

A comparison between gravimetric and in situ spectroscopic methods to measure the sorption of CO₂ in a biocompatible polymer

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Abstract

In situ ATR-IR spectroscopy was used to simultaneously measure the sorption and swelling of carbon dioxide at high pressures in a biocompatible acrylate copolymer poly(methylmethacrylate-co-ethylhexylacrylate-co-ethyleneglycoldimethacrylate), P(MMA-EHA-EGDMA). The ν_3 band of CO₂ dissolved in the polymer (at 2335 cm⁻¹) was used to calculate the sorption data and the polymer swelling was determined by analyzing the changes in the absorbance of the $\nu(\text{C}=\text{O})$ band (at 1730 cm⁻¹) of the polymer. Transmission spectroscopy in the near-IR region was also used to study the sorption of CO₂ in the polymer using combinational and overtone bands. The experiments were carried out in a pressure range of 2.0–12.0 MPa and in a temperature range of 27–40 °C. The data for CO₂ sorption in this polymer obtained by in situ spectroscopic methods have been compared to the data obtained by the gravimetric technique.

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1. Introduction

The knowledge of the phase behaviour of different polymers in supercritical media, mainly in supercritical carbon dioxide, has been widely studied in recent years. The manipulation of the physical properties of polymers as well as their selective control has become an area of interest in polymer science, particularly in polymer synthesis and processing using supercritical fluids [1].

It is well known that when a substance with a low molecular weight comes into contact with a polymer, sorption of this substance by the polymer often occurs. Carbon dioxide at high pressures can easily be dissolved in a polymeric matrix; the result is the swelling of the polymer since molecular forces between polymer chains are reduced. Thus, using supercritical (sc) fluid conditions is of great interest due to the possibilities of modifying the morphological and functional properties of polymers by swelling in scCO₂. Carbon dioxide is used as a temporary plasticizer to assist the

absorption of additives into glassy or rubbery polymers [2] as it facilitates mass transport in the polymer and enhances the kinetics of absorption of the diffusing substances. Another great advantage of supercritical media is that the commonly used fluids are often gases at room temperature and atmospheric pressure. They rapidly disappear from the polymer upon depressurisation of the system, leaving no toxic solvent residue in the polymer, and thus can be easily recovered upon release of pressure [2,3]. Finally, there is a drive towards the use of scCO₂ in processing and synthesis instead of using organic solvents because of the environmentally friendly properties of supercritical carbon dioxide. The knowledge of CO₂ sorption and polymer swelling is important not only for designing polymeric materials, but also for implementing a number of chemical processes, such as polycondensation, foaming, creation of polymer composites, impregnation, modification of polymers to name a few [4].

The impregnation of pharmaceutical compounds in polymeric matrices can take advantage of the increased diffusivity in CO₂-plasticized polymers. Plasticization results in an increase of free volume in the polymer matrix (since there is an increase in freedom of motion of polymer

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chains) enabling the entrapment of more drug than otherwise possible and more importantly the achievement of molecularly dispersed drug in the polymer matrix [5,6].

Supercritical fluid impregnation of bio-active substances into polymeric optical lens or personal care products has been proposed [7]. However, prior to studying such impregnation processes we need to analyse the behaviour of polymeric matrices subjected to scCO_2 . In this paper, we describe combined gravimetric and spectroscopic study of CO_2 sorption and swelling of one specific polymer which is suitable as a matrix for optical lens. A biocompatible acrylate copolymer, poly(methylmethacrylate-co-ethylhexylacrylate-co-ethyleneglycoldimethacrylate) or P(MMA–EHA–EGDMA), has been proposed by Mariz [8] as a possible matrix for controlled release systems designed for ophthalmic applications.

In situ spectroscopy has proven to be one of the most powerful techniques to give an insight into interactions between CO_2 and polymers at a molecular level. In addition, in situ spectroscopy also provides quantitative information on sorption and swelling of polymers and impregnation of polymers under high pressure [9].

Sorption and swelling of polymers are frequently measured using different methods. Literature data on the sorption of carbon dioxide into polymers refer various apparatus and methods to perform the measurements. The use of a quartz-crystal microbalance and a simple in situ gravimetric method or a barometric method are the most commonly used [10,11]. Transmission IR spectroscopy has also been used to measure CO_2 sorption in polymers [12,13]. The direct optical observation of the sample's dimensions is usually widely used to study polymer swelling [1].

