



In situ FTIR micro-spectroscopy to investigate polymeric fibers under supercritical carbon dioxide: CO₂ sorption and swelling measurements



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ABSTRACT

An original experimental set-up combining a FTIR (Fourier Transformed InfraRed) microscope with a high pressure cell has been built in order to analyze in situ and simultaneously the CO₂ sorption and the polymer swelling of microscopic polymer samples, such as fibers, subjected to supercritical carbon dioxide. Thanks to this experimental set-up, we have determined as a function of the CO₂ pressure (from 2 to 15 MPa) the CO₂ sorption and the polymer swelling at $T=40^{\circ}\text{C}$ of four polymer samples, namely PEO (polyethylene oxide), PLLA (poly-L-lactide acid), PET (polyethylene terephthalate) and PP (polypropylene). The quantity of CO₂ sorbed in all the studied polymers increases with pressure. PEO and PLLA display a significant level of CO₂ sorption (20 and 25% respectively, at $P=15\text{ MPa}$). However, we observe that a lower quantity of CO₂ can be sorbed into PP and PET (7 and 8% respectively, at $P=15\text{ MPa}$). Comparing their thermodynamic behaviors and their intrinsic properties, we emphasize that a high CO₂ sorption can be reached if on one hand, the polymer is able to form specific interaction with CO₂ in order to thermodynamically favor the presence of CO₂ molecules inside the polymer and on the other, displays high chains mobility in the amorphous region. PLLA and PEO fulfilled these two requirements whereas only one property is fulfilled by PET (specific interaction with CO₂) and PP (high chains mobility). Finally, we have found that for a given CO₂ sorption, the resulting swelling of the polymer depends mainly on its crystallinity.

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1. Introduction

Replacing the traditional organic solvents with supercritical carbon dioxide (scCO₂) is currently an attractive field in polymer processing [1–3]. Actually, scCO₂ possesses numerous advantages particularly a high diffusivity, a low cost, a polymer plasticizing effect and a low environmental impact. Moreover, it enables to recover a final material free of any solvent residues as the solvent can be easily removed by depressurization. Thus, ScCO₂ has been widely used in polymer processing and in particular as a blowing agent to create foams [4–6], in extraction of molecules from polymeric matrix [7], in impregnation of solute such as drugs and dyes [8,9], in polymer blends [10,11] and in creation of polymer particles from molten polymer [12].

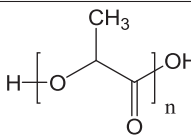
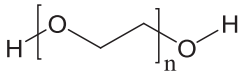
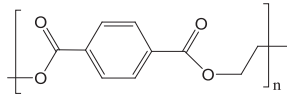
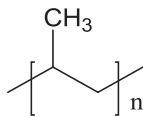
In order to design and optimize these processes, it is necessary to investigate the behaviors of the polymers when subjected to high-pressure CO₂ and particularly the amount of CO₂ sorbed into the polymer and the swelling, since these two parameters directly influence the processes efficiency. As an example, high CO₂ sorption and high polymer swelling will facilitate and accelerate the impregnation or extraction processes [8].

To investigate the thermodynamic properties of polymers subjected to high-pressure CO₂, different technics are frequently used in the literature. These methods can be classified in two families. The first family is composed of technics that only measure the CO₂ sorption, such as the gravimetric technic [13,14] which is the simplest and main technic implemented, the Quartz Crystal Microbalance technic [15,16] and the pressure decay method [17]. All these methods need to be coupled with an optical measurement or an equation of state (for example Sanchez-Lacombe) to estimate polymer swelling.

The second family is constituted by the spectroscopic technics, which enable to determine simultaneously and in situ the

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Table 1
Physical and chemical properties of the studied polymers.

