

# Sorption/Desorption Of Carbon Dioxide Into Amorphous And Semicrystalline PEEK Films

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## ABSTRACT

Sorption/Desorption experiments of carbon dioxide in amorphous and semicrystalline PEEK (Polyetheretherketone) film were carried out in autoclave at 15 MPa and at 80°C, 50°C and 35°C. The thickness PEEK film was 100 µm.

A standard experimental test consists in the following steps: loading of PEEK samples into the reactor, pressurizing with CO<sub>2</sub> up to the prefixed value and heating to the prefixed temperature; the system was allowed to reach equilibrium for 24 h and then the reactor was depressurized.

Sample mass loss was recorded during desorption.

The sorption of CO<sub>2</sub> into PEEK films was estimated from the desorption data and ranged from 2.76% at T=80°C to 6.77% at T=35°C for amorphous film; and from 2.03% at T=80°C to 4.78% at T=35°C for semicrystalline films. The results are reported in table 1.

The diffusion coefficients of carbon dioxide in PEEK were also estimated according to Crank equation [1 - 3].

## INTRODUCTION

Supercritical carbon dioxide is well known as polymers swelling agent and it can be used as a carrier gas in impregnation processes with additive substance like monomers, metal organic compounds, fragrances or colours [4 ÷ 6].

Saturation of polymers with supercritical carbon dioxide and subsequent desorption at elevated temperatures can lead to microcellular foams production [7, 8].

Polymeric foams are widely used as heat insulators, support materials and food trays, as they have high impact strength, low thermal conductivity and light weight. To produce polymeric foams a blowing agent to induce nucleation and growth of cells is required. CFC-11 (trichlorofluoromethane) and CFC-12 (dichlorodifluoromethane) were used as physical blowing agents in foaming processes, but recently international regulatory has been issued that limits the use of such gases and supercritical fluids as carbon dioxide can be considered a valid alternative as blowing agent [9].

Sorption/desorption and diffusion coefficient at different temperatures and pressures are needed to describe mass transfer of SCF in polymers.

Muth et al. [1] evaluated CO<sub>2</sub> diffusion coefficients into PVC for sorption processes at temperatures from 40° to 70°C and pressure from 20 to 40 MPa by MLA (Mass Loss Analysis) method.

Schnitzler and Eggers [10], using MLA method, studied the CO<sub>2</sub> diffusion in PET at temperatures in the range 40° - 120°C and pressure from 5 to 35 MPa. CO<sub>2</sub> desorption data

were obtained by recording sample weight decrease after sorption process. These data allow to calculate the CO<sub>2</sub> diffusion coefficient.

Sato et al. [9] measured solubility and diffusion coefficients of carbon dioxide in PVAc at temperature from 40° to 100°C and pressures up to 17.5 MPa by magnetic suspension balance (MSB).

Aubert [11] demonstrated the possibility to have accurate measurements of carbon dioxide solubility in polymers at high pressure used a QMC (quartz crystal microbalance).

In this work sorption/desorption experiments are performed in order to estimate the carbon dioxide uptake into PEEK amorphous and semicrystalline (30%) films and to study carbon dioxide diffusion process using the MLA method.

## MATERIALS AND METHODS

PEEK films were supplied by Victrex in form of amorphous or semicrystalline films, 100 μm thickness. Carbon dioxide was supplied by Rivoira (99,99%).

Experimental tests were carried out using a Nova Swiss reactor.

In a standard experimental procedure, PEEK sample was weighed and then loaded into the vessel, the reactor was heated and filled with CO<sub>2</sub>. Pressure was increased up to the prefixed value and after the time necessary to reach equilibrium conditions was elapsed, the reactor was depressurized. The samples weight loss due to desorption was measured using a analytical balance (10<sup>-4</sup> g).

According Fickian diffusion for a polymeric film of thickness *l*, the diffusion of CO<sub>2</sub> can be described with the Crank equation [2]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2 \cdot n + 1)^2 \cdot \pi^2} \cdot \exp\left(\frac{-D \cdot (2n + 1)^2 \cdot \pi^2 \cdot t}{l^2}\right) \quad (1)$$

where  $M_t$  is the sorption amount of CO<sub>2</sub> in polymer at time *t* (g CO<sub>2</sub>/g polymer)

$M_\infty$  is the equilibrium sorption amount of CO<sub>2</sub> in polymer

*D* = Diffusivity

*l* = sample thickness.