A new method based on attenuated total reflectance (ATR)-IR spectroscopy has been developed by Flichy et al. [14] for simultaneous measurement of sorption and swelling. At different operational conditions a single spectrum of the polymer and the gas sorbed in the polymer is acquired. A change in the spectral band of the polymer corresponds to a change in the polymer density and therefore to a volume change (swelling of the polymer). On the other hand, the absorbances of IR bands of the gas correspond to the sorption (solubility) of the gas in the polymer. To avoid the overlapping of the polymer–gas mixture spectrum with that of the pure gas, a good contact between the polymer sample and the ATR crystal is essential. Recently, near-IR transmission spectroscopy was used in situ to calculate both CO_2 sorption and swelling for liquid polymers [15]. In this paper, near-IR spectroscopy was utilised to study CO_2 sorption in solid polymer and to validate the data obtained by ATR-IR spectroscopy.

In this work, the gravimetric method was compared to two in situ spectroscopic techniques used to measure the sorption of carbon dioxide in P(MMA–EHA–EGDMA). The gravimetric method is advantageous in the simple experimental procedure, whereas the spectroscopic techniques offer the advantage of in situ measurements with

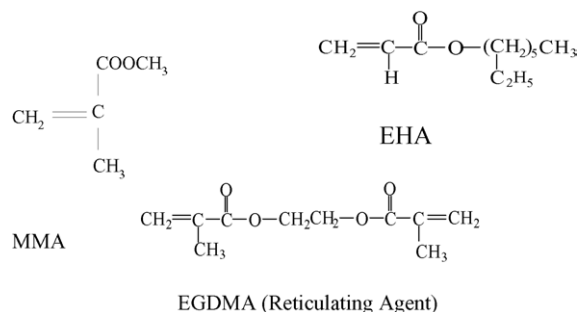


Fig. 1. The three monomer constituents of P(MMA–EHA–EGDMA).

easy operation by means of good accuracy and insight on molecular interactions between CO_2 and the polymer.

2. Experimental

2.1. Materials

Films of P(MMA–EHA–EGDMA) with ~ 0.15 and 1 mm thickness and ~ 18 mm diameter were kindly supplied by H.C. de Sousa (Universidade de Coimbra, Portugal). Copolymer P(MMA–EHA–EGDMA) were prepared by adding 40% of MMA, 60% EHA and 7.5% (wt% of total mass of MMA+EHA) of the reticulating monomer, EGDMA. The value of T_g of this copolymer is -4°C . Carbon dioxide (99.998 mol%) was supplied by BOC. All products were used without further purification. Three monomer constituents of this copolymer are shown in Fig. 1.

2.2. Apparatus

2.2.1. Gravimetric measurements

A simple gravimetric procedure, similar to the one described by Berens et al. [2] was performed. The high-pressure apparatus is schematically presented in Fig. 2.

A high-pressure stainless steel cell was immersed in a thermostatic water-bath, heated by means of a controller that maintained temperature within ± 0.1 K. The sample

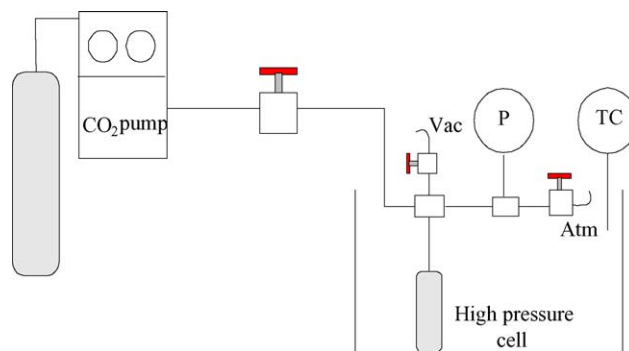


Fig. 2. Schematic diagram of the high-pressure sorption apparatus (P—pressure transducer; TC—temperature controller).

was loaded in a small stainless steel basket and the initial weight was recorded. The basket was placed inside the cell, which was then evacuated for 15 min. Carbon dioxide was pumped into the cell using a pneumatic compressor until the desired pressure was attained. The pressure inside the cell was measured with a pressure transducer within ± 0.5 bar. The samples were submitted to high pressure for 5 h. After impregnation, the vessel was quickly depressurised and the basket with the sample was transferred to the balance for recording weight changes during desorption at atmospheric pressure. The experiments were carried out in a pressure range from 2.0 to 20.0 MPa and in a temperature range from 27 to 40 °C.

