

## Kinetic and thermodynamic study of supercritical CO<sub>2</sub> sorption within polymers used in medical devices and their packaging

Y. Masmoudi,<sup>a,\*</sup> T. Tassaing,<sup>b</sup> M. B. Abdou,<sup>b</sup> M. Lerest,<sup>c</sup> P. Raymond,<sup>d</sup> E. Badens,<sup>a</sup>

<sup>a</sup>Aix Marseille Univ, CNRS, Centrale Marseille, M2P2, Marseille, 13451, France

<sup>b</sup> Université de Bordeaux, ISM, UMR CNRS 5255, Talence 33405, France

<sup>c</sup> Lattice Medical, Loos 59120 France

<sup>d</sup> Cousin Surgery, Wervicq-Sud, 59117, France

\*Corresponding author: yasmine.masmoudi@univ-amu.fr

### 1. Introduction

Optimization of supercritical (sc) processes for polymer treatment requires a good knowledge of their behavior in the presence of scCO<sub>2</sub>. Indeed, CO<sub>2</sub> sorption in the amorphous regions of a polymer promotes its chain mobility by weakening intermolecular interactions, inducing a plasticizing effect and a volume swelling. These phenomena depend on the nature of the polymer (degree of crystallinity, free volume, molecular weight, chemical structure, the presence of functional groups interacting with CO<sub>2</sub>, etc.). CO<sub>2</sub> sorption and polymer swelling vary depending on pressure and temperature conditions. They are generally favored by increasing the pressure as CO<sub>2</sub> density is increased. By increasing the temperature, CO<sub>2</sub> density is reduced which can limit sorption phenomena. However, polymer chain mobility is improved above the glass transition temperature (T<sub>g</sub>), favoring CO<sub>2</sub> sorption and swelling phenomena. Since sorption is not an instantaneous phenomenon, kinetic study is important to determine the times required to reach thermodynamic equilibrium.

In this work, a thermodynamic and kinetic study of scCO<sub>2</sub> sorption in various polymer medical devices and their packaging and the swelling of the latter was investigated under pressure using *in situ* FTIR spectroscopy.

### 2. Materials and Methods

**Chemicals:** Several polymers used in medical devices and their packaging were characterized. As medical devices, medical grade silicones wedges and sheetings as well as polypropylene (PP) meshes were supplied by Cousin Surgery (Wervicq-Sud, France) and Poly(L-lactide-co-ε-caprolactone) (PLA:PCL) implants by Lattice Medical (Loos, France). As packaging for medical devices, pouches and blisters were supplied by Cousin Surgery (Wervicq-Sud, France). They are made of one side Tyvek® (high density polyethylene - HDPE) and one side low density polyethylene and polyethylene phthalate blends (PET/PE) peel for pouches or polyethylene terephthalate glycol-modified (PETG) for blisters sealed together.

**Methods:** CO<sub>2</sub> sorption within polymers and the subsequent swelling of the latter were measured *in situ* using an experimental set-up combining a FTIR microscope (Perkin-Elmer spotlight 400) operating in a transreflection mode, and a high-pressure cell equipped with sapphire window and a polished stainless-steel mirror<sup>1</sup>. In the high-pressure cell, a 2- or 4-mm diameter polymer sample was placed facing the sapphire window and supported at its center by the mirror. After filling the cell with CO<sub>2</sub> to the desired pressure (8, 14 and 20 MPa), infrared spectra were recorded under isothermal conditions (40 and 50°C) until reaching thermodynamical equilibrium, allowing thus to follow the kinetic of CO<sub>2</sub> sorption within the polymer. After selecting a wavenumber for CO<sub>2</sub> and a spectral range for the polymer, the Beer-Lambert law was applied to quantify the concentration of CO<sub>2</sub> sorbed within the polymer (C<sub>CO<sub>2</sub></sub> in mol.L<sup>-1</sup>) and the volume swelling of the polymer as detailed by Dubois *et al.*<sup>1</sup> and Guadagno and Kazarian<sup>2</sup>. When the raw density of the polymer is known, it was also possible to quantify the mass fraction of CO<sub>2</sub> within the polymer (w (%)).

### 3. Results and discussion

For each material, the absorbance of the selected peak for CO<sub>2</sub> and the integrated area of the spectral range selected for the polymer were recorded as a function of time for the different selected operating conditions.

An increase in the absorbance of CO<sub>2</sub> peak was observed indicating an increase of CO<sub>2</sub> sorption within the polymer, before reaching a plateau characteristic of the establishment of thermodynamic equilibrium. In parallel, the integrated area of the polymer spectral range decreases, indicating an increase in the volume swelling before stabilizing when the thermodynamic equilibrium is reached (Figure 1).

