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A Novel Gas Chromatographic Method to Measure Sorption of Dense Gases into Polymers

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A novel experimental approach to determine the solubility of gaseous compounds inside polymers is here described. The method is based on the gas chromatographic determination of the composition of the fluid phase at equilibrium with the polymer. To take into account the effect of the volume swelling on the measurement a suitable probe, nonabsorbable by the polymer, was added to the fluid phase. Under the adopted configuration the apparatus can operate up to 35 MPa and 80°C. This experimental technique has been used to determine the solubility of carbon dioxide in poly(vinylidene fluoride) using argon as a probe. The latter was chosen because it is negligibly absorbed by the polymer and does not significantly alter the chemical potential of CO_2. The uncertainty of the method in the determination of the solubility was estimated for each experimental points by error analysis. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2243–2253, 2006

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Introduction

The measurement of sorption of low molecular weight compounds in polymers is a research topic of critical relevance from both scientific and technological perspectives. The availability of reliable data of solubility of penetrants in macromolecular matrices is indeed a cornerstone for the validation of models to predict mass uptake and dilation of the material. The problem becomes particularly challenging in the case of glassy polymers where the nonequilibrium configuration of the system must be taken into account. In these cases the adoption of order parameters in addition to classical thermodynamic quantities (temperature, pressure, chemical composition) has been proposed to define models more related to fundamentals with respect to the usually adopted phenomenologically based dual-mode sorption model. It is clear that not only the procedure of validation of these models, but also their further amelioration requires that an abundance of experimental data on sorption and swelling of polymers, under a wide range of operative conditions, are available.

Beside the aforementioned theoretical consideration, the investigation of sorption and swelling of polymers is of paramount relevance for a number of applications. The use of polymeric membranes in separation processes, the extraction or impregnation of additives, and the modification and synthesis of polymers in supercritical solvents are some relevant examples. In all these cases knowledge of the solubility of the solvent and of the penetrant inside the polymer matrix is mandatory for the proper design and conduction of the process.

Indeed several experimental methods have already been described in the literature to study sorption and swelling of polymers that come in contact with high-pressure fluid systems.

A conceptually simple method is based on the measurement of the pressure decay accompanying the sorption of the gaseous compound inside the matrix.[1-3] In this technique, the amount of gas dissolved in the polymer is determined from the mass balance of the gas in contact with the polymer, by evaluating the initial and final mass of the component from pressure measurements, using suitable equations of state to determine the density of the fluid phase. To ensure the reliability of the technique an accurate calibration of the volume of the sorption cell and a precise and accurate measurement of the pressure are vitally important. As the volume of the polymer increases of

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the amount V_{Sw} for the swelling effect of the dissolved gas, its equilibrium value $V_P = V_P^0 + V_{Sw}$ is calculated using the Sanchez–Lacombe equation of state (S-L EOS). The prediction of V_{Sw} and the correlation of the solubility are done simultaneously, using an iterative method, because the measured solubility changes with the predicted V_P value.

A positive feature of the method is that the apparatus is simple and inexpensive. However, its reliability decreases at high temperatures, especially for polymer melts, because the accuracy of the pressure sensors is negatively affected by higher temperatures and no sensor with suitable performances is currently available. One further source of errors is intrinsic to the estimation of the swelling of the polymer obtained using an iterative method based on the use of an EOS. As a result the method is not entirely based on experimental determination, but depends on the accuracy of the S-L EOS, which is hardly estimable.

Other experimental apparatuses have been proposed to be used in situ gravimetric techniques for the measurement of the amount of gaseous compounds dissolved into polymers.

The simplest approach is based on the use of a quartz spring method, originally adopted at pressure < 10 MPa by Wissinger and Paulatis[4] and later extended to more dense supercritical systems.[5] In this technique the amount of gas sorbed is evaluated from the length extension of the spring, provided that its elastic constant k is known. A substantially similar approach is based on the use of an electro- or microbalance to perform the weighting of the polymer sample directly in the dense fluid atmosphere.[6,7] All these techniques can be considered rather sensitive and fast because they require only a small amount of sample, although at high densities of the gaseous medium, they suffer from substantial errors arising from the variation in the buoyancy effect as a result of swelling of the polymer, which compels the operator to have accurate swelling volume data of the polymer together with an accurate determination of the gas density at the adopted experimental conditions.

