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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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Highlights

> Simultaneous CO_2 sorption and swelling of elastomers using high pressure FTIR microscopy.

> Investigation of seven elastomers for T=50 to 110°C from P=5 to 15MPa

> All the elastomers displays a significant level of CO_2 sorption about 20% at P=15MPa.

> The resulting swelling is linearly correlated to the CO_2 sorption.

> Weak dependence of swelling and CO_2 sorption upon temperature variation.

ABSTRACT

An FTIR (Fourier Transform InfraRed) microscope combined to a high pressure cell has been used to determine the CO_2 solubility in several common elastomers: EPDM, CR, IR, SBR, EVM and NBR. 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 EVM in the same conditions. The resulting percentage of swelling of the elastomers is significant and nearly equal to the CO_2 mass uptake for most of the studied elastomers. The effect of temperature has been studied for EPDM, between T=50°C and T=110°C (P=5-15MPa) and demonstrate that the swelling and CO_2 sorption of EPDM displays only a weak variation in this temperature range. Few data are available in the literature for elastomers.

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, 74 bars. 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 CO2/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.

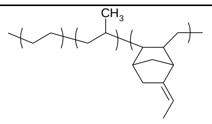
In this study we rely on a well-established technique (high pressure near infra-red microcopy –NIR µscopy) and we develop this technique to extract several data dealing with diffusion, swelling and solubility of CO_2 / unfilled elastomer systems (various Pressures and Temperatures). It is an in-situ method, providing a one-step measurement, applicable to any sample thickness. An expected drawback is that diffusion is not unidirectional.

We chose a panel of engineering elastomers (EPDM, CR, EVM, IR) 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

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

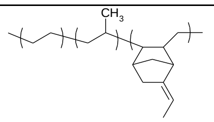
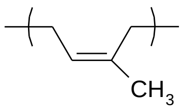
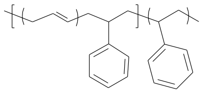
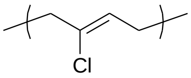
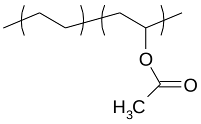
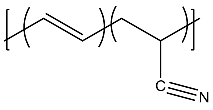
EPDM 2		0.86	*amorphous*	-51	112 000	low molecular weight
IR		n.d.	*amorphous*	-70	271 000	///
SBR		n.d	*amorphous*	-55	110 000	
CR		1.23	*Semi-cristalline*	-40	540 000	///
EVM		1.07	*amoprhous*	-11	196 000	*Vinyl acetate content: 70%*
NBR/PVC *Physical blend,* *NBR matrix*		*Poorly characterized (P.C.)*	*P.C.*	*P.C*	*P.C*	*P.C*

Table 1: Physical and chemical properties of the studied elastomers

2.2. Infrared micro-spectroscopy

2.2.a. 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 µm². Single beam spectra recorded with a 4 cm^{-1} resolution were obtained after the Fourier transformation of 50 accumulated interferograms. The home-made stainless steel vessel was equipped with a sapphire window and a mirror in between the polymer sample was maintained as shown in Figure 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.b. Experimental Procedure

From the bulk polymeric sample, a piece was cut with a thickness of about 0.5 mm, a width of about 1.5mm 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 Figure 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. Figure 2 is an example of the evolution of absorbance at 50°C et 5 MPa for every elastomers.

