Test Method

Simultaneous experimental evaluation of solubility, diffusivity, interfacial tension and specific volume of polymer/gas solutions

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Abstract

We present a new methodology, based on the coupling of a gravimetric method and Axisymmetric Drop Shape Analysis (ADSA), which allows for the simultaneous measurement of solubility, diffusivity, specific volume and interfacial tension of molten polymer/gas solutions. This approach, besides supplying information on useful material properties, significantly enhances the reliability of the values of the single measured properties. In fact, the evaluation of the specific volume of molten polymer/gas solutions can be used to accurately account for the buoyancy correction to be applied in both the gravimetric sorption experiment and in the evaluation of interfacial tension.

In this work, we illustrate the details of this combined technique highlighting the advantages of these simultaneous measurements and, as an example, we report the results obtained in the case of molten poly(()-caprolactone)/carbon dioxide solutions.

1. Introduction

Information on the properties of polymer/gas solutions is of great importance both for the development of theories of polymer based mixtures and for several technological applications including, among others, polymer recycling, durability of polymers in gaseous environments and gas foaming of polymers [1]. With reference to this latter technology, knowledge of solubility and diffusivity of gases in molten polymers and of interfacial tension of molten polymer/gas mixtures is of paramount importance to properly design the process and to optimize the foam structure [2].

Accurate evaluation of these properties is often affected by assumptions that are needed for a proper re-elaboration of the experimental measurements. Moreover, measurement of different properties of the polymer-gas mixture of interest, for example solubility and interfacial tension, are frequently performed in different types of apparatus with the consequence that the working conditions of the measurements (actual pressure and actual temperature of the sample) could be not very close, thus affecting also reliable correlations between the measured properties.

Regarding the experimental evaluation of solubility in polymers of gases at relatively high pressures, reliability of results often suffers from the unavailability of data on specific volume of the polymer/gas solutions, which are needed to correct sorption data for buoyancy effects [3] when measurement of gas sorption is performed by means of a microbalance operating in a controlled environment. In fact, when the polymer (either in the glassy [4,5] or in the rubbery [6] state) is exposed to a gaseous penetrant, its volume changes as a consequence of sorption of gas and the compressive action of pressure, thus modifying the buoyancy effect due to gravity. An incorrect evaluation of this effect in turn leads, unavoidably, to an inaccurate evaluation of the sorption data. A possible way to circumvent this difficulty is to perform an error analysis of experimental data performed by combining the
gravimetric measurements with the theoretical prediction of the equilibrium mixture density obtained from solution theories grounded on statistical thermodynamics (e.g. Sanchez and Lacombe [7–9] or Simha and Somcynsky [10] equations of state, to mention a few). However, the scarcity of experimental swelling data and, consequently, the actual validation of the effectiveness of the adopted models in correctly predicting the volume of the specific mixture under analysis, do suggest a certain caution in using these procedures [11]. As a consequence, a reliable evaluation of the amount of sorbed gas can only be obtained if a direct experimental evaluation of the specific volume of the molten polymer/gas mixture is available.

The determination of the interfacial tension of the separation surface between the molten polymer/gas mixture and the surrounding gas can be performed by using the well established Axisymmetric Drop Shape Analysis (ADSA), which is based on the evaluation of the shape of an axisymmetric pendant drop [12]. This technique consists of fitting the shape of an experimental drop to the theoretical drop profile according to the Laplace equation [13,14], properly modified to account for the action of the gravitational field [15–17]. Details of the recent advances in the numerical methods introduced to solve this non-linear differential problem can be found elsewhere [15–17]. The ADSA procedure provides the interfacial tension of polymer/gas solutions once the specific volume of the gas saturated polymer drop, the specific volume of the fluid surrounding it and the coordinates of several points of the drop profile are available. In order to evaluate the specific volume of the mixture, both reliable gas solubility data and total volume of the polymer-gas mixture are needed [18,19]. To this aim, the volume of the drop can be first obtained from image analysis of the drop itself by integrating the drop profile. Since the starting weight of the drop of neat polymer is known, this measured volume can be used to evaluate also the corresponding volume of the polymer/gas mixture contained in the weighing crucible, thus allowing the calculation of the related buoyancy lift. As will be discussed in detail in the following, the quantitative evaluation of this buoyancy effect allows for the reliable calculation of the actual amount of gas sorbed (from gravimetric measurements). At this stage, both the volume and the weight of the drop can then be estimated, thus allowing the evaluation of the requested equilibrium specific volume of the polymer-gas mixture at the pressure of interest. The specific volume of the surrounding fluid, which is also needed for ADSA, can be calculated either on the basis of reported data for the density of the fluid as a function of temperature and pressure or by concurrent direct measurement, with the microbalance assembly, of the weight of a non adsorbing metal piece of known-volume. Finally, the calculation of interfacial tension can be performed by ADSA, by coupling the information on specific volumes with the acquired drop profile.