A simplified form of Crank equation for long sorption times is obtained truncating the summation at the first term:

$$\frac{M_s}{M_\infty} = 1 - \frac{8}{\pi^2} \cdot \exp\left(\frac{-D_s \cdot \pi^2 \cdot t_s}{l^2}\right) \quad (2)$$

where  $M_s$  is the sorption amount of CO<sub>2</sub> in the polymer at the time *t<sub>s</sub>* (g CO<sub>2</sub>/g pol),  $M_\infty$  is the equilibrium sorption amount of CO<sub>2</sub> in polymer.

The Crank equation for short desorption times has the following expression [3]:

$$\frac{M_d}{M_\infty} = -\frac{4}{l} \cdot \sqrt{\left(\frac{D_d \cdot t_d}{\pi}\right)} \quad (3)$$

where  $M_d$  is the residual amount of  $\text{CO}_2$  in polymer at the time  $t_d$  (g  $\text{CO}_2$ /g pol).

For a Fickian diffusion,  $M_d$  is a linear function of the square root of the desorption time  $t_d$  and a linear fit gives  $M_\infty$  at zero  $t_d$ .

The desorption diffusivity  $D_d$  can be determined by plotting  $(M_d/M_\infty)$  against  $\sqrt{t_d}$ .

## RESULTS

PEEK samples were treated with carbon dioxide at 15 MPa for 24 h at three different temperatures: 35°C, 50°C and 80°C.

In figure 1, 2 and 3 are reported the desorption data at 15 MPa and at 35°C, 50°C and 80°C for amorphous and semicrystalline samples.

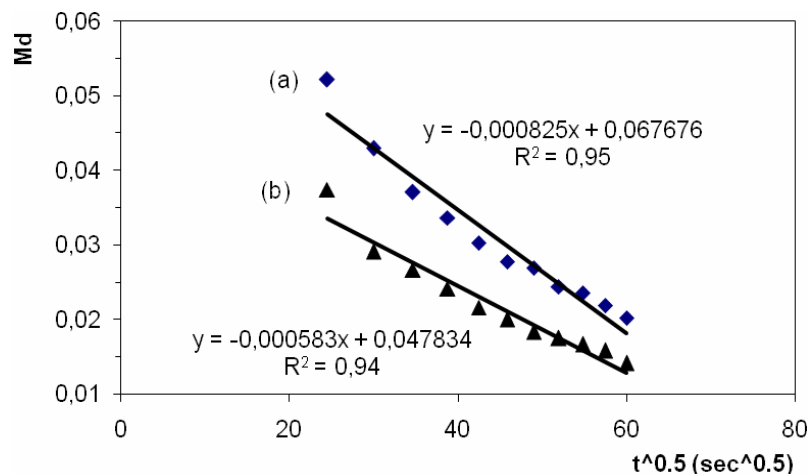
The high value of correlation coefficient of the linear fit of experimental data confirms that diffusion of  $\text{CO}_2$  in PEEK for the chosen experimental conditions is of the Fickian type.

In table 1 are reported the equilibrium  $\text{CO}_2$  weight % in polymer samples, evaluated by extrapolating the linear fit of  $M_d$  vs  $t_d^{0.5}$  to  $t_d=0$ . They ranged from 2.76% (at 80°C) up to 6.77% (at 35°C) for amorphous PEEK film and from 2.03% (at 80°C) up to 4.78% (at 35°C) for semicrystalline PEEK film. The difference between the equilibrium carbon dioxide concentration in amorphous and semicrystalline PEEK increases with decreasing temperature, ranging from about 2% at 35 °C to 0,73% at 80 °C.