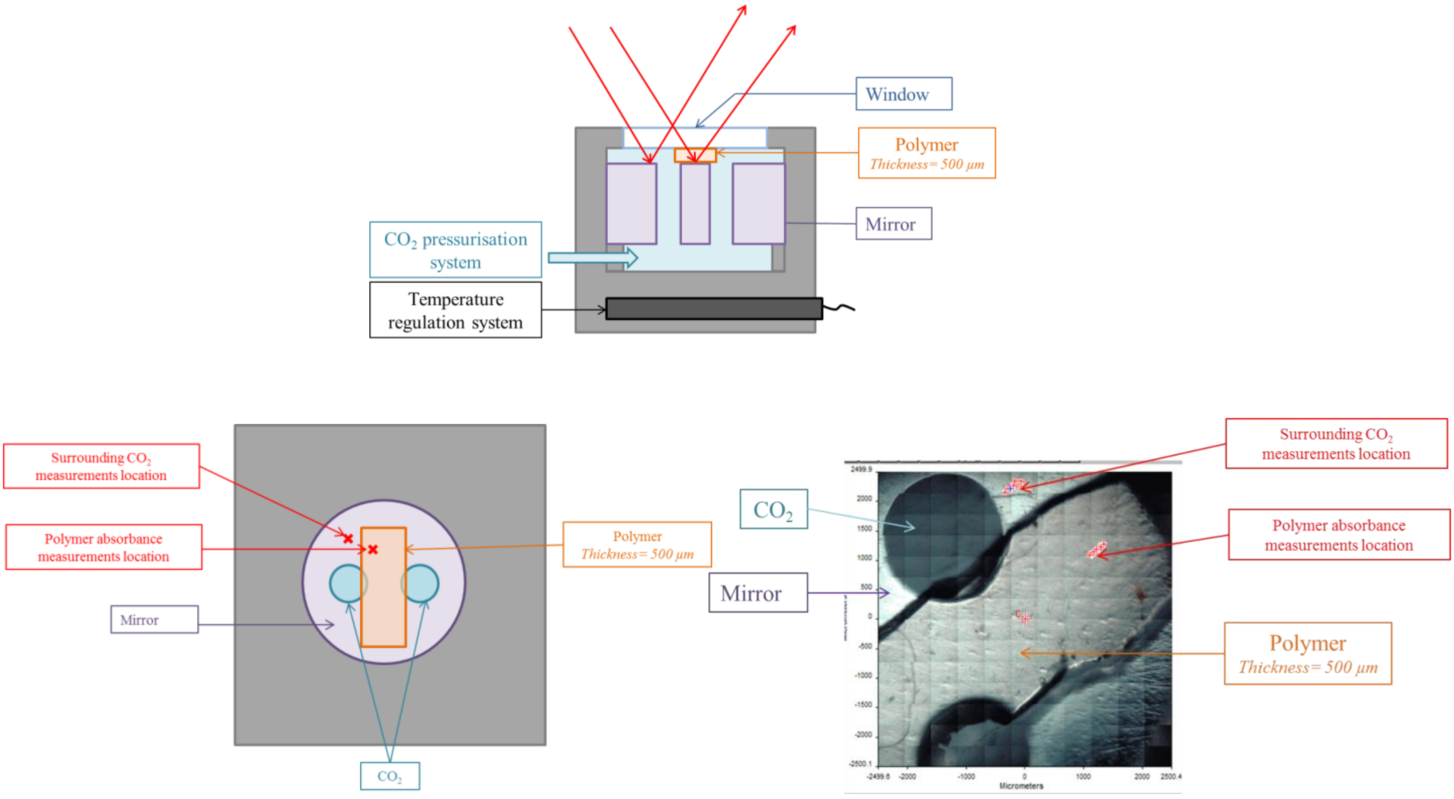


Figure 1 Experimental setup

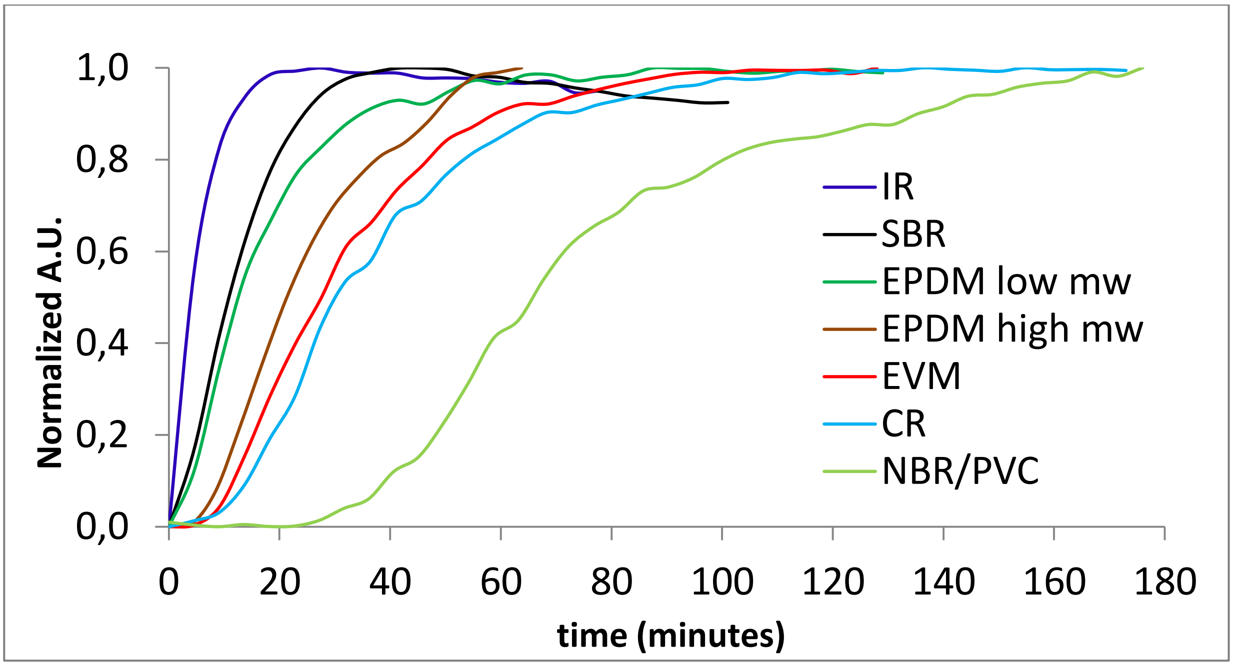


Figure 2 Evolution of the absorbance of the peak centered at 4950 cm-1 (this band is assigned to CO_2, it is expressed in normalized unit) at T=50°C and P=5 MPa

3 – INFRARED SPECTRA AND DATA PROCESSING

3.1. Infrared absorption spectra

Polymer

The infrared spectra of the different polymers swelled by CO_2 were recorded at 50°C for various pressures ranging between 0.1 and 15 MPa. Figure 3 displays the typical changes of the EPDM 1 or 2 infrared spectra that can be observed upon an increase of CO_2 pressure. A number of significant peaks associated with fundamental and combination modes of CO_2 and polymer can be observed. Regarding the polymer, the peaks detected in the range 2900-3100 cm^{-1} are associated to fundamental C-H stretch vibrations, that observed in the range 4000-4500 cm^{-1} are associated to C-H combination modes and finally the contribution detected in the range 5500-6000 cm^{-1} is associated to C-H overtones. We emphasize that all polymers investigated in this study displays the same characteristic infrared bands. The peaks observed at about 3000 cm^{-1} are saturated in our experimental conditions. Besides, the group of peaks observed in the range 4000-4200 cm^{-1} strongly overlapped making difficult their analysis to get accurate quantitative information. Consequently, we have used the peaks associated to C-H overtones centered at about 5800 cm^{-1} to determine the swelling of EPDM subjected to scCO$_2$.

