

Simultaneous Measurement of Solubility, Diffusivity, Interfacial Tension and Specific Volume of Molten PCL/CO₂ Solutions

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The aim of this contribution is to present a new, purely-experimental approach allowing for the direct and concurrent determination of solubility, diffusivity, interfacial tension and specific volume of polymer/gas solutions, without relying on any theoretical assumption or equation of state at any stage of the properties evaluation. The new experimental set-up consists of a high pressure and temperature magnetic suspension balance equipped with a view cell where both gravimetric and interfacial tension measurements are performed at the same time. The pendant drop method (a molten polymer drop hanging from a rod) has been coupled with the classical gravimetric measurement performed on samples placed in a cylindrical crucible. In this experimental configuration, while the balance is measuring the weight change during sorption, a high resolution digital camera acquires the profile of the pendant drop, at the same temperature and pressure, and Axisymmetric Drop Shape Analysis (ADSA) is used to calculate interfacial tension. In particular, this coupling of the two techniques allows for the measure of the specific volume of molten polymer/gas solutions, a key property that is rarely measured and, conversely, is necessary for the accurate buoyancy correction, needed in both the gravimetric sorption experiment and in the ADSA. We herein illustrate this experimental set-up and related procedures and report results for poly(ϵ -caprolactone)/carbon dioxide system at 80°C and at pressures up to 4.2 MPa.

INTRODUCTION

In the last decades gas foaming technologies have been drawing increased attention since the extremely wide range of application of polymeric foams in several fields such as packaging, acoustic and thermal insulation, tissue engineering and separation [1]. Furthermore, the development of supercritical fluid foaming technique paved the way to the production of microcellular foams, which are characterized by improved mechanical and impact properties as compared to standard foams, since the very small dimension of pore diameter (smaller than 10 μ m) and a population density that is larger than 10⁹ cells per cm³ [2]. In fact, the density and the morphology of a foam determine the final properties of the foam itself. The fine tuning of processing conditions and the selection of the blowing agent allows for the tailoring of the structure of a foam and, consequently, of its final properties. Hence, a careful selection of the proper combination of polymer/foaming agent system and the proper coordination of the individual steps in the process are required in the manufacturing of foamed products. Several pieces of literature provide a qualitative frame for the investigation of the effect of working conditions (e.g. temperature and gas pressure) and thermodynamic and mass

transport properties of polymer/gas solutions of interest in this process on the kinetic of foam formation and on final pore structure of the foam [3-8]. In particular, the properties which play a role in the homogeneous bubble nucleation in polymeric thermoplastic foaming are: solubility, mutual diffusivity, interface tension and specific volume of the polymer/gas solution [3,8]. In a previous paper, we have presented a purely experimental approach allowing the direct and concurrent determination of all of these aforementioned properties of interest, without relying on any theoretical assumption or equation of state at any stage of the properties evaluation [9]. The proposed approach is based on the coupling of gas sorption and Axisymmetric Drop Shape Analysis (ADSA) measurements, allowing for the simultaneous measure of those properties in a single experiment. The new experimental set-up consists of a magnetic suspension balance equipped with a high pressure and temperature view cell where both gravimetric and interfacial tension measurements are performed synchronously. The pendant drop method (a molten polymer drop hanging from a rod) has been coupled with the classical gravimetric measurement performed on samples placed in a cylindrical crucible. In this experimental configuration, while the magnetic suspension balance is measuring the weight change during sorption of the sample placed in the crucible, the profile of the pendant drop, at the same temperature and pressure, is monitored with a high resolution camera, giving information about volumetric and shape changes.

Here we illustrate the results of our investigation performed with this new, fully experimental methodology on molten PCL/CO₂ solutions. The choice of this binary system is strongly connected to the recent increasing interest in 'eco-friendly' foaming processes, that involve two environmental issues: a biodegradable polymer matrix, that is used as scaffolds in tissue engineering and that also represent a valid alternative to common packaging materials, and the use of supercritical carbon dioxide as a blowing agent, that is an alternative to the traditional blowing agent that belong to the class of chlorofluorocarbons, that are known to contribute to seriously deplete the ozone layer.

Simultaneous measurements of solubility, diffusivity, interfacial tension and specific volume of PCL/CO₂ solutions have been performed at three different temperatures (80, 90 and 100°C) and at CO₂ pressures up to 4.2 MPa.