An improvement of the aforementioned gravimetric techniques is based on the use of the so-called magnetic suspension balance (MSB), conceived by Kleinrahm and Wagner,[8] for accurate measurements of fluid densities. The apparatus can be easily used to measure sorption of gases into polymers. In this case the measuring strength is transmitted contactlessly by a magnetic coupling from the pressurized chamber, containing the polymer sample, to the microbalance. Through this approach the latter can be located outside the high-pressure measuring chamber under room pressure conditions.

This type of instrumentation can be used to measure the gas solubility and diffusivity in polymers at high temperature and pressure, although it suffers from the same buoyancy effect previously described in the case of other gravimetric techniques; thus in this case, too, the volume swelling of the polymer must be known or measured by a different technique. A commonly adopted choice is to compute the volume swelling of the sample by visual observation of the polymer contained in a suitable view cell, under the assumption of isotropic dilation. Apart from the uncertainty in the measurement of the characteristic length used to estimate the swelling, other potential sources of error can arise from the method adopted to sustain the sample and from the effect of residual stresses originating from the machining process. Several authors have used this experimental apparatus to determine the solubility and diffusivity of gaseous components in solid polymers.[9-12]

Another interesting family of methods adopted to study the sorption of gaseous molecules inside polymers is based on the measurement of the resonant frequency of a suitable mechanical system made solidal to the polymer specimen and immersed in the supercritical phase. The underlying principle is that the response of a physical system to an external periodic driving force depends on its inertial mass so that any variation arising from sorption of the gas corresponds to a variation in the resonance frequency that can be correlated with the mass uptake, provided that suitable mechanical models are available. To this family can be ascribed measurements performed with quartz crystal microbalances[13,14] and with the vibrating beam technique.[16] Moreover, as clearly explained by Briscoe et al.,[15,16] measurements obtained with these methods suffer from the uncertainty arising from the swelling of the polymer. In the case of dense gaseous media the variation in the areas of the specimen normal to the plane of vibration leads to a variation in the apparent mass of the sample, not related to the sorption process, but rather depending on the variation in the amount of the mass of gas displaced by the movement of the system. This means that in this case, too, to provide correction for the aforementioned effect, independent data on the swelling of the polymer must be available to correct the measurement.

A conclusion that can be drawn from analyses of all the techniques is that, even if characterized by different degrees, all of them are affected by the uncertainty arising from the difficulty of evaluating the volume dilation of the polymer sample during the sorption measurements. This can be a relevant source of error in the evaluation of solubility of the penetrant. Moreover, all of them cannot be used to measure sorption of penetrants in multicomponent systems because it is difficult to discriminate between the effects of dissolution of different compounds. With this awareness we have tried to set up an experimental approach that can give the sorption data, intrinsically taking into account the effect of swelling of the polymer, and that is potentially useful to operate in the presence of fluid mixtures.

To reach this goal a limited amount of a nonabsorbable molecule, to be used as an internal standard to compute the polymer swelling, was added in the fluid phase. The amount of CO_2 dissolved in the polymer is determined by solving the mass balance equations of the two components, using their relative concentrations evaluated by gas chromatographic (GC) analyses of the gaseous mixture after attainment of the equilibrium condition. The use of GC made the method potentially extendable to mixtures without modification of the hardware. To test the validity of this approach we have started to investigate the solubility of carbon dioxide in poly(methylmethacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF). The acrylate polymer was chosen because it has been widely investigated with other techniques, thus offering a model system to validate our methodology. With respect to the fluorinated polymer, the investigation reported in this work was the first step of research aimed to find a reliable and simple experimental method to investigate the solubility of carbon dioxide and vinylidene fluoride in PVDF exposed to dense gaseous mixtures of such components, to obtain information on the partitioning of these species between the fluid and polymer phases. This research activity was part of a wider project, financed by the European Union, and directed to investigate the possibility of performing the surfactant-assisted polymerization of fluoromonomers in supercritical carbon dioxide. Given the heterogeneous character of the polymerization, the knowledge of such information becomes crucial for the definition of a reliable kinetic model of the process, considering that two different polymerization loci (continuous fluid medium and dispersed polymer-rich phase) can be considered a priori.

