ELSEVIER

On the CO_2 sorption and swelling of elastomers by supercritical CO_2 as studied by in situ high pressure FTIR microscopy
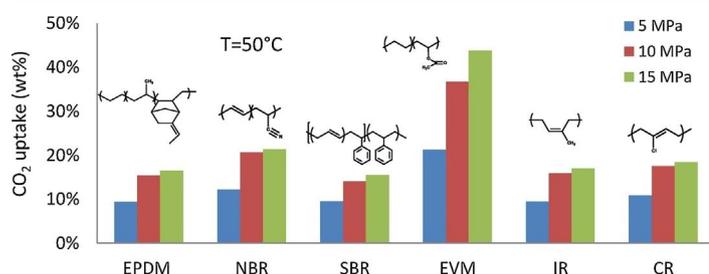
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GRAPHICAL ABSTRACT

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An FTIR (Fourier Transform InfraRed) microscope combined to a high pressure cell has been used to determine the CO_2 uptake in several common elastomers. Both the CO_2 sorption and the resulting swelling of the elastomers have been determined as function of pressure (P = 5–15 MPa) at constant temperature (T = 50 °C). A significant quantity of CO_2 is sorbed in all studied elastomers, between 15 and 20% at T = 50 °C and P = 15 MPa for most elastomers and up to 30% for Ethylene Vinylacetate (EVM) in the same conditions. The resulting percentage of swelling of the majority of studied elastomers is significant (up to 30%), and varies quite proportionally with the CO_2 mass uptake (linear variation with a slope equal to 1). The effect of temperature has been studied for Ethylene Propylene Diene (EPDM), between T = 50 °C and T = 110 °C (P = 5–15 MPa) and demonstrate that the swelling and CO_2 sorption display only a weak variation in this temperature range.

1. Introduction

Supercritical (sc) fluids have long been known as good solvents, good reaction media, extraction, separation or degradation media, molecular carriers, mass and heat transport media [1–3]. Among sc fluids, the CO_2 molecule switches easily between the liquid, gas and supercritical (sc) states, the critical point being rather low at 31 °C, 7.4 MPa. Although CO_2 is the primary greenhouse gas emitted through human activities, it is an industrially used molecule in its sc state as a reaction solvent [4], as a blowing agent [5], as a transport medium for

the introduction of active ingredients or for the extraction of toxic ingredients [6,7] in all kinds of solids. At a given pressure and temperature within the sc state, when such a low molar mass molecule flows into a solid polymer, several types of physical phenomena occur: sorption, absorption, diffusion, solubility and swelling [8–11]. These phenomena are governed by the polymer/CO_2 interactions and the particular properties of the sc state. Indeed the supercritical state enhances the CO_2/polymer interactions because sc CO_2 combines simultaneously a very good solvent capability and a very good diffusion capacity. But depending on the polymer, the knowledge of CO_2/

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polymer interactions is more or less accessible or sometimes poorly affordable. Glassy amorphous polymers are the most studied polymers [12,13], semi crystalline polymers are commonly studied [13–16] whereas reinforced, filled, or biphasic materials are becoming more and more studied [14,17,18]. However studies (e.g refs [16,19–22]) are rather scarce when dealing with the behavior of elastomers (neat or filled) in CO_2. The reasons are twofold: i) rubbery polymers are expected to be highly deformable in CO_2 (involving a high swelling), ii) the sorption/desorption stages are fast. Swelling may not be isostatic and elastomers may even creep. All of this makes data recovery and studies difficult.