EXPERIMENTAL

Coupled measurement methodology and experimental setup. Simultaneous measurement is based on the coupling of ADSA and gas sorption experiment performed into a custom-designed apparatus. Information about sorption were gained from a sorption experiment: in a high temperature-high pressure view cell of a magnetic suspension balance (Rubotherm Prazisionsmesstechnik GmbH, Germany) the polymer contained in a crucible was continuously weighed. Concurrently, the investigation of the swelling of the molten polymer/gas solution was performed by the optical monitoring of a pendant drop placed in the same view cell, allowing the acquisition of drop shape and size to be used also for the evaluation of buoyancy and for the determination of interfacial tension (by means of ADSA). By properly combining the information collected in these two measurements, it is possible to obtain a fully experimental and reliable measure of solubility, diffusivity, specific volume and interfacial tension of the polymer/gas solution. Details of the methodology and of the whole data treatment chain are well described in a previous work [9].

Briefly, a custom-designed sample holder, consisting of a rod to which the polymer-gas solution drop is stuck (for ADSA) and a crucible containing a few grams of polymer-gas solution (for weight monitoring), was placed in the high temperature-high pressure view cell. The crucible hangs from the hook of the balance weight measuring unit while the rod is fixed

inside the cell. Two optical quality windows, mounted perpendicular to the axis of the cell, allow for the drop monitoring, that is performed by using an adjustable high resolution CCD camera, equipped with a modular zoom lens system. The optimal threshold for digitizing the drop image is achieved by a uniform bright background, that is provided by light emitting diodes. The CCD camera is connected to a computer, and commercial software is used to analyze drop profile. Details of the equipment and the description of the preliminary experimental phases (i.e. drop preparation, optimization of CCD parameters and image calibration) are reported in a previous paper [9].

Sorption and ADSA experiments were carried out by isothermal step-change pressure increments up to 4.2 MPa, at 80 °C, then 90 and 100 °C. Step-wise increments of the gas pressure (about 0.5 MPa steps) were performed with pre-heated gas, after the attainment of equilibrium sorption in the previous step. Concurrently, during each pressure step, image acquisition of the pendant drop was performed every 10 min.

Materials. Poly(ϵ -caprolactone), a biodegradable polymer with a melting point of ca. 60 °C, was supplied by Solvay Interlox Ltd. (PCL CAPA 6800) and used as received. High purity grade carbon dioxide and nitrogen were supplied by SOL (Italy).

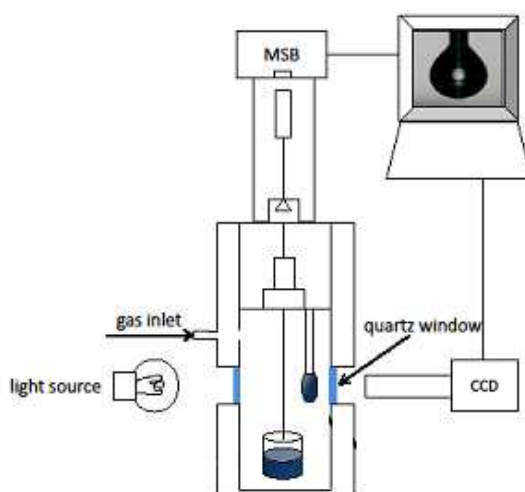


Figure1: Schematic illustration of experimental equipment used in the simultaneous measurement

RESULTS AND DISCUSSION

The sequence of data flow necessary to calculate solubility, diffusivity, specific volume and interfacial tension of the polymer/gas solution is summarized in the following. For further details, the reader is recommended to refer to Ref. 9.

First, from the sorption experiment, apparent solubility (i.e. not yet corrected to account for the effect of change of sample buoyancy due to sorption and compressive action of gas) was measured as a function of gas pressure. Concurrently, from ADSA, the volume of the pendant polymer/gas drop was computed. Having assumed that, at equilibrium, drop curvature has negligible effects on specific volume and local gas concentration [24-26] and, consequently, that the drop and the sample in the crucible reach the same volume per unit mass of starting polymer, it was possible to calculate the volume of the polymer/gas solution contained in the crucible, thus allowing for the correction of sorption data with the proper buoyancy force and, consequently, for the calculation of actual solubility and diffusivity of the polymer/gas solution. Gas sorption amount and solution volume per unit mass of polymer were then used

to calculate the specific volume of the polymer/gas solution. As a final step, this value was fed to the ADSA software to calculate the actual interfacial tension.