2.2.2. ATR-IR spectroscopy

A heated “Golden Gate” ATR-IR accessory (diamond crystal with an incident angle of 43°, ZnSe focusing lenses) was used to determine the sorption and swelling of carbon dioxide in the polymeric film. A specially designed “covering-cap” high-pressure cell, compatible with the single-reflection ATR accessories (Specac Ltd., UK) was used [14].

2.2.3. Transmission spectroscopy

A high-pressure optical cell with two CaF₂ windows was used to study the sorption of carbon dioxide in the polymer [15]. The path length of the cell was 5 mm. The experiments performed with this cell were carried out only at room temperature (ca. 27 °C) and in a pressure range of 2.0–10.0 MPa. The high-pressure cells, for both ATR-IR and transmission measurements, were pressurised by means of a manual syringe pump (HIP, Model 62-6-10).

All the spectra were recorded with the use of a Bruker Equinox 55 FT-IR spectrometer with a mercury–cadmium–telluride (MCT) detector [14]. The resolution was 4 cm⁻¹. Equilibrium was assumed when the observed band absorbance remained constant for more than 30 min.

2.2.3.1. Choice of spectral bands. The choice of spectral bands depends on whether ATR-IR or transmission near-IR measurements are performed.

For the ATR-IR measurements, the analysis of the spectra was focused on the ν_3 band of CO₂, which is characteristic of carbon dioxide sorbed in the polymer (at 2335 cm⁻¹), and the carbonyl band of the polymer (at 1730 cm⁻¹) to determine the swelling. The carbonyl band was chosen because it was easier to quantify as it is an isolated band (Fig. 3).

In the case of near-IR spectroscopy (transmission mode), due to the dense fluid phase, very strong absorbances were observed in the mid-IR spectral region. To overcome this problem, the $\nu_1 + 2\nu_2 + \nu_3$ (4965 cm⁻¹) band of CO₂ in the near-IR region (>4000 cm⁻¹) was used for measuring the sorption of CO₂ in the polymer. Although this band of the fluid phase CO₂ surrounding the polymer film is quite strong, it remains on-scale (Fig. 4) allowing the spectral subtraction.

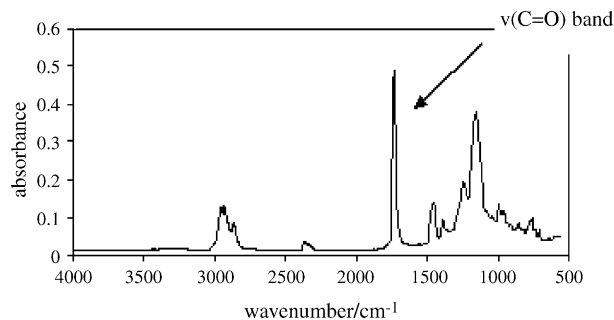


Fig. 3. The ATR-IR spectra of P(MMA–EHA–EGDMA).

The procedure was similar to that described by Brantley et al. [13].

3. Results and discussion

3.1. CO₂ sorption

In regards to gravimetric measurements, the amount of carbon dioxide present in the polymer was evaluated from the data analysis using diffusion equations. The data set describing the mass of CO₂ present in the samples as a function of time after the pressure release, recorded by the balance, was exported to an ASCII file, as described elsewhere [16]. An equation derived from Fick’s second law of diffusion is used to model the experimental data and to estimate the sorption of carbon dioxide. This equation describes the time dependence of the diffusing substance out of the sample, which in this study was a slab of thickness l [4,17–19].

$$M(t) = \frac{8M_0}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\left[\frac{(2n+1)\pi}{l}\right]^2 Dt}$$

where D is the diffusion coefficient, l the film thickness, $M(t)$ the mass of diffusing substance at time t and M_0 is the mass of diffusing substance at $t = 0$ which is the time when cell was depressurised.