Polymer	Structure	Density (g cm ⁻³)	Crystallinity, χ (%)	E (MPa)	T_g (°C)	T_m (°C)
PLLA		1.25	52	4930	61	168
PEO		1.21	70	Low	-55	69
PET		1.38	43	8578	79	254
PP		0.91	41	3858	-16	167

amount of CO₂ into the polymer and the swelling. Moreover, the spectroscopic technics are suitable to have an insight of molecular interactions. Nowadays, the two main spectroscopic technics that are generally used are the Near and mid-FTIR (Fourier Transformed InfraRed) and ATR-IR (Attenuated Total Reflectance InfraRed) spectroscopies. FTIR spectroscopy is more adapted to liquid and/or large samples (cm³) [18–21]. Besides, ATR-IR spectroscopy requires melting the samples to shape it into films in order to ensure a good contact between the polymer and the crystal [22]. Consequently, the melting step changes the polymer structure and so its behavior under scCO₂.

In the literature, a large part of the studied polymers processed with supercritical carbon dioxide has implied thin polymeric films or fibers (50–1000 μ m) [22–29]. However, FTIR and ATR-IR technics are not well suited to analyze directly thin film or fibers without changing their shape. Thus, in order to allow the in situ analysis of the CO₂ sorption and polymer swelling of microscopic polymer samples (~5–500 μ m), we have developed a new and original method. The experimental setup consists in a FTIR microscope coupled with a high pressure cell that enables to operate up to 15 MPa and under a controlled temperature. As the FTIR microscope technic leads to adjustable size and focus of the IR beam, this technic is adapted to analyze microscopic scale samples.

The present study is part of a project that aims at impregnating various sutures (150 μ m diameter) with anti-inflammatory drugs using scCO₂. Thanks to the newly developed technic, we determine as a function of the pressure and at 40 °C, the swelling and the CO₂ quantity adsorbed in various polymeric sutures made of PLLA, PET and PP. A PEO sample is selected to validate the developed experimental setup and data processing. The thermodynamic behaviors of these four polymers are compared and discussed regarding to their physical and chemical properties.

2. Experimental details

2.1. Materials

Carbon dioxide N45 (purity 99.95%) was supplied by Air Liquide. PEO (Mw = 1 000 000 g mol⁻¹) was purchased from Sigma. PET, PP and PLLA fibers (diameters of 90, 150 and 150 μ m, respectively) were purchased from Covidien. Structures and properties of the polymers used in this study are displayed in Table 1.

2.2. Infrared micro-spectroscopy

2.2.1. Experimental set-up

A schematic representation of the experimental set-up is presented in Fig. 1. The set-up consists in a FTIR microscope working in transfection mode coupled with a high pressure cell. The infrared absorption measurements were performed using a ThermoOptek interferometer (type 6700) equipped with a global source and KBr/Ge beamsplitters coupled to an Infrared microscope (NicPlan, Nicolet) equipped with an MCT (Mercury Cadmium Telluride) detector in order to investigate the spectral range (400–7500 cm⁻¹). Single beam spectra recorded with a 2 cm⁻¹ resolution were obtained after the Fourier transformation of 50 accumulated interferograms. The home-made stainless steel was equipped with a sapphire (or CaF₂) window and a mirror in between the polymer sample was maintained as shown in Fig. 1. A 100 μ m Kapton[®] foil was placed between the window and the cell body to compensate for any imperfections between the two surfaces. Two thermocouples were used, the first one located close to a cartridge heater for the temperature regulation and the second one close to the sample area to measure the temperature of the sample with an accuracy of about 1 °C. The cell was connected via a stainless steel capillary to a hydraulic pressurizing system, which permits the pressure to be raised up to 50 MPa with an absolute uncertainty of ± 0.1 MPa and a relative error of $\pm 0.3\%$. The stabilization of the operating conditions was controlled by recording several consecutive spectra. The experiments were performed at fixed temperature of 40 °C and in a pressure range from 2 to 15 MPa. To take into account distinct polymer geometries, the size of the IR beam was tuned thanks to a rectangular diaphragm with adjustable opening.

2.2.2. Experimental procedure

First of all, the polymeric sample (fiber or film) was fitted into the cell and held in contact between the window and the mirror thanks to a spring disposed between the mirror and the bottom of the cell as one can see in Fig. 1. The mirror used was made of stainless steel polished to obtain a good reflection of the IR beam. In this set-up, the CO₂ diffused into the polymer from its lateral sides to its center. Once the cell was mounted, it was placed under the infrared beam and successive adjustments were performed in order to optimize infrared spectra (see the supporting information a).

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