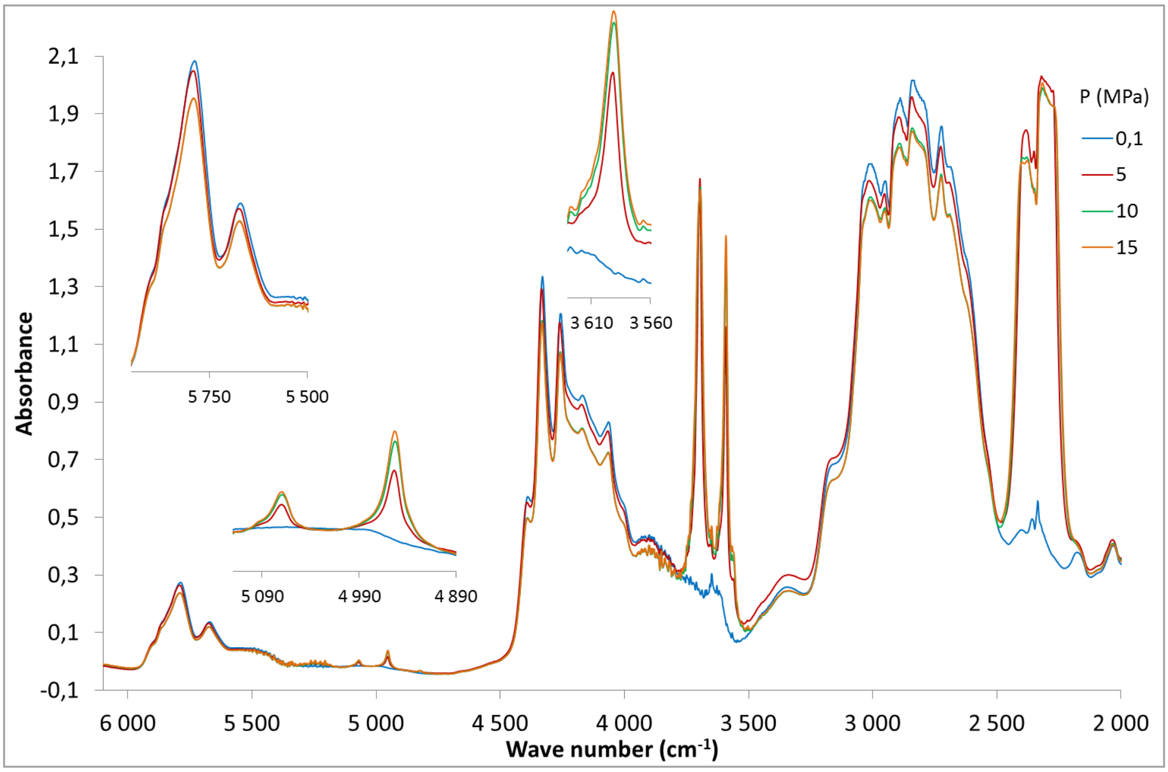


Figure 3: Infrared spectra of EPDM 1 at 50°C under a CO$_2$ pressure of 0.1 MPa, 5 MPa, 10 MPa and 15 MPa

Concerning CO_2, five peaks can be detected. Peak at 2300 is assigned to the antisymetric stretch ν_3, 3590 is assigned to combination modes $2\nu_2+\nu_3$, , 3695 assigned to combination mode $\nu_1+\nu_3$, 4950 cm^{-1} is assigned to combination mode $\nu_1+2\nu_2+\nu_3$ and 5030 is assigned to $2\nu_1+\nu_3$ of CO_2 molecule.

Most intense peak, centered at 2300 cm^{-1}, is saturated in our experimental conditions and cannot be used for our purpose. The peak centered at 3590 cm-1 could be used for quantitative measurements but only for pressures below 5 MPa. Above this pressure, peak is saturated and linearity hypothesis between the IR absorbance and the concentration is not valid anymore. To sum up, the bands at 3590 cm^{-1}, 3695 cm^{-1} , 4950 cm^{-1} and 5066 cm^{-1} were used to estimate the evolution of the weight percentage of CO_2 sorbed into the polymers, depending on the saturation or not of the peak at 3590 cm^{-1} . Besides, we emphasize that these peaks can be assigned unambiguously to CO_2 sorbed into the polymer and not to surrounding CO_2, since the peaks of surrounding CO_2 are detected at higher wavenumbers (3610, 3710 and 4970 cm-1 and 5100 cm-1 for the combination modes) as depicted in Figure 4. This kind of shift was also reported in the literature [23].

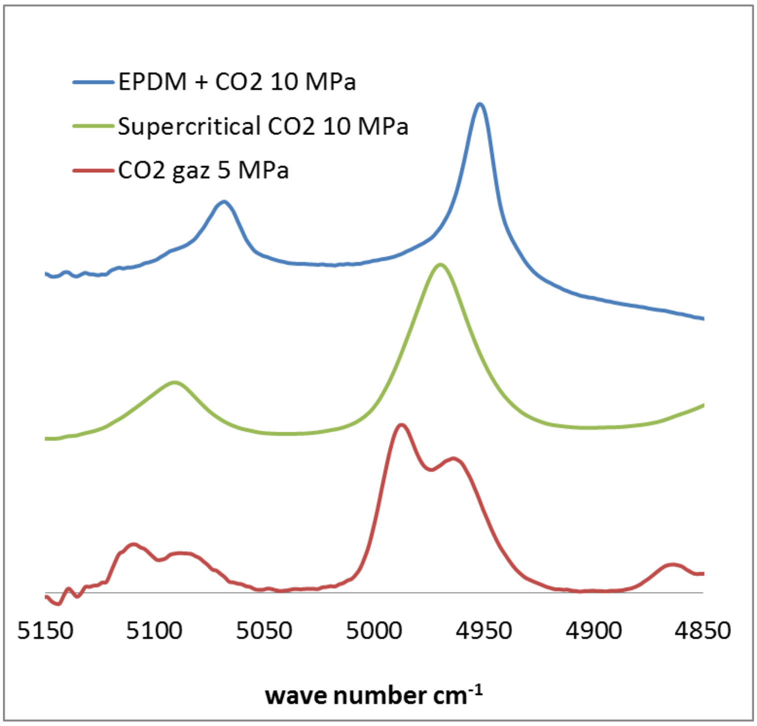


Figure 4: Infrared spectra of CO_2 at T=50°C and P= 5MPa (neat gaseous CO_2), P=10 MPa (neat $scCO_2$) and P=10 MPa (CO_2 in EPDM)

3.2 Determination of polymer swelling and CO_2 sorption: data processing

3.2.a. Polymer swelling

Guadagno et al [24] has proposed a calculation of the polymer swelling via the absorbance of a specific band of the polymer before and during exposure to CO_2, and based on the Beer-Lambert law.

$$A_0 = \varepsilon . l . C_0 \quad (1) \qquad\qquad A = \varepsilon . l . C \quad (2)$$

where A_0 and A are the absorbances of the polymer bands before and after exposure to CO_2, respectively; l is the pathlengths (cm); C_0 and C are the concentration of polymer before and after exposure to CO_2, respectively (mol.L^{-1});ε is the molar extinction coefficient of the polymer band (mol.L^{-1}.cm^{-1}). The molar extinction coefficient ε is considered to be independent of the CO_2 density. In addition, the pathlength was fixed because the elastomeric sample was held between the window and the mirror and swelling occurred in two dimensions only.