In the case of spectroscopic studies, the concentration of carbon dioxide in the polymeric sample was determined by

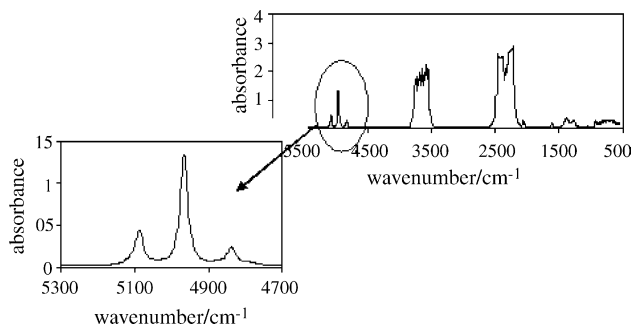


Fig. 4. Transmission IR spectra of high-pressure CO₂ at 10 MPa showing the near-IR region of the spectrum and the $\nu_1 + 2\nu_2 + \nu_3$ (4965 cm⁻¹) band of CO₂.

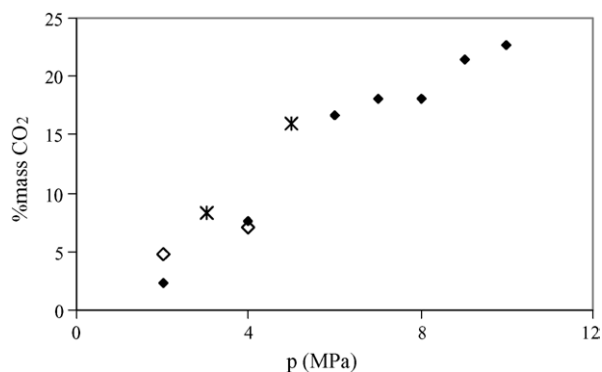


Fig. 5. Sorption of CO₂ in P(MMA–EHA–EGDMA) at 27 °C (✱) gravimetric measurements (◇) ATR-IR spectroscopy and (◆) transmission spectroscopy.

the Beer-Lambert law:

$$A = \varepsilon cl$$

where A is the absorbance, ε the molar absorptivity, c the concentration of sorbed CO₂ and l is the path length.

The integrated molar absorptivity of combination bands can be considered independent of the carbon dioxide density in the range of pressures and temperatures studied, as it has been demonstrated elsewhere [20], and its value is ca. 1×10^4 cm/mol for the near-IR measurements.

In mid-IR experiments, the molar absorptivity based on the peak absorbance of the ν_3 band of carbon dioxide dissolved in other solvents at high-pressure can be used (ca. 1×10^6 cm²/mol [14]).

In the case of near-IR experiments, the path length corresponds to the thickness of the polymer. Regarding the ATR-IR experiments, a thickness that would give the same absorbance in transmission is required in order to apply the Beer-Lambert law. This constant is expressed in terms of the effective thickness of unpolarized light and can be calculated based on the refractive index of the crystal, the refractive index of the sample, the angle of incidence and the wavelength of the incident beam. With a simple computer program (“CrystalCalc”—Harrick Scientific Corporation), it was possible to calculate this effective thickness. The estimated refractive index of the sample is 1.45 (this was achieved with measurements using diamond and Germanium crystals following procedure by Flichy et al. [14]) and it was considered to be constant during experiments. The refractive index of the crystal diamond is known to be 2.4, the incident angle

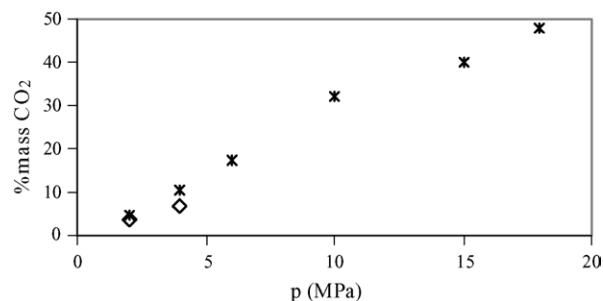


Fig. 6. Sorption of CO₂ in P(MMA–EHA–EGDMA) at 40 °C (✱) gravimetric measurements and (◇) ATR-IR spectroscopy.

was estimated to be 43° and the wavenumber of the incident beam corresponding to the ν_3 band of CO₂ is equal to 2335 cm⁻¹.

The results of the CO₂ sorption experiments at the different operational conditions are shown in Figs. 5 and 6.