From this brief description, it is evident how the interfacial tension and sorption measurements are strongly interconnected, and how a reliable evaluation of solubility and interfacial tension would certainly benefit from a concurrent volume and weight evaluation in a single experiment under identical experimental conditions.

Some recent pieces of scientific literature describe various strategies and experimental apparatus utilized to couple different measurements on polymer/gas solutions in order to evaluate specific volume and, hence, correct sorption as well as interfacial tension data. For instance, Wulf et al. [20] coupled sessile drop and pendant drop methods in a single experiment, using the former to evaluate interfacial tension and then, by inverting the ADSA algorithm, the latter to evaluate specific volume of the solution. Ohshima et al. used a modified magnetic suspension balance to measure the buoyancy force exerted on a platinum plate submerged in the gas/polymer solution [21]. However, the two approaches do not allow for the concurrent measure of gas sorption and interfacial tension. Park et al. [22] and Tomasko et al. [23], conversely, provided data on both sorption and interfacial tension on PS and PLGA, respectively, by performing independent measurements made with different apparatus for sorption and interfacial tension. It is worth noting that their approach relies upon data obtained with different apparatus and, hence, with working conditions that are not guaranteed to be really the same. More importantly, it is a “hybrid” method, as it is based on the combined use of experimental and theoretical evaluation of the specific volume of the polymer/gas solution from the Sanchez and Lacombe equation of state. As a consequence, as already mentioned, the reliability of the results is strictly dependent on the capability of the adopted equation of state to describe the thermodynamic behavior of the solution.

The aim of this contribution is to describe a different, purely experimental approach allowing the direct and concurrent determination of all of the relevant properties of interest (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. In fact, the proposed approach is based on a coupling of sorption and ADSA measurements, allowing for the simultaneous measure of those properties in a single experiment. 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. 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.

2. Experimental section

2.1. Coupled measurement methodology

Concurrent sorption measurement and ADSA have been performed by using a custom-designed apparatus. Gas sorption experiment was conducted by continuously
weighing the polymer contained in a crucible placed in a high temperature/high pressure (HTHP) view cell. At the same time, the optical monitoring of a pendant drop hanging from a rod placed in the same view cell was performed, based on the ADSA technique, allowing the acquisition of drop shape and size to be used for the determination of interfacial tension and to follow the swelling of the molten polymer/gas solution. By properly combining the information from the two measurements, it was possible to obtain a fully experimentally based and reliable measure of solubility, diffusivity, specific volume and interfacial tension of the polymer/gas solution. The sequence of data flow necessary to calculate the properties of the polymer/gas solution is summarized in the diagram shown in Fig. 1.

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 pressure) was measured as a function of gas pressure (box A). Concurrently, from ADSA, the volume of the pendant polymer/gas drop was computed (box B). It was 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. On this basis, it was possible to calculate the volume of the polymer/gas solution contained in the crucible, 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 at each gas pressure (box C). Having determined gas sorption amount and solution volume per unit mass of polymer, these results were then used to calculate the specific volume of the polymer/gas solution (box D). As a final step, this value was used as input to the ADSA software to perform the calculation of the actual interfacial tension (box E).

