MASS SWELLING OF PERFLUORINATED POLYMERS EXPOSED TO SUPERCRITICAL CARBON DIOXIDE

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Preliminary results of the investigation of the mass swelling of PVDF contacted with supercritical carbon dioxide are here reported. The amount of CO_2 absorbed has been measured using the gravimetric method developed by Berens. Experiments performed until now induce to hypothise non Fikean diffusion of the penetrant inside the polymer matrix. Mass equilibrium mass uptake up to 7.2 % w/w was determined under adopted experimental conditions.

1. INTRODUCTION

Polymeric materials may exhibit a wide range of interactions with supercritical carbon dioxide ($scCO_2$); the action of such molecule on polymers is, as a rule, confined within the amorphous regions of the macromolecular structure and results in the modification of the internal forces among the chains with consequent swelling and changes of the mechanical and physical properties of the polymers.

The plasticization has a strong impact on many processing operations. In so far as the viscosity reduces, this influences polymer extrusion and blending; additionally the presence of $scCO_2$ into the structure enhances both the diffusion of additives through the polymer matrices for impregnation and extraction, or the monomer diffusion for polymer synthesis.

Plasticization also influences the foaming of polymers, and changes in polymer morphology due to the induced crystallization.

Poly(vinylidene fluoride), denoted PVDF, is a potential candidate, for its remarkable chemical and mechanical resistance, for the construction of the containers used in chemical engineering or building construction or in oil recovery. In particular, PVDF is used as a liquid –proof casing barrier for flexible tubes, transporting hydrocarbons and gas, such as carbon dioxide, at high pressure and high temperature. It was observed that this material can be blistered and cracked by brutal decompression. Hence, a detailed study of the behaviour of PVDF in contact with supercritical carbon dioxide may be useful to understand possible applicative limitation of such material. Furthermore, it was previously observed that precipitation polymerisation of VF2 to PVDF in supercritical carbon dioxide can be described with an homogeneous free radical kinetics model [1-2], despite the heterogeneous nature of the polymerisation, evidentiated by the onset of an acceleration period in system initiated by gamma rays [2]. Even if some hypotheses have been expressed to explain this behaviour no definitive interpretation is currently available. One possibility is that carbon dioxide swells the PVDF coagulum increasing free volume and chain mobility and enhancing mass transfer controlled polymerisation steps. In this context the investigation of PVDF mass swelling contacted with carbon dioxide can be useful to ascertain the validity of this hypothesis,

moreover giving complementary information for the modelling of the polymerisation kinetics. Briscoe et al. have investigated carbon dioxide – PVDF interactions using vibrating beam technique to measure the gaseous mass uptake [3].

We have made an attempt to investigate mass swelling of PVDF contacted with supercritical carbon dioxide at 50 and 70 C° in the range of pressure 200-300 bar with a simple approach proposed by Berens [4].

Preliminary results are here reported.

2. METHODS

Materials. Carbon dioxide is SOL 2.7. PVDF HYLAR M10 polymer samples were kindly supplied from Solvay under the form of films (thickness 1 mm)

Mass swelling. The procedure for swelling experiments is that adopted by Berens and coworkers [4]. Mass swelling determinations have been performed on polymer samples of HYLAR M10 at 50°C AND 70 °C and from 200 to 300 bar.

Experiments were performed using the extraction chamber of an ISCO SF10X supercritical extractor fitted with a pressure transducer and inserted on line to an air driven Maximator pump to deliver dense CO_2.

After the insertion of the polymer film in the vessel, it was purged with gaseous subcritical carbon dioxide, heated at the operating temperature and pressurised through the Maximator pump up to the setting pressure.

After the attainment of the set-up conditions a slow flow rate (12 ±2 NL/h) of $scCO_2$, measured by a flowmeter totalizer Bronkhurst F-11C-GD-00-V, totalizer Seneca S164, was maintained during the whole duration of the exposure.

At the end of the sorption period, the vessel was vented to room pressure and the polymer film rapidly transferred on the pan (18-22s) of a fast-response electronic scale (Sartorius CP 225 D, accuracy 0.01 mg) interfaced with a PC to monitor the CO_2 desorption from the film. The mass of CO_2 dissolved inside the polymer film at the end of the sorption period was obtained by a linear extrapolation of the plot to zero desorption time. By repeating the procedure at different sorption times the absorption curve can be obtained.