CO₂ sorption isotherm in molten PCL. The actual sorption isotherms of CO₂ in PCL at the three temperatures is shown in Figure 2. As expected, ω_{ACT} increases with the pressure and decreases with the temperature. It is important to highlight the importance of the effect of the swelling of the gas saturated polymer during sorption for the proper buoyancy correction and the evaluation of actual sorption data: in the whole temperature and pressure range, ω_{ACT} remains ca. 2% higher than ω_{APP} for each MPa of increase of CO₂ pressure (data not shown) [9], this error summing up to 10% ca. at the highest pressure investigated in this work.

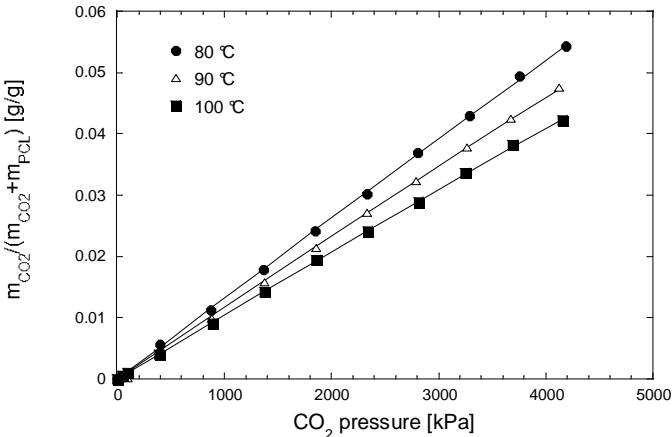


Figure 2: Actual sorption isotherms for the PCL/CO₂ systems

Evaluation of CO₂ mutual diffusivity. The values of \bar{D} of carbon dioxide in PCL are reported in Figure 3, as a function of CO₂ mass fraction. Within the investigated pressure range, it was found that \bar{D} exhibits a slight dependence on CO₂ concentration, showing a maximum value at a CO₂ mass fraction equal to 0.02

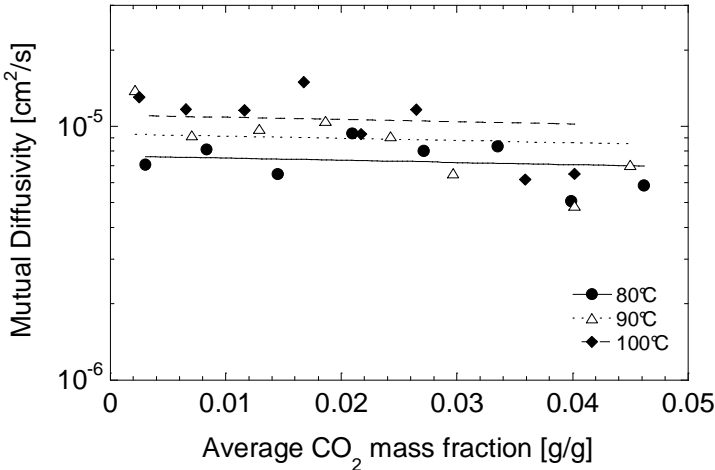


Figure 3. Mutual Diffusivity for the PCL/CO₂ solution as a function of CO₂ concentration.

Specific volume of PCL/CO₂ solutions. Figure 4 shows the specific volume of the PCL/CO₂ solutions as a function of CO₂ mass fraction. A peculiar trend has been highlighted for V_s : initially, it is found to decrease with gas concentration; then, for a CO₂ mass fraction approximately higher than 0.025, it starts increasing. In order to understand this behavior, it is important to consider that, when a molten polymer is exposed to a high-pressure gas, two mechanisms compete in affecting the specific volume: on one hand, the external gas exerts a mechanical action leading to the compression of the gas saturated polymer melt, on the other hand, gas solubilization is responsible to mass and volume increases. Finally, the overall variation of the specific volume of the solution is the result of the combination of both the mass increase and the volume changes. The final balance of mass and volume contributions giving the non monotonic profile of the effect of gas pressure on the specific volume.