This trend was observed for all the investigated polymers except for PETG for which an increase in the CO<sub>2</sub> peak intensity was observed before a decrease in the latter in all the experimental conditions explored. The contact duration before this decrease varies according to the pressure and temperature conditions and was higher than 500 min. This specific behavior could be explained by a partial recrystallization of the amorphous zones of the polymer<sup>3</sup>.

For all the characterized polymers, CO<sub>2</sub> concentration and polymer swelling after reaching the thermodynamic equilibrium were compared. Under isobaric conditions, non-significant variations were observed while varying the temperature from 40 to 50°C. An increase in pressure from 8 to 20 MPa under isothermal conditions was favorable to CO<sub>2</sub> sorption and to polymer swelling.

Silicone wedges and sheetings present the highest values of CO<sub>2</sub> concentrations (5.3 to 11.4 mol.L<sup>-1</sup>) and of polymer swelling (25 to 62%). This behavior can be explained by a high chain mobility for elastomers<sup>1</sup>. In addition to being completely amorphous, silyl ethers groups in their molecular structure have a good affinity with CO<sub>2</sub> promoting its sorption within the polymer.

CO<sub>2</sub> sorption in PLA:PCL implants was also significant with concentrations varying between 3.8 and 5.7 mol.L<sup>-1</sup> and polymer swelling varying between 32 and 54% which can be explained on the one hand by a low crystallinity rate of 15% as well as a high chain mobility in the amorphous region and on the other hand by the presence of carbonyl groups that can interact with CO<sub>2</sub><sup>4</sup>.

Although being initially amorphous and despite the presence of carbonyl groups in its structure, PETG presented lower CO<sub>2</sub> sorption and swelling. This could be explained by a lower chain mobility and a potential partial recrystallization during contact with CO<sub>2</sub>.

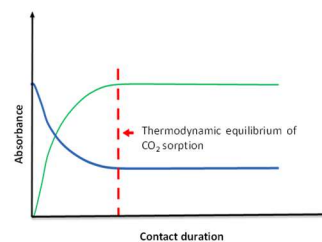
For polypropylene meshes as well as Tyvek® (HDPE) and PET/PE peels, sorption and swelling phenomena were low. These results can be explained on the one hand by a high crystallinity rate of these 3 polymers, despite a low glass transition temperature of the amorphous zones for PP and polyethylene. Furthermore, these polymers do not have functional groups exhibiting a specific chemical affinity with CO<sub>2</sub><sup>5,6</sup>.

#### 4. Conclusions

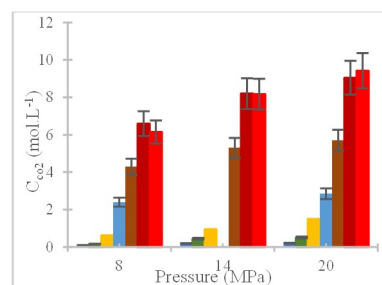
Kinetic and thermodynamic study of scCO<sub>2</sub> sorption within polymers and the subsequent swelling of the latter are important guidelines for supercritical processing of these materials. These phenomena were investigated under pressure for several polymers used in medical devices and packaging using in situ FTIR spectroscopy. This study highlighted the importance of simultaneously fulfilling two criteria to promote CO<sub>2</sub> sorption and polymer swelling, chemical affinity of the polymer with CO<sub>2</sub> and high chain mobility.

#### References

1. J. Dubois, E. Grau, T. Tassaing, M. Dumon, *J. Supercrit. Fluids* **2018**, 131, 150–156.
2. T. Guadagno, S.G. Kazarian, *J. Phys. Chem. B* **2004**, 108, 13995–13999.
3. N. H. Brantley, S. G. Kazarian, C., *J. Appl. Polym. Sci.* **2000**, 77(4), 764–775.
4. S. G. Kazarian, M. F. Vincent, F. V. Bright, C. L. Liotta, and C. A. Eckert, *J. Am. Chem. Soc.* **1996**, 118(7), 1729–1736.
5. M. Champeau, J.-M. Thomassin, C. Jérôme, T. Tassaing, *J. Supercrit. Fluids* **2014**, 90, 44–52.
6. L.H. Ohyabu, Y. Sato, H. Inomata, R.L. Smith Jr., *J. Supercritical Fluids* **2007**, 40, 452–461.



**Figure 1.** Evolution of the absorbance/integrated surface of the peak/spectral range selected for CO<sub>2</sub> (—) /the polymer (—)



**Figure 2.** CO<sub>2</sub> sorption at 40 °C in ■ silicone wedge, ■ silicone sheeting, ■ PLA:PCL, ■ PETG, ■ PET/PE peel, ■ PP meshes, ■ Tyvek®