If V and $V + \Delta V$ are the volume of the polymer before and after exposure to gas respectively, one can write:

$$\frac{c_0}{c} = \frac{V+\Delta V}{V} = 1 + \frac{\Delta V}{V} = 1 + S \quad (3)$$

Finally, after combination of these three equations (1), (2) and (3), the swelling S is given by:

$$S = \frac{A_0}{A} - 1 \quad (4)$$

For studied elastomers, peak around 5800 cm^{-1} have been used to calculate polymer swelling. As shown on Figure 3, the intensity of the peak decreases with the CO_2 sorption.

3.2.b. CO_2 sorption

In order to determine the concentration of CO_2 (C_{CO_2}) sorbed into the polymer, the Beer-Lambert law has been applied to the CO_2 peaks. In order to directly use the concentration of CO_2 for further calculation, it has been calculated in g.cm^{-3} using the equation 6:

$$C_{CO_2} = \frac{A}{\varepsilon . l} \times M_{CO_2} \times 10^{-3} \quad (6)$$

where A is the absorbance of the CO_2 band; ε is the molar extinction coefficient; l is the pathlength; M_{CO2} is the molar mass of CO_2 and equal to 44 g.mol^{-1}.

The characteristic peaks of CO_2 centered at 3715 and 4950 cm^{-1} were used for the absorbance measurements. For 4950 cm-1 peak, both the height and the integrated area were used. Concerning the other peaks (3590, 3695 and 5066 cm-^{1}) the peak heights were used instead of integrated area because the baseline choice produces larger errors.

The molar extinction coefficient considering the peaks height were estimated to be about $\varepsilon_{3695cm-1}$= 8.28 L.mol^{-1}.cm^{-1}; $\varepsilon_{3590cm-1}$= 4.6 L.mol^{-1}.cm^{-1} and $\varepsilon_{4950cm-1}$= 0.25 L.mol^{-1}.cm^{-1} and $\varepsilon_{5066cm-1}$= 0.086 L.mol^{-1}.cm^{-1}. Concerning the 4950 cm^{-1} peak integrated area, the molar extinction coefficient is estimated to be about $\varepsilon_{4950cm-1}$= 7 L.mol^{-1}.cm^{-2} [23][11][25]

Regarding the determination of the pathlength, as the elastomeric polymers are quite soft, it cannot be measured before introduction in the IR cell. Indeed, the elastomeric samples are significantly compressed when held between the mirror and the window. That is why the pathlength l has been evaluated by recording a spectrum of the surrounding CO_2 right next to the polymeric sample for the 3 different pressures as shown in Figure 5. Thanks to the Beer-Lambert law, the pathlength can be determined using the following equation:

$$l = \frac{A_{CO2}}{\varepsilon * C_{CO2}}$$

Where A_{CO2} *is the* absorbance of the characteristic peak of CO_2 and C_{CO2} the concentration of CO_2. for the given pressure and temperature that is known from the literature [26].

In order to determinate l, the integrated area of the peak at 4950 cm^{-1} was used. For each experiment, absorbance as function of CO_2 concentration has been plot and *l* has been determined thanks to the chart slope which is equal to *ε.l* (Fig 6).

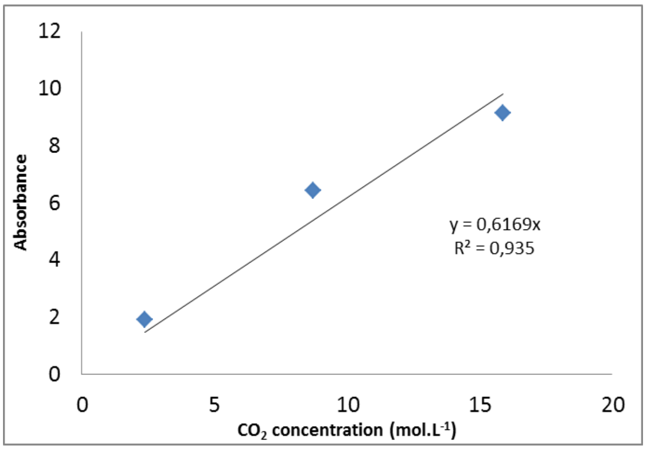


Figure 5 : CO_2 concentration (neat CO_2) as function of integrated area OR absorbance of 4950 cm^{-1} peaks for path length calculation, at T= 50°C

Finally, for a direct comparison with the literature data, the weight percentage of CO_2 *(%massCO_2)* sorbed into the polymer was calculated using the following equation:

$$\%mass_{CO_2} = \frac{C_{CO_2}}{C_{CO_2} + \frac{\rho_{pol}}{1+S}} \quad (7)$$

where ρ_{pol} is the initial polymer density (g.cm-3) and S the swelling.

For each elastomer and for every pressure, four values of absorbance at least have been taken into account: height of peak at 5066 cm^{-1}, 4950 cm^{-1} and 3590 cm^{-1} and integrated area of peak at 4950 cm^{-1}. At 5 MPa, a fifth value could be added: the height of the peak à 3693 cm-1. Figure 6 give the example of determination of % mass CO_2 in EPDM 1 or 2. For each condition, the four or five values calculated thanks to the different peaks are in a good agreement hence validating our methodology. In following paragraphs, the average value of % mass uptake is given.