It is worthy of note that it would have been obviously preferable to perform both the weight and shape acquisition on the drop itself, having the rod directly mounted on the balance hook (rod-hook-balance coupling), to avoid the assumption reported above. However, several practical reasons make gravimetric measurements difficult when carried out directly on the pendant drop:

- the drop is very small in size and weight (order of 10 μL and 10 mg) and measurement of weight increase as a consequence of gas sorption is less accurate (nominal balance precision being equal to ±0.01 mg) as compared to the same measurement performed on the polymer contained in the crucible (sample weight of the order of 1g);
- the positional lability of the rod-hook-balance coupling is responsible for continuous oscillation of the hanging sample, especially at high gas pressures; these oscillations would impede a reliable optical monitoring of the drop shape. Moreover, the associated inertial forces would complicate the force balance used to determine the drop shape.

2.2. Experimental set-up and apparatus

The experiments were carried out by using a custom-designed measuring device, consisting of a rod to which the polymer solution drop is stuck and a crucible containing a few grams of polymer solution for weight monitoring (see Fig. 2 where a photograph of the two “sample holders” is shown), placed in a high-temperature and high-pressure view cell of a magnetic suspension balance (Rubotherm Prazisionsmesstechnik GmbH, Germany). In this type of balance, the electronics and weight measuring unit work at room conditions since they are fully separated from the measuring chamber where high pressure/temperature conditions can be safely used. The coupling

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![Fig. 1. Schematic illustration of data flow used in the coupled measurement.](image1)

![Fig. 2. Photograph of the pendant drop fixed to the rod and the crucible.](image2)
between the sample weighing equipment and the microbalance itself is operated via a magnetic system. Computer control ensures the correct positioning of the weighing assembly to allow the best magnetic coupling with the microbalance. In detail, the crucible hangs from the hook of the balance weight measuring assembly and the rod is fixed inside the cell in such a way as to avoid any interference with the gravimetric measurement and to allow the reliable continuous acquisition of the drop shape. The temperature inside the cell is controlled by a heating bath circulator and a temperature controller to an accuracy of ±0.05 °C. Two optical quality windows, mounted perpendicular to the axis of the cell, allow for the acquisition of the image through an adjustable high resolution CCD camera (BV-7105H, Appro), equipped with a modular zoom lens system (Zoom 6000, Navitar), installed on a manual XYZ lead screw stage. Light emitting diodes provide a uniform bright background, achieving an optimal threshold for digitizing the drop image. The CCD camera is connected to a computer, and commercial software (FTA32 Video 2.0, First Ten Angstroms) is used to analyze drop profile.

Drop preparation is a fundamental step in ADSA technique. First, size is a critical aspect: if the drop is too small and close to spherical shape, numerical problems may arise in the fitting procedure [27]; conversely, if the drop is larger than a critical value, it will neck and detach (“necking effect” [22]). Titanium rods were chosen as drop holders (diameter 1.789 mm). This paramagnetic material assures that no interaction establishes between the rod and the magnetic field produced by the balance electromagnetic coupling. The rod was polished to achieve a very smooth and planar bottom surface, necessary for good drop axisymmetry. Before drop creation, the rod was cleaned with ethanol to avoid contamination. The drop was formed in an oven, by melting a weighed amount of polymer on top of the polished surface of the rod, and then, turning around the system to avoid any polymer drainage. The oven was then cooled down to room temperature and, finally, the rod with the drop was fixed inside the HTHP view cell.

Before starting an experiment, image quality was enhanced by optimizing CCD parameters (such as working distance, zoom and contrast) and the optimal magnification was selected in order to achieve good drop profile edge detection. The pixel/µm calibration was then performed by evaluating the number of pixels corresponding to the rod diameter (actual diameter known to be 1.789 mm from digital micrometer measurement). Also, a preliminary validation with a calibrated steel sphere was performed to verify any presence of image distortion due to the CCD lens and optical windows. After having placed both the crucible containing the polymer and the rod with the drop in the HTHP view cell, sorption and ADSA experiments were carried out by step-change pressure increments up to 4.2 MPa, at 80 °C. In detail, during each pressure step, image acquisition of the pendant drop was performed every 10 min and drop volume was calculated. In order to achieve good accuracy in drop volume determination, the baseline between the rod and the drop was manually positioned. It was found (by a pixel-step shift of the baseline) that the calculated value of volume is affected by less than 0.15% error.