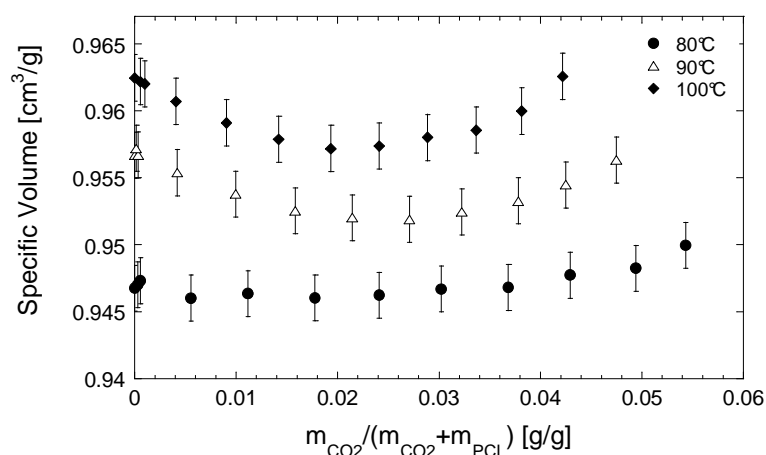


Figure 4. Specific volume of the solution PCL/CO₂ as a function of CO₂ mass fraction. Error bars evaluated by accounting for the error propagation in the whole measurement chain.

Interfacial tension. The interfacial tension of the polymer/gas solution, as evaluated on the basis of the described procedure, are shown in Figure 5 as a function of CO₂ concentration. In the selected experimental range, interfacial tension of the solution is found to be a nearly linear decreasing function of the CO₂ pressure. This trend of the interfacial tension with the gas concentration has already been reported elsewhere [10, 11] and is generally attributed to the plasticizing action of carbon dioxide on molten polymer. Also temperature drives the interfacial tension down: it was also estimated that, for the pure PCL, the interfacial tension decreases with a temperature coefficient of -0.059 mNm/°C as compared to -0.073 mNm/°C for the mixture (see inset of the Figure 5).

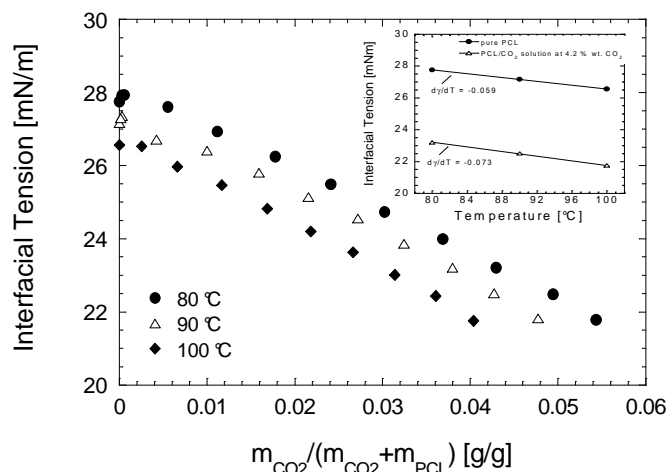


Figure 5. Effect of CO₂ concentration on the interfacial tension of PCL in CO₂. Inset: Effect of temperature on the interfacial tension of the solution PCL/CO₂ as a function of CO₂ mass fraction.

CONCLUSIONS

The simultaneous measurement of solubility, diffusivity, specific volume and interfacial tension of molten PCL/CO₂ solutions has been performed at three different temperatures and at CO₂ pressures up to 4.2 MPa. The coupling of the gravimetric measurement (performed using a magnetic suspension microbalance equipped with a pressurizable view cell) with the ADSA-based monitoring of a polymer pendant drop allows for a fully-experimental determination of the aforementioned properties, without resorting to any predictive modeling. The effect of temperature on CO₂ sorption isotherm and on interfacial tension was studied. Mutual diffusivity coefficients have been found to have a weak dependence on CO₂ concentration and to increase with temperature. Specific volume of the PCL/CO₂ solution was found to show a non monotonic profile than can be ascribed to the final balance of the two contribution of the effect of gas pressure (volume and mass changes). Interfacial tension of the solution was found to decrease linearly with gas concentration and with temperature.

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