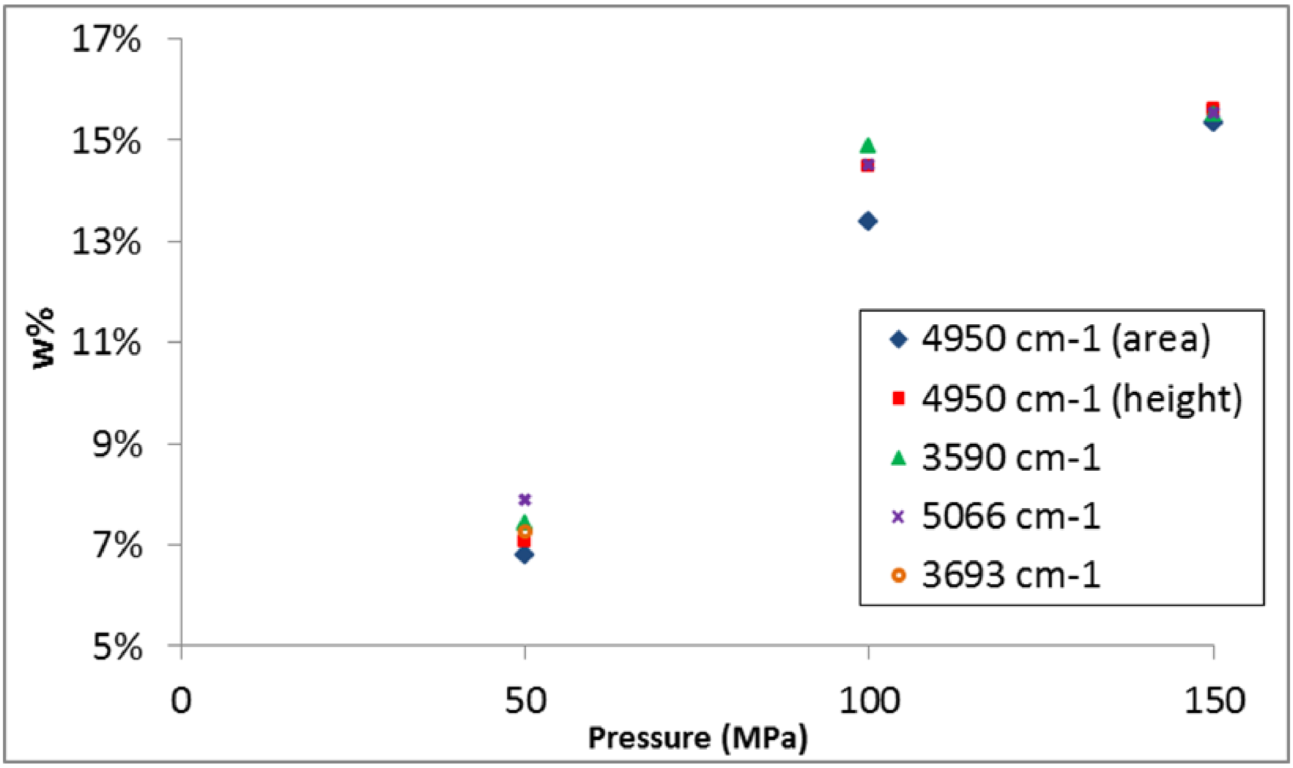


Figure 6 : % mass CO_2 in EPDM data points at 50, 100 and 150 bars and 50°C, calculated thanks to every CO_2 specific peaks.

Taking into account all the source of errors associated with our methodology (baseline correction, constant molar extinction coefficient, spectrometer stability), we have evaluated a relative standard uncertainty $u_r(C_{CO2})=0.1$ on our concentration values. We emphasize that the reliability of such methodology has already been demonstrated in previous investigations [23] [25].

4- Results and discussion

4.2 CO_2 sorption and swelling

CO_2 sorption and swelling measurements have been performed at 50°C and at 5 MPa, 10 MPa and 15 MPa for every studied elastomer. Maximum CO_2 mass uptake (% mass CO_2) at equilibrium has been calculated thank to Equation 7. On Figure 7% mass CO_2 as function of pressure has been represented for each polymer.

CO_2 sorption is quite similar for all studied elastomer except in the case of EVM. At 15 MPa and 50°C, a maximum CO_2 mass uptake is between 15% and 20% for most of the studied elastomer and about 45% for EVM.

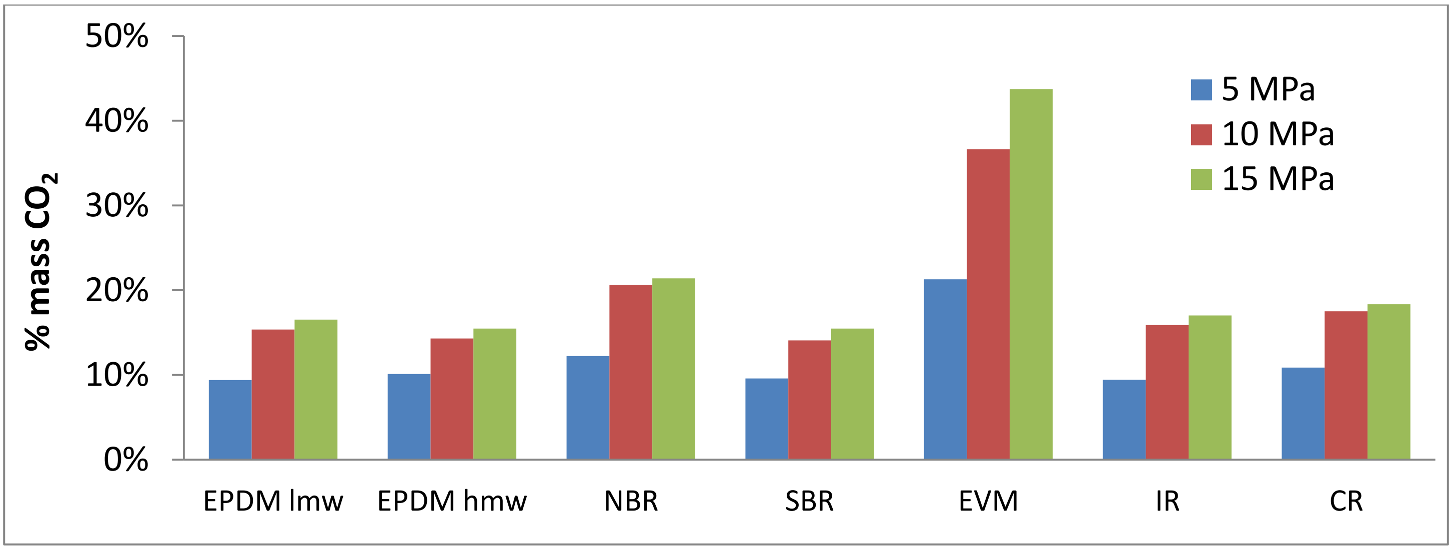


Figure 7 : CO_2 mass uptake (% mass CO_2) as function of pressure, in every studied elastomer, at T= 50°C, P=5 MPa, P=10 MPa and P=15 MPa

Although there are very few data concerning measurements of CO_2 absorption and swelling in general-purpose elastomers. Mickaeli et al [27] measured CO_2 absorption in an EPDM through in-situ gravimetric method (magnetic suspension balance). Their EPDM sample (Buna EP G 3550) has similar physico-chemical properties (molar mass, ENB content) as the two EPDM samples investigated here. At 65°C and 100 bars, their EPDM sample exhibits a mass uptake of about 20% which is in good qualitative agreement with our result.

