Thus, the solubility results for PLA 98:2 were corrected by a factor of 1.15, considering that the crystalline regions do not accommodate any CO\textsubscript{2}. The solubility of carbon dioxide increases with pressure and decreases with temperature for both polymers, showing the same behavior found in the low pressure region [4]. For PLA 80:20, it was only possible to measure up to 2.5 MPa due to the large amount of film used. For higher pressures, the carbon dioxide mass sorbed stopped the crystal to vibrate. The solubility of carbon dioxide in PLA 98:2 is smaller than solubility in PLA 80:20. The same results were found bellow 0.1 MPa and it was attributed to the existence of crystallites in PLA 98:2 that probably do not allow a further relaxation of the polymer chain, fact that happened in PLA 80:20 that is totally amorphous. The dual-mode sorption model was used to correlate the experimental results with an AAD of 3 % for PLA 98:2 and 5 % for PLA 80:20.
Figure 3: Solubility of carbon dioxide in Poly(lactic acid) with L:D content of 80:20.

Figure 4: Solubility of carbon dioxide in Poly(lactic acid) with L:D content of 98:2.
Conclusions

A QCM for measuring high pressures solubilities of gases in polymers was constructed successfully. The apparatus was tested with the system carbon dioxide in polystyrene with and overall AAD around 5%. The solubility of carbon dioxide in poly(lactic acid) 80:20 and 98:2 was measured between 303 and 323 K and pressures up to 5 MPa. The role of crystallinity in the static free volume of the polymer was addressed.


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