

MASS SWELLING OF PVDF EXPOSED TO SUPERCRITICAL CARBON DIOXIDE

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Mass swelling of PVDF contacted with supercritical carbon dioxide at 50 and 70 C° in the range of pressure 50-300 bar was investigated with two simple experimental approaches based respectively on gravimetric and chromatographic methodologies. The gravimetric method, based on Berens approach, was developed in order to investigate the solubility of pure carbon dioxide in the polymer. The second methodology based on “in situ” analytical measurements (GC) and on the use of a molecular probe has been developed in order to investigate the solubility in multi component system.

INTRODUCTION

Polymeric materials may exhibit a wide range of interactions with supercritical carbon dioxide (scCO₂); 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 scCO₂ 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, evidenced 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 two simple approach based respectively on gravimetric and chromatographic methodologies. The gravimetric method, based on Berens approach [4], was developed in order to investigate the solubility of the carbon dioxide alone in the polymers. The second methodology based on “in situ” analytical measurements (GC) and on the use of a molecular probe has been developed in order to investigate the solubility of both carbon dioxide and monomer.

Preliminary results are here reported.

I - MATERIALS AND METHODS

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

I.1 Gravimetric methodology

Mass swelling determinations have been performed on polymer samples of HYLAR M10 at 50°C AND 70 °C and from 50 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 CO₂.

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 scCO₂, 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 CO₂ desorption from the film. The mass of CO₂ 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.

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

Where M_∞ is the corresponding quantity after infinite time (obtained by weighting the samples after exposure to scCO₂ followed by treatment under vacuum at 40°C for 24 hours)

I.II Chromatographic methodology

The polymer film was inserted in a chamber filled to the desired pressure, P_s , with CO_2 and eventually other gaseous components at determinate temperature. The initial mass of the gaseous components were weighted with an high accuracy electronic scale ($\pm 0.01g$).

As shown by equations 2 and 3, in order to determinate the mass swelling it is necessary to evaluate the concentrations of gaseous components in the fluid phase and the volume swelling V_s . According with an homogeneous distribution of gaseous components in the system the concentration of these components can be, simply, evaluated by GC measurements.

$$M_{CO_2}^0 = M_{CO_2}^P + C_{CO_2}^F (V_R - V_P - V_S) \quad (2)$$

$$M_{VF_2}^0 = M_{VF_2}^P + C_{VF_2}^F (V_R - V_P - V_S) \quad (3)$$

V_R = Reactor volume; V_P = Polymer volume; V_S = Swelling volume; M^0 = initial mass (weighted); M^P = mass absorbed in the polymer; C^F = concentration in the fluid phase

Hence, if $V_S \sim 0$ these data are sufficient to calculate the mass swelling. If V_s is not negligible, mass swelling can be computed measuring by GC the concentration of a not absorbable gaseous probe (see eq. 4 and 5) as Argon in the fluid phase.

$$M_{Probe}^0 = C_{Probe}^F (V_R - V_P - V_S) \quad (4)$$

$$M_{CO_2}^0 = M_{CO_2}^P + (C_{CO_2}^F / C_{Probe}^F) * M_{Probe}^0 \quad (5)$$

In this case, as shown, by eq. 5 the value of mass swelling should be more accurate for two reasons:

- The value of V_s is not neglected;
- Mass swelling measurement is not affected by the reactor and polymer volumes; the effect of the free volume is, in fact, included in the slope of calibration curves

The concentration of gaseous components during the adsorption was, hence, evaluated by gas chromatography. The GC was connected to the system by a high pressure six position valve equipped with an high pressure loop of 6 micro L.

CONCLUSION

Gravimetric methodology

Experiments were performed according to the method of Berens [4], as previously described in the experimental section. Excellent Fickian behaviour was exhibited during desorption by all the investigated samples and sample weight extrapolation to instant zero was done with good accuracy. Otherwise mass uptake of carbon dioxide in PVDF up to about 7% was determined, significantly lower than that obtained by Briscoe et al. with different methodology. Hence, in order to verify the results we focused our attention on the second system based on Gas Chromatography approach.

Chromatographic methodology

Carbon dioxide absorption in PVDF was tested at 50°C and 60°C in a range of pressure between 80 and 300 bar in absence and in presence of argon as a probe. Preliminary results will be reported.

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REFERENCES :

- [1] CHARPENTIER, P. A., DESIMONE, J. M., ROBERTS, G. W., *Ind. Eng. Chem. Res.*, vol. 39, **2000**, p. 4588.
- [2] GALIA, A., CAPUTO, G., SPADARO, G., FILARDO, G., *Ind. Eng. Chem. Res.*, vol. 41, **2002**, p. 5934.
- [3] BRISCOE, B., J., LORGE, O., WAJS, A., DANG, P., *Journal of Polymer Science: Part B: Polymer Physics*, vol. 36, **1998**, p. 2435.
- [4]. BERENS, A., R., HUVARD, G., S., KORSMEYER, R., W., KUNIG, F., W., *J. Appl. Pol. Sci.*, Vol. 46, **1992**, 231.
- [5] CRANCK, J., *The Mathematics of Diffusion*, 2nd Ed. Clarendon Press, Oxford, **1975**.
- [6] BRUNNER G., *Gas Extraction*, Springer, **1994**, p. 15.