The higher CO_2 sorption of EVM compare to the other polymers reported in this study is in agreement with the work of Jacobs et al [28]. Indeed, they performed some measurements on EVA with a vinyl acetate content of 40 % through pressure decay method. For a CO_2 pressure of 15 MPa at 50°C, a CO_2 mass uptake of about 36% is reported versus a mass uptake of about 45% for our EVM sample (vinyl acetate content of 70%). Therefore, the higher the vinyl acetate content in an EVM sample, the higher the CO_2 sorption as previously discussed in the study of Jacobs et al. This behaviour can be explained by the well-known good affinity between CO_2 and acetate function that is exploited for the design of CO_2 philic polymers [29].

Concerning the relation between the pressure increase and the amount of CO_2 absorbed in elastomer matrix: as expected, the CO_2 mass uptake raise with the CO_2 pressure increase but in a non-linear way. Indeed, for every polymer, the CO_2 mass uptake is increased by about 40 to 72% when the CO_2 pressure is raised from 5 MPa to 10 MPa whereas only a modest increase of about 4 to 20% CO_2 mass uptake is observed between 10 MPa and 15 MPa. This nonlinear relation between the solubility and the pressure increase has been reported for other rubbery polymers [22, 27, 30–32]. Tomasko et al.[33] explained that at high pressure, CO_2 sorption is no longer proportional to CO_2 pressure. Indeed, at low pressure, CO_2 sorption follows Henry's law: $C_{CO_2} = k_H P_{CO_2}$where k_H is the Henry's coefficient which is dependent of the temperature and the polymer. At high pressure, k_H is no longer constant and becomes dependent of the CO_2 sorption.

Regarding the corresponding swelling of the polymer that results from the CO_2 sorption for a given pressure and temperature, it has been calculated thanks to the polymer peak around 5800 cm^{-1} and the equation 4. As well as the CO_2 mass uptake, the maximum swelling at equilibrium (S%) at 50°C, has been plot for every elastomer and for a CO_2 pressure of 5, 10 and 15 MPa (see Figure 8)

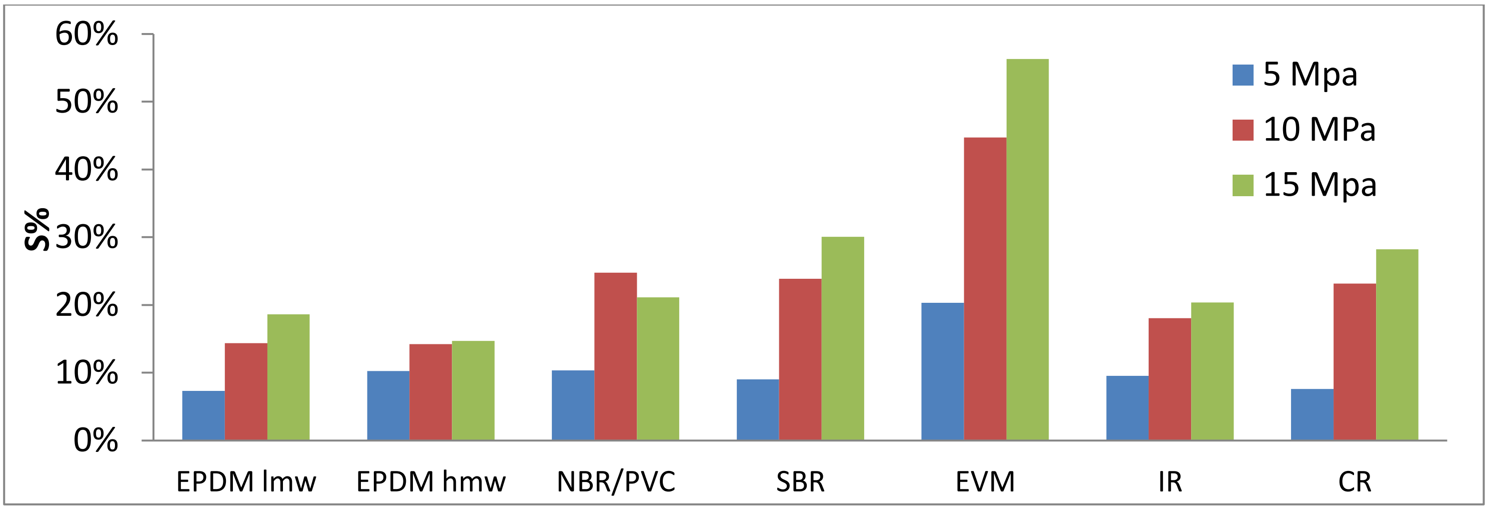


Figure 8 : Polymer swelling as function of pressure, at T= 50°C

Therefore, it seems that the swelling value is directly related to the CO_2 mass uptake of the studied polymers. In order to quantify the correlation between the swelling of a given polymer and its CO_2 mass uptake, we have reported on Figure 9 the swelling as function of CO_2 mass uptake for every elastomer. Concerning most ~~of~~ elastomers, the data are around the dashed line which means that the swelling is directly proportional to the CO_2 mass uptake. In contrast, CR, SBR and EVM exhibit a higher swelling value compare to CO_2 mass uptake. Although the swelling is a complex phenomenon which involve not only the effect of chemical affinity of the polymer with carbon dioxide but also polymer chain mobility and free volume, such behavior can be qualitatively explained by a probable higher chain mobility of CR, SBR and EVM compared to the other polymers investigated in this study. This is particularly true for EVM that contains vinyl acetate groups and is known to display low polymer-polymer interaction thus favouring its swelling and solubility in $scCO_2$ [34].