Experimental limitations did not allow the measurement of sorption of carbon dioxide at higher temperatures using the transmission cell. ATR-IR measurements for higher pressures are not presented because the contact between the film and the diamond ATR crystal was lost to collect the spectra. The success of Flichy et al. [14] study on ATR-IR measurement of sorption and swelling was based on the use of a liquid polymer which inherently had a good contact with a diamond crystal.

The sorption isotherms presented as a function of pressure indicate an increase in the solubility with increasing pressure. For the same pressure, the sorption decreases with increasing temperature. This kind of behaviour has been reported by other authors [15,21,22] and is expected as there are some exothermic interactions between carbon dioxide and some polymers [23]. The seeming inflection point in the trend of data in Fig. 5 cannot be a result of the polymer glass transition, as observed in some previous studies [11], because this polymer is in a rubbery state due to its low glass transition temperature. Our combined approach to measure sorption shows that there is a good agreement between all three methods at low pressures (up to 5–6 MPa). However, the gravimetric approach provides somewhat higher values for CO₂ sorption compared to in situ near-IR spectroscopy. We believe that the reasons for discrepancy are related to the approximation of Fickian diffusion used in the gravimetric calculations which led to the overestimation of CO₂ sorption. This also points out the intrinsic advantage of the in situ spectroscopic method in that it does not require removal

Table 1

Sorption and swelling measurements using gravimetric, transmission and ATR-IR methods at 27 and 40 °C under a range of pressures

| Temperature (°C) | Pressure (MPa) | Mass sorption (%) | | ATR-IR | |
|------------------|----------------|-------------------|--------------|-------------------|--------------|
| | | Gravimetric | Transmission | Mass sorption (%) | Swelling (%) |
| 27 | 2 | | 2.3 | 4.7 | 7.7 |
| | 4 | | 7.6 | 7.1 | 18.5 |
| 40 | 2 | 4.9 | | 3.6 | 15.4 |
| | 4 | 10.3 | | 8.9 | 25.4 |

of the sample with consecutive approximation of the amount of sorbed CO₂. It is clear that this effect would be stronger at higher pressures, and thus a greater discrepancy between gravimetric and spectroscopic results.

The results of the experiments performed are summarized in Table 1.

3.2. Polymer swelling

Polymer swelling can be determined from the ATR-IR experiments. The change of the absorbance of the carbonyl band of the polymer is a measure of the polymer swelling. As the pressure increases, there is a decrease in the polymer band absorbance as a result of the polymer swelling. Assuming that the molar absorptivity is constant, the absorbance of the polymer band follows the Beer-Lambert law:

$$A_0 = \varepsilon c_0 l_0, \text{ before exposure to gas;}$$

$$A = \varepsilon c l, \text{ during exposure to carbon dioxide.}$$

Considering that the sample occupies a volume V before exposure to carbon dioxide and $V + \Delta V$ during exposure, the swelling (S) can be defined according to the following equation:

$$\frac{c_0}{c} = \frac{V + \Delta V}{V} = 1 + \frac{\Delta V}{V} = 1 + S$$

Combining this equation with the Beer-Lambert law, the degree of swelling is defined as:

$$S = \frac{A_0 l}{A l_0} - 1$$

The swelling can be calculated directly from the measurement of the absorbance of the band at 1730 cm⁻¹ because the path length has been considered to be constant with increasing pressure.

The swelling was measured at 27 and 40 °C for 2.0 and 4.0 MPa and the data are presented in Table 1.

4. Conclusions

The sorption of carbon dioxide in the biocompatible polymer of interest to ophthalmic applications, P(MMA–EHA–EGDMA), was measured using three different techniques, a gravimetric method and two in situ spectroscopic techniques (ATR-IR and transmission spectroscopy). This is first time that three different methods have been applied to study CO₂ sorption and swelling for the same polymer sample. It is shown that the gravimetric method, using a simple procedure, gives consistent data when compared to in situ spectroscopic methods at relatively low pressures of CO₂. The ATR-IR approach was challenging to use for this polymeric sample due to the contact issues with ATR crystal, and therefore no measurements at higher pressures were presented. However, the ATR-IR method provided quantitative information about polymer swelling which

was not accessible via the two other approaches. The in situ near-IR spectroscopic method provided reliable information on CO₂ sorption over the pressure range studied. Information for CO₂ sorption and swelling in the studied biocompatible polymer will be useful for optimization of impregnation processes of this material with bioactive substances.

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