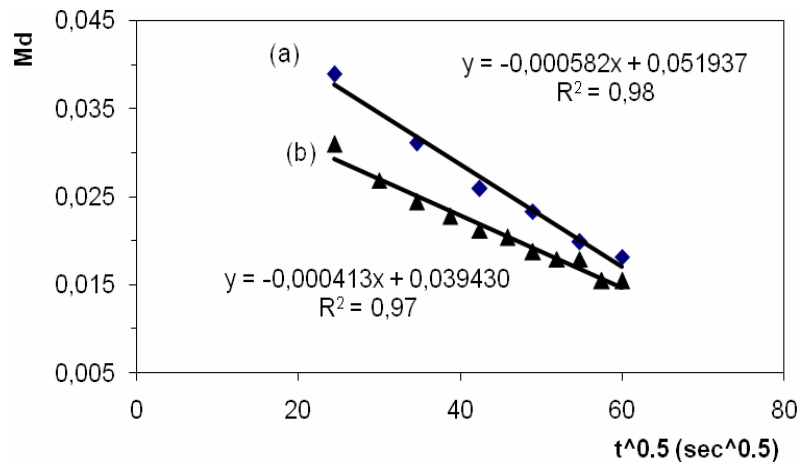
In figure 4 and 5 are reported the experimental  $(M_d/M_\infty)$  vs  $t_d^{0.5}$  at 50°C and 15 MPa for amorphous and semicrystalline PEEK, respectively.

By a linear fit of experimental  $(M_d/M_\infty)$ , carbon dioxide diffusivities have been evaluated according to Eq. (3). The diffusivity data are reported in table 1.

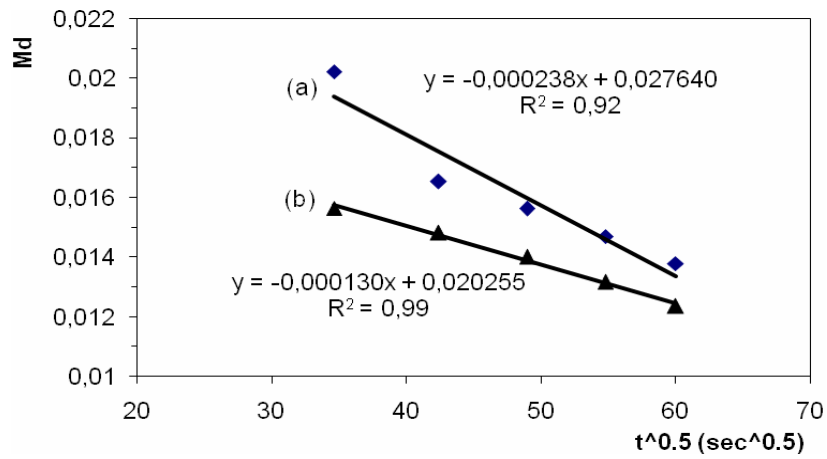
The desorption diffusivities increase with decreasing temperature, showing the same behaviour reported by Tang et al. [3] for desorption of carbon dioxide from Polycarbonate samples. The same trend was observed by Muth for PVC [1]. The desorption diffusivities data for Polycarbonate are reported in table 2, the data for PVC are reported in table 3.



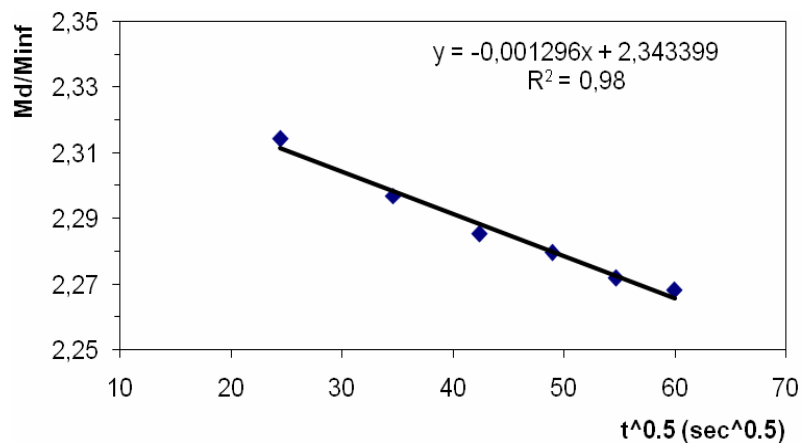
**Figure 1** -  $\text{CO}_2$  weight fraction ( $M_d$ ) vs  $t_d^{0.5}$ . (a): Amorphous; (b): semicrystalline. Sorption conditions: 15 MPa, 35°C, 24 h.