2.3. Materials

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

3. Data acquisition and treatment and results

In order to validate the ADSA technique, the interfacial tension of water at room temperature and at atmospheric pressure was first measured. The measured value (73.2 mN/m) was consistent with the data found in the literature (72.14 mN/m [28]). Furthermore, a preliminary investigation of the effect of drop size on the validity of ADSA result [27] was also carried out by performing experiments on molten PCL drops (at 80 °C and under vacuum). It was found that drops as small as 6 mg do induce a considerable error in fitting the drop profile; conversely, drops larger than 11 mg gave rise to the necking effect. In light of this analysis, 9 mg-sized drops were chosen for this investigation. Experiments were repeated five times in order to assess the reproducibility of the measure of interfacial tension, which was found to be within ±2.6%. A borosilicate glass rod has also been used to verify the effect of rod material on the interfacial tension measure on neat PCL. It was found that rod material had no effect on this measured value.

Results will be described in the following according to the measurement flow chart reported in the scheme of Fig. 1.

3.1. Apparent sorbed amount, \( \omega_{\text{APP}} \)

Sorption measurements were conducted by performing step-wise increments of the gas pressure (about 0.5 MPa steps) with pre-heated gas, after the attainment of equilibrium sorption in the previous step. Sample weight data were collected by the balance software and apparent gas weight fraction, \( \omega_{\text{APP}} \), at the end of the transient sorption, at each pressure, was computed according to the following expression:

\[
\omega_{\text{APP}} = \frac{W_{\text{APP}}}{W_0 + W_{\text{APP}}} \tag{1}
\]

where the apparent gas weight gain, \( W_{\text{APP}} \), is calculated as by eq. (2):

\[
W_{\text{APP}} = BR_e - BR_e^0 + \rho_{\text{gas}} (V_0 + V_h) \tag{2}
\]

Buoyancy correction was performed on the basis of CO\(_2\) density (\( \rho_{\text{gas}} \)) [29], volumes of crucible and hook (\( V_h \) and initial volume of the neat polymer sample (\( V_0^c \)). \( BR_e \) is the Rubotherm balance reading at equilibrium at each pressure (polymer/gas solution), \( BR_e^0 \) is the initial balance reading at equilibrium (under vacuum) and \( W_0 \) is the initial weight of the sample contained in the crucible (neat polymer) as measured by an analytical balance with a sensitivity of 10^{-3} g (Mettler AE240). The overall volume of crucible and hook and of the initial volume of the sample was previously
determined by evaluating the buoyancy effect in a blank test with helium. As already mentioned, the proper correction of buoyancy to account also for the volume change associated with solubilized gas and compression due to pressure isotropic stress was possible only after having performed the measurement of the volume of the molten polymer/gas mixture, as described below.

3.2. Evaluation of the volume of polymer/gas solution

Fig. 3 reports the volume of the drop, \( V_d \), as a result of the drop volume integration, performed by the ADSA software, at CO\(_2\) sorption equilibrium for each investigated pressure. Selected images of the drops taken at sorption equilibrium for several pressures are reported at the bottom of the volume plot. It is possible to note a 6% volume increase for the PCL/CO\(_2\) solution at 80 °C and 4.2 MPa as compared to the starting polymer volume.

As it has been described in the experimental section, the volume of the polymer/gas solution contained in the crucible, \( V_c \), at equilibrium, can be calculated as:

\[
V_c = V_d \frac{W_0^d}{W_0^c} \tag{3}
\]

where \( V_d \) is the volume of the drop, \( W_0^d \) is the initial weight of the polymer forming the drop (neat polymer) as measured by an analytical balance.