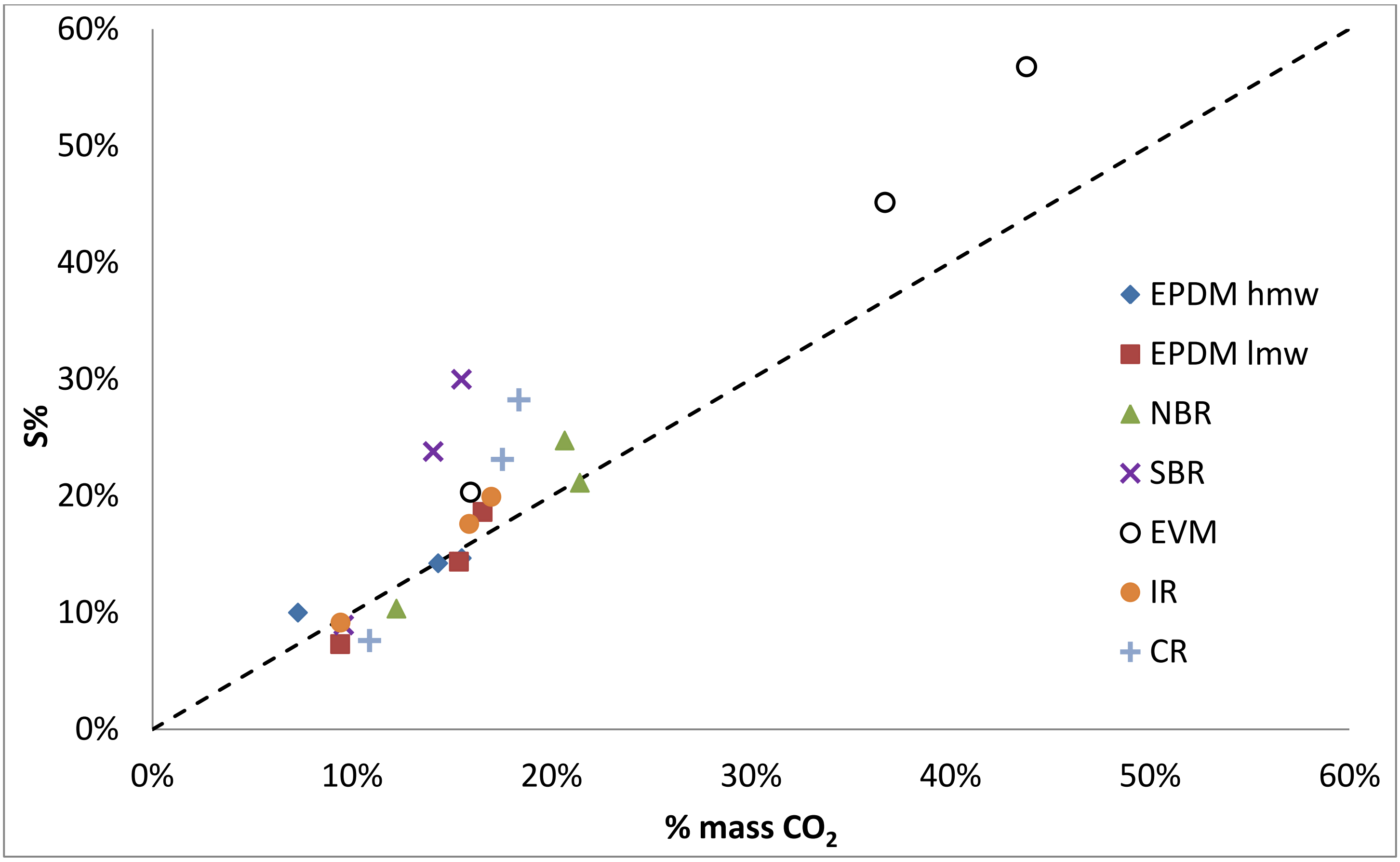


Figure 9 : Polymer swelling (S%) as function of CO_2 mass uptake (%mass CO_2), at T= 50°C

4.3 Effect of temperature on absorption and swelling

For EPDM1, we have performed additional experiments at different temperatures 65°C, 80°C, 95°C and 110°C in order to evaluate the temperature influence in CO_2 mass uptake and swelling. On Figure 10, the maximum CO_2 mass uptake at equilibrium is plotted at each temperature and for a CO_2 pressure of 5MPa, 10 MPa and 15MPa. Thus, it shows that temperature has only a low effect on mass uptake: from 50 to 110°C, the mass uptake only decreases from 18 to 16.5% at 15 MPa. Such a low effect of the temperature on CO_2 mass uptake has already been reported for HTPB [11], a polymer of similar physico-chemical properties as our elastomer. Indeed, at 15 MPa, it shows a modest reduction of mass uptake from about 14% to 11.5 % for a temperature increase from 40°C to 100°C, which is comparable to our polymers.