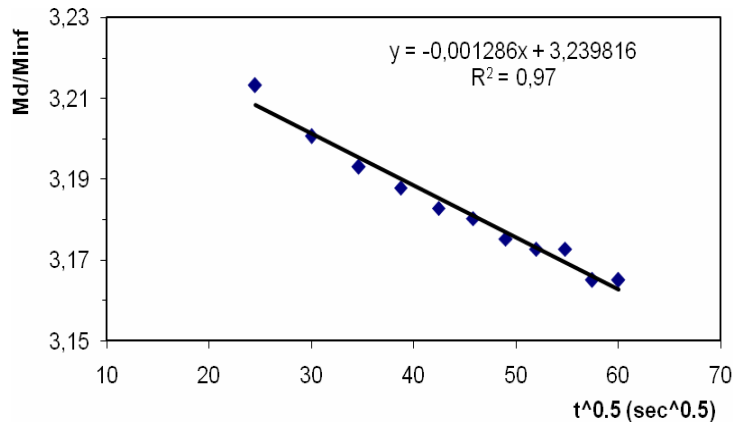
**Figure 2** - CO<sub>2</sub> weight fraction ( $M_d$ ) vs  $t_d^{0.5}$ . (a): Amorphous; (b): semicrystalline. Sorption conditions: 15 MPa, 50°C, 24 h.



**Figure 3** - CO<sub>2</sub> weight fraction ( $M_d$ ) vs  $t_d^{0.5}$ . (a): Amorphous; (b): semicrystalline. Sorption conditions: 15 MPa, 80°C, 24 h.



**Figure 4** - Plot of  $(M_d/M_\infty)$  vs  $t_d^{0.5}$  for determination of sorption diffusivities according to Eq. (3). Amorphous PEEK,  $T=50^\circ\text{C}$  and  $P=15 \text{ MPa}$ .



**Figure 5** - Plot of  $(M_d/M_\infty)$  vs  $t_d^{0.5}$  for determination of sorption diffusivities according to Eq. (3). Semicrystalline PEEK,  $T=50^\circ\text{C}$  and  $P=15\text{ MPa}$ .

$T$ ( $^\circ\text{C}$ )	<i>Amorphous PEEK</i>		<i>Semicrystalline PEEK</i>	
	% wt. $\text{CO}_2$	$D_d$ ( $10^{15}\text{ m}^2/\text{s}$ )	% wt. $\text{CO}_2$	$D_d$ ( $10^{15}\text{ m}^2/\text{s}$ )
80	2.76	1.72	2.03	1.19
50	5.19	3.29	3.94	3.24
35	6.77	4.12	4.78	4.21

**Table 1.** Equilibrium sorption amount and desorption diffusivity for PEEK samples treated at 15 MPa and different temperatures.

$T$ ( $^\circ\text{C}$ )	$P$ (MPa)	$D_d$ ( $10^{11}\text{ m}^2/\text{s}$ )
40	20	2.01
50	20	1.61
60	20	1.67
40	30	2.16
50	30	1.85
60	30	1.70
40	40	2.55
50	40	2.07
60	40	2.07

**Table 2** - Equilibrium sorption amount and desorption diffusivity for PC samples treated at various experimental conditions (Tang et al. [3]).

$P$ (MPa)	$T$ ( $^\circ\text{C}$ )	$D_d$ ( $10^{11}\text{ m}^2/\text{s}$ )
20	40	0.24
20	50	0.19
20	60	0.19
20	70	0.08

**Table 3** - Equilibrium sorption amount and desorption diffusivity for PVC samples treated at various experimental conditions (Muth et al. [1]).

## CONCLUSION

Sorption and diffusion of supercritical carbon dioxide in amorphous and semicrystalline PEEK films at temperature from 35° to 80°C at 15 MPa were studied. The CO<sub>2</sub> sorption amount into samples decreased with increasing temperature, from 6.77 to 2.76 % for amorphous PEEK and from 4.78 to 2.03% for semicrystalline PEEK.

The desorption diffusivity decreases with increasing temperature, reaching the maximum value of  $4.21 \cdot 10^{-15}$  m<sup>2</sup>/s at 35°C for semicrystalline PEEK.

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