3.3. Actual solubility and diffusivity

Data from section A and B can now be used for a proper correction of apparent sorption data, to obtain \( \omega_{ACT} \), the actual gas weight fraction in the gas/polymer solution, as by eq. (4).

\[
\omega_{ACT} = \frac{W_{ACT}^{gas}}{W_c + W_{ACT}^{gas}} \tag{4}
\]

where the actual gas weight gain, \( W_{ACT}^{gas} \) is calculated as by eq. (5):

\[
W_{ACT}^{gas} = BR_e - BR_0^e + \rho_{gas}(V_c + V_b) \tag{5}
\]

The actual sorption isotherm, obtained on the basis of this correction, and the apparent sorption isotherm as determined on the basis of eq.(1) are compared in Fig. 4. We can note that the correction is as large as 8% at the highest pressure, where the swelling of the solution and, in turn, the correction due to the buoyancy effect are relevant.

The kinetics of sample weight increase in step-wise sorption experiments was analyzed to gather information on the value of carbon dioxide diffusivity as a function of carbon dioxide concentration in the molten polymer. Since the value of penetrant diffusivity could depend upon penetrant concentration, data should be properly analyzed to derive meaningful diffusion coefficients from step-change experiments. In this investigation, we adopted a method proposed by Vrentas et al. [30] to obtain the value of mutual diffusivity, \( D(C) \), at a penetrant concentration, \( C \), which is between the initial and final concentrations of each step sorption experiment. The method is based on the evaluation of an average mutual diffusivity \( \langle D \rangle \) from the initial rate of sorption. Since the system under investigation follows Fickian behaviour, the expression for \( D \) takes the form [31].

\[
D = \frac{\pi L^2}{4} \left( \frac{d(BR_t/BR_e)}{d(\sqrt{t})} \right)^2 \tag{6}
\]

where \( BR_t \) is the balance reading at time at time \( t \), \( BR_e \) is the balance reading at equilibrium and \( L \) is the actual sample thickness (sample is exposed to the gas phase on one side.

![Fig. 3. Drop volume vs. CO\(_2\) pressure at sorption equilibrium and sample images of the polymer solution drops taken at equilibrium at the reported CO\(_2\) pressure.](image)

![Fig. 4. Actual (square symbols) and apparent (empty circles) sorption isotherms. Error within 0.4%. Inset: difference between actual and apparent solubility.](image)
only). The value of \( \bar{D} \) calculated through eq. (6) corresponds to the value of the carbon dioxide mutual diffusivity, \( D(C) \) at an intermediate concentration, \( C \), the value of which can be calculated according to the procedures proposed by Vrentas et al. [30]. Since \( L \) increases as the sorbed amount of carbon dioxide increases due to sample swelling, the actual sample thickness used in this analysis was evaluated on the basis of the arithmetic average of initial and final measured equilibrium volume of the polymer-gas solution. Evaluation of diffusivity was based on balance reading, and the buoyancy correction was applied only to correct for the initial lift promoted by the additive gas entering the measuring cell during the step pressure increase. Actually, the lift changes also during sorption due to the weight and, in turn, volume increase of the polymer-gas mixture. However, in view of the slight weight increase during a step sorption, this correction was not applied. In Fig. 5, the diffusivity values, as obtained from eq. (6), are reported as a function of \( C \) mass fraction. In the inset, a Fick’s plot for a typical sorption experiment is also reported. It was found that, in the investigated \( C \) pressure range, \( \bar{D} \) had no significant dependence on \( C \) concentration, with an average value of \( 7.6 \times 10^{-6} \text{ cm}^2/\text{s} \).

### 3.4. Specific volume of the solution

Data from sections B and C allowed for the direct calculation of the specific volume of the polymer/gas solution, \( v_s \), as by eq. (7).

\[
v_s = \frac{V_c}{W_c} = \frac{V_c}{W_0 \left( 1 + \frac{1}{\alpha_{ACT}} \right)}
\]  

where \( W_c \) is the weight of the sample contained in the crucible.