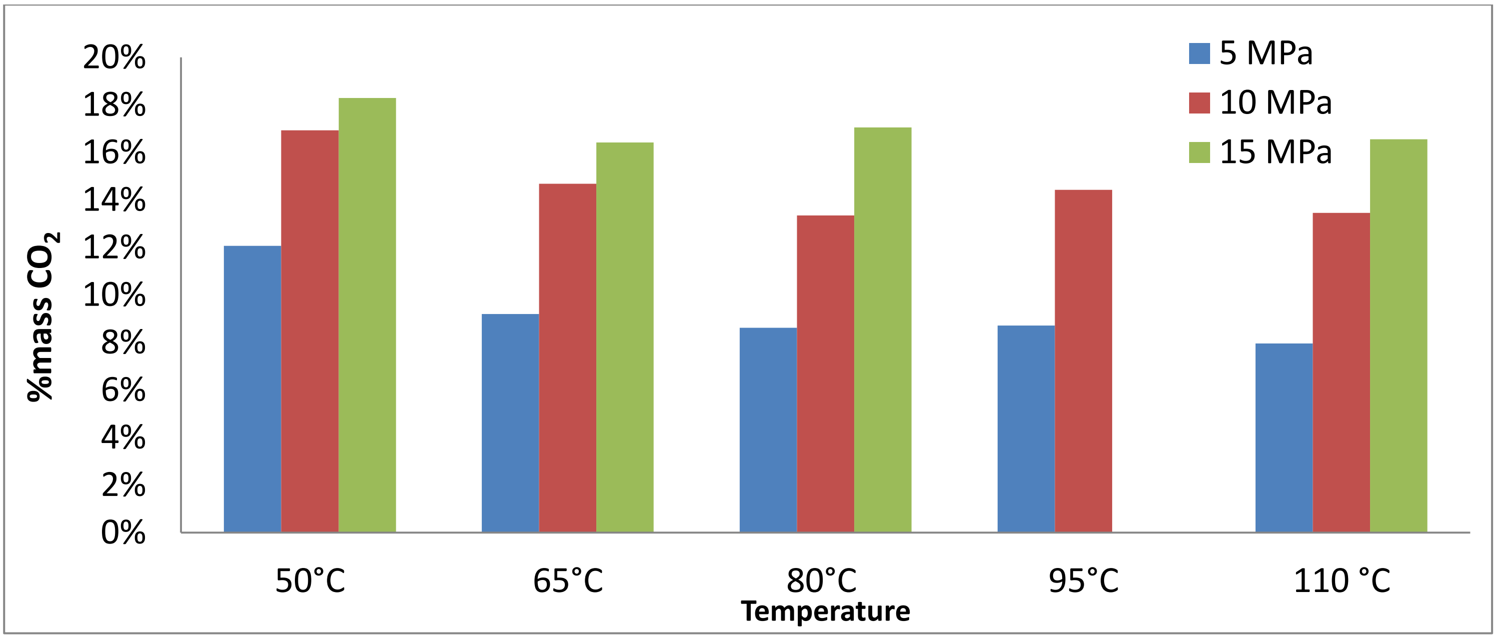


Figure 10 : CO_2 mass uptake (%mass CO_2) in EPDM1 as function of CO_2 pressure and temperature

The swelling of EPDM has also been calculated at T=50, 65, 80, 95 and 110°C and for 3 different pressures (see Figure 11). The effect of temperature on the swelling is similar to that reported above for the CO_2 mass uptake as it displays only a modest reduction of the swelling upon increase of temperature.

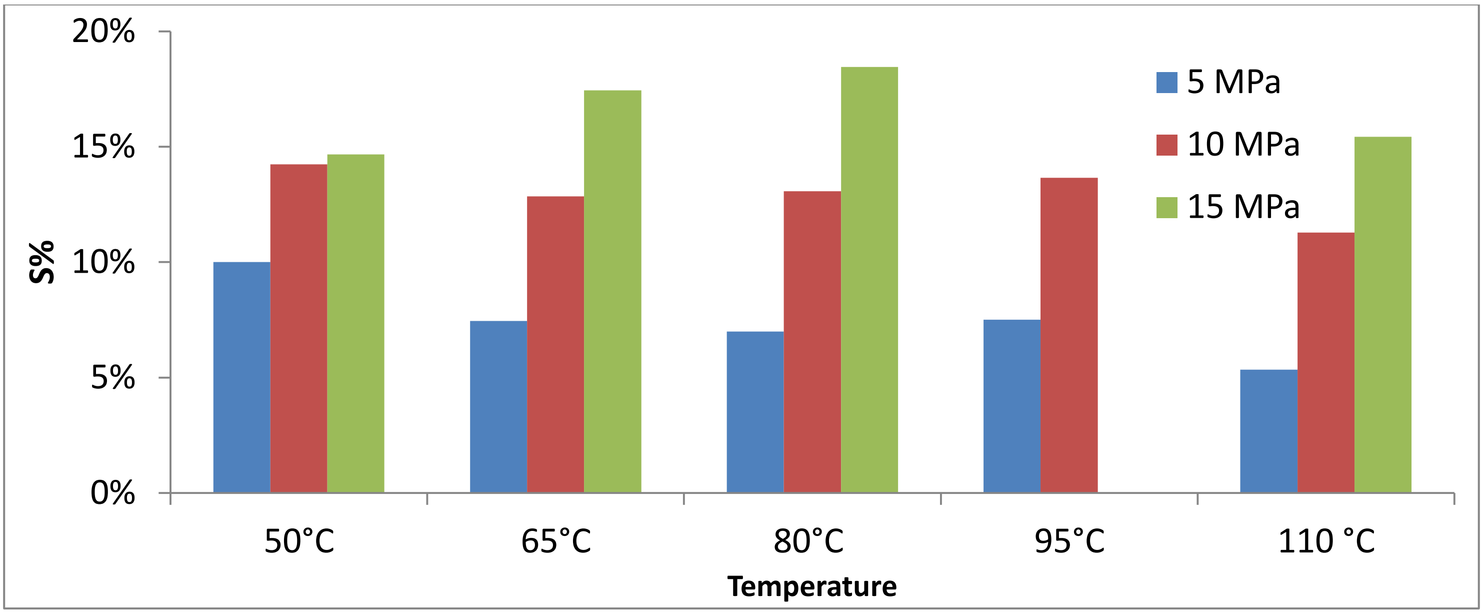


Figure 11 : Swelling of EPDM 1 as function of CO_2 pressure and temperature.

CONCLUSION

In order to determine *in-situ and simultaneously* the CO_2 sorption and swelling of elastomers by supercritical CO_2, we have used an FTIR microscope combined with a high pressure cell. The isothermal behaviour (T=50°C) as a function of pressure (from 5 to 15 MPa) of several common elastomers (EPDM, CR, IR, SBR, EVM and NBR) was investigated in order to understand the key parameters governing CO_2 sorption and elastomer swelling. The effect of temperature (from 50 to 110°C) as a function of pressure (from 5 to 15 MPa) has been studied for EPDM. The quantity of CO_2 sorbed in all the studied elastomers increases with pressure. All the elastomers display a similar significant level of CO_2 sorption between 15 and 20% wt at T=50°C and P=15 MPa. However, we observe that a quite higher quantity of CO_2 can be sorbed in EVM in the same conditions (30%wt). This behaviour was explained by the well-known good affinity between CO_2 and the acetate function present in EVM.

The resulting swelling behaviour of most elastomers displays almost the same percentages as ~~than~~ the CO_2 *mass uptake. In contrast, CR, SBR and EVM exhibit higher swelling values compared to the* CO_2 *mass uptakes. The swelling behavior of most elastomers follows the same trend as the mass uptakes and reaches the same quantitative levels (there is a quasi linear relationship between CO2 uptake % and swelling %). In contrast for elastomers having more interactions with* CO_2 *(i.e elastomers containing chlorine or carbonyl groups, CR, EVM), swelling ratios are higher mass uptakes.* Besides such behavior can be qualitatively explained by a probable higher chain mobility of CR, SBR and EVM compared to the other elastomers investigated in this study.

Finally, the swelling and CO_2 sorption of EPDM displays only a weak variation upon a temperature increase from 50°C to 110°C.

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Figure captions