In this study we rely on a well-established technique (high pressure near infra-red spectroscopy) [11,23,24] that we have developed at a microscopic scale to extract several data dealing with diffusion, swelling and solubility of CO_2/unfilled elastomer systems at various pressures and temperatures. It is an in-situ method, providing a one-step measurement for the simultaneous measurement of the swelling and CO_2 sorption. We chose a panel of engineering elastomers (Ethylene Propylene Diene rubber (EPDM), Chloroprene rubber (CR), Isoprene rubber (IR), Styrene Butadiene rubber (SBR), Ethylene Vinylacetate rubber (EVM) and a blend of Nitrile Butadiene Rubber/Poly-VinylChloride (NBR/PVC)) from raw uncrosslinked rubbers to thermoplastic elastomers, with different chemical interacting groups towards CO_2 (different polarities).

2. Experimental details

2.1. Materials

Carbon dioxide N45 (purity 99,95%) was supplied by Air Liquide. EPDM (s), CR, EVM, IR, SBR, NBR/PVC were purchased from international companies. Structures and properties of the polymers used in this study are displayed in Table 1.

2.2. Infrared micro-spectroscopy
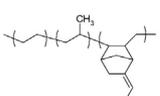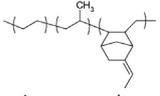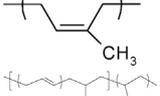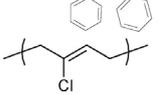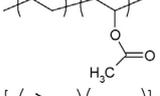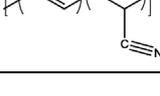
2.2.1. Experimental set-up

The set-up consists in a FTIR microscope working in transflection mode coupled with a high pressure cell. The infrared absorption

measurements were performed using an Infrared microscope Perkin Elmer Spotligh 200 that allows investigating the spectral range (800–6500 cm^{-1}) with a spatial resolution of 100 μm^2. Single beam spectra recorded with a 4 cm^{-1} resolution were obtained after the Fourier transformation of 50 accumulated interferograms. The homemade stainless steel vessel was equipped with a sapphire window and a mirror in between the polymer sample was maintained as shown in Fig. 1. This cell was designed in order to withstand a pressure of about 20 MPa for temperature ranging between 20 and 150 °C. A 100 μm Teflon 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 a standard uncertainty u(P) = 0.1 MPa. The stabilization of the operating conditions was controlled by recording several consecutive spectra. The experiments were performed at fixed temperature of 50 °C and in a pressure range from 5 to 15 MPa.

2.2.2. Experimental procedure

From the bulk polymeric sample, a piece was cut with a thickness of about 0.5 mm, a width of about 1.5 mm and a length of about 4 mm. The sample was placed between the window and the mirror, the position of which could be adjusted in order to hold a good contact between the window and the mirror (see Fig. 1). The mirror used was made of stainless steel polished to obtain a good reflection of the IR beam. Under this geometry, CO_2 could diffuse into the polymer from the four lateral sides of the polymer sample. Then, the cell was heated up to the required temperature. The spectra were recorded for the polymer sample alone then CO_2 was added up to the desired pressure. During the stabilization of the operating conditions, consecutive spectra were recorded every 5 min. For each series of measurements, absorption IR spectra have been plotted as function of time to check that the equilibrium has been reached typically after a period of time between 30 and 150 min depending upon the temperature and pressure conditions and the nature of the polymer. Fig. 2 is an example of the evolution of absorbance at 50 °C et 5 MPa for every elastomers.

Table 1
Physical and chemical properties of the studied elastomers.

Polymer	Structure	Density (g cm^{-3})	Crystallinity	T_g (°C)	M_n (g mol^{-1})	Supp. Info
EPDM 1		0.86	*amorphous*	−44	165 000	high molecular weight
EPDM 2		0.86	*amorphous*	−51	112 000	low molecular weight
IR		n.d.	*amorphous*	−70	271 000	///
SBR		n.d	*amorphous*	−55	110 000	
CR		1.23	*Semi-cristalline*	−40	540 000	///
EVM		1.07	*amoprhous*	−11	196 000	*Vinyl acetate content: 70%*
NBR/PVC *Physical blend, NBR matrix*		*Poorly characterized (P.C.)*	*P.C.*	*P.C*	*P.C*	*P.C*