Fig. 6 shows the results of test conducted at 80 °C up to 4.2 MPa. As a final step, these data were fed to the ADSA software to evaluate interfacial tension, as described in Section E.

### 3.5. Interfacial tension of the polymer/gas solution

Using the previously determined specific volume, the equilibrium value of interfacial tension was calculated at each value of \( C \) pressure by using the ADSA software. For a pendant drop in a gaseous environment, the mechanical equilibrium is ruled by the balance of gravitational forces, pressure and interfacial tension. Consequently, a modified Laplace equation has to be used to evaluate the interfacial tension. In particular, the ADSA software uses the Bashforth–Adams equation [see references [15-17] for details]. This equation requires knowledge of the specific volumes of the gas saturated polymer drop and of the fluid surrounding it, as well as the experimental drop profile. Fig. 7 reports the dependence of the interfacial tension of the polymer/gas solution on carbon dioxide concentration, as evaluated on the basis of this procedure. The observed decrease in the interfacial tension with the gas concentration has already been reported elsewhere [18,32] and was attributed to the plasticizing action of carbon dioxide on molten polymer. In the selected experimental range, interfacial tension of the PCL was a nearly linear decreasing function of the \( C \) pressure, with a reduction of almost 16% for a 5% b.w. \( C \)-polymer mixture as compared to neat molten polymer.
4. Conclusions

We developed a new methodology for the simultaneous measurement of solubility, diffusivity, specific volume and interfacial tension of molten polymer/gas solutions. It is based on the monitoring of weight increase of molten polymer/gas solution as a consequence of step-wise increase of gas pressure. Measurements were performed using a magnetic suspension microbalance equipped with a pressurizable view cell, coupled with the ADSA-based monitoring of a polymer pendant drop located in the same cell. Preliminary measurements performed on a reference fluid (water) and on neat molten PCL indicate the reliability and reproducibility of the interfacial tension measuring device. The coupling between gravimetric and optical measurements allows for a fully-experimental determination of the aforementioned properties, without resorting to any predictive modeling, as is typically done to evaluate the specific volume of the polymer/gas solution which is needed to calculate sorbed amount and interfacial tension. Using this approach, we were able to concurrently measure solubility, diffusivity, specific volume and interfacial tension of PCL/CO₂ solutions, at 80 °C at pressures up to 4.2 MPa.

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References


List of symbols

ω_{\text{app}}: apparent gas weight fraction in the gas/polymer solution
ω_{\text{act}}: actual gas weight fraction in the gas/polymer solution
ρ_{\text{gas}}: gas density
BR_{\text{t}}: initial equilibrium Rubotherm balance reading (under vacuum)
BR_{\text{s}}: equilibrium Rubotherm balance reading at each gas pressure
W_{\text{c}}: initial weight of the sample contained in the crucible (neat polymer) as measured by the analytical balance
W_{\text{c}}: weight of the sample contained in the crucible (polymer/gas solution)
W_{\text{d}}: initial weight of the polymer drop (neat polymer) as measured by the analytical balance
W_{\text{app}}: apparent gas weight gain
W_{\text{act}}: actual gas weight gain
V_{\text{d}}: initial volume of the drop
V_{\text{s}}: volume of the gas-saturated polymer drop
V_{\text{c}}: initial volume of the sample contained in the crucible (neat polymer)
V_{\text{c}}: volume of the sample contained in the crucible (polymer/gas solution) at equilibrium
V_{\text{h}}: volume of the sample holders (crucible + hook)
D(C): polymer/gas mutual diffusivity as a function of gas concentration,
C: gas concentration in the polymer/gas solution
D: average polymer/gas mutual diffusivity
L: actual sample thickness
BR_{\text{t}}: balance reading at time t
BR_{\text{w}}: balance reading at equilibrium
V_{\text{c}}: specific volume of the neat polymer
V_{\text{c}}: specific volume of the polymer/gas solution