Experimental data were fitted by the equation derived for diffusion in a plane sheet of thickness L with uniform initial distribution [5], in order to obtain the total amount M of diffusing compound entered the sheet at time t and the diffusion coefficient D of the species inside the sheet.

$$\frac{M}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \boldsymbol{p}^2} \exp - \left\{ \frac{D(2n+1)^2 \boldsymbol{p}^2 t}{L^2} \right\} \tag{1}$$

Where M_∞ is the corresponding quantity after infinite time (obtained by weighting the samples after exposure to $scCO_2$ followed by treatment under vacuum at 40°C for 24 hours)

3. RESULTS AND DISCUSSIONS

Experiments were performed according to the method of Berens [4], as previously described in the experimental section.

Excellent Fickean behaviour was exhibited during desorption by all the investigated samples and sample weight extrapolation to instant zero was done with good accuracy, so that an

experimental method simpler than that adopted by Brisco et al. [3] can be used for the determination of the CO_2 mass uptake.

Figure 1. Absorption curve of carbon dioxide in PVDF film at 50 °C and 200 bar
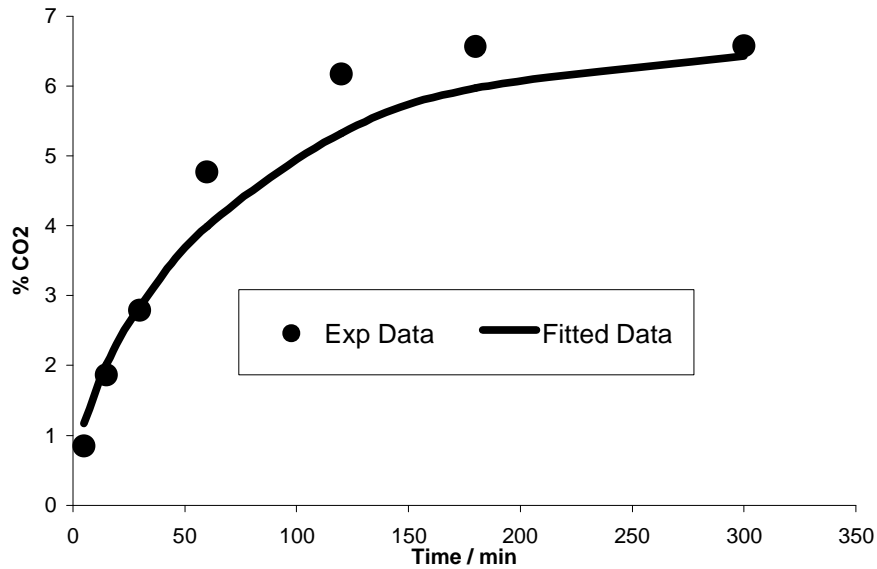
In figure 1 is reported the mass sorption profile for PVDF HYLAR MP10 at 50 °C and 200 bar. As a result of the fitting with the eq.1 for n = 0 to 4 a diffusion coefficient of 2.05 10^{-7} cm^2/s was estimated. It is observed that fitting based on a Fikean behaviour is not accurate. Actually, fitting of experimental points at short soaking time (< 50 min) leads to diffusion coefficient around 1.7 10^{-7} cm^2/s while fitting at longer time (> 50 min) leads to diffusion coefficient around 4.6 10^{-7} cm^2/s. Similar results were obtained also at other T and P investigated and they could be tentatively explained on the basis of a diffusion coefficient increasing with the concentration of the penetrant.

As shown in table 1, the CO_2 Equilibrium concentration at fixed temperature increased with the density of the fluid phase while a slightly decrease was observed at 200 bar by increasing temperature at 70 °C probably due to the decreased density of the supercritical fluid.

Table 1: Mass swelling experiments of PVDF samples at 50 °C .

Temperature (°C)	Pressure (Mpa)	Density[a] (g/cm^3)	Diffusion coefficient $10^{-7}cm^2$/s	CO_2 Equilibrium concentration (%w/w)
50	200	0.78	2.05	6.57
50	250	0.83	2.02	6.83
50	300	0.87	1.98	7.20
70	200	0.66	5.04	6.39

a estimated with the Bender equation of state [6]

4. REFERENCES

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