Moreover, in our opinion, the choice of PVDF can be rewarding also from a theoretical perspective. In fact PVDF is a macromolecular material of wide applicative interest characterized by a semicrystalline structure and concerning which literature data of sorption and swelling are already available.[16,17]

Experimental

Materials

Poly(methylmethacrylate) (PMMA) was purchased from Aldrich in the form of powder with weight-average molecular weight (M_w) = 350,000 and glass-transition temperature (T_g) = 122.0°C. PMMA sheets (~1 mm thick; 10 × 10 cm) were prepared from the powder by compression molding in a laboratory press: the powder was kept at 185°C for 5 min, after which the polymer specimens were cooled to room temperature by cold water running through the press plates. The sheets were then cut in small pieces to be inserted in the sorption cell in the proper amount (about 30 g of polymer). Poly(vinylidene fluoride) Solef 1010 [melting temperature 173.2°; crystallinity 55%; number-average molecular weight (M_n) = 120,600; M_w = 298,300 (molecular weight obtained using polystyrene standard)] was kindly donated by Solvay Solexis and used in the form of cylindrical pellets [diameter (d) = 2 mm, d/h = 1]; before the insertion in the sorption vessel the polymer (30 g) was heated to 140°C for 3 h and then slowly cooled to room temperature (cooling time 3–5 h). The adopted CO_2 (Air Liquide) was 99.998 pure; the Ar, selected as a nonabsorbable probe (see below), was Air Liquide 5.0. Both gases were used without further purification. The carrier gas for the GC analyses, carried out with a thermal conductivity detector (TCD), is hydrogen 6.0 produced by a Parker electrolytic gas generator.

Polymer characterization

Calorimetric analyses of selected PVDF samples were done by use of a Shimadzu DSC-60 calorimeter. A preweighted amount of the polymer (mass ≈ 10 mg) was loaded into a suitable aluminum pan. An aluminum lid was placed over the polymer and this assembly was pressed slightly with a metal plunger. Then the sealed pan was placed in the DSC holder under N_2 atmosphere. The sample was heated twice from 10 to 200°C at a heating rate of 10°C/min. The cooling rate between the two scans was also 10°C/min. Analyses were performed on the virgin material, both before and after the thermal pretreatment, and on the fluoropolymer recovered at the end of the sorption period. Polymer crystallinity was found from calorimetric curves using λ = 105 J/g[18] as the latent heat of crystallization of an ideal PVDF crystal.

Sorption measurements apparatus

The experimental apparatus used to measure the sorption of dense CO_2 in polymer samples, schematically depicted in Figure 1, was assembled in our laboratory using commercial elements.

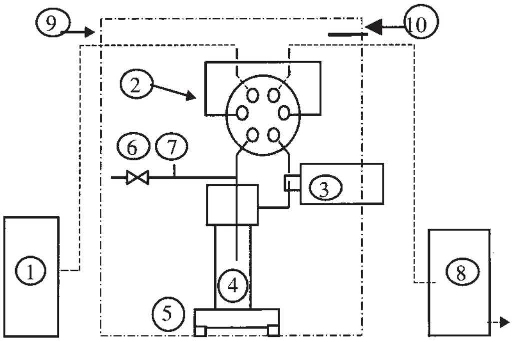

Figure 1. Representation of the experimental apparatus adopted to measure sorption of carbon dioxide in polymers.

(1) Hydrogen generator, (2) switching valve equipped with 6 μL gas sampling loop, (3) high-pressure recirculation pump, (4) sorption vessel, (5) magnetic stirrer, (6) gas inlet valve, (7) high-accuracy pressure transducer, (8) GC analyzer, (9) electronically controlled oven, (10) temperature sensor.

It is composed of a high-pressure sorption cell consisting of a Parr high-pressure vessel (Model 2670, nominal free volume 72 mL) fitted with a high-pressure transducer (Sensotec Model: STJE/1890–20A) with accuracy ±0.05 MPa. The sorption cell is part of a closed loop prepared with 1/16-in. OD AISI 316 tubing and equipped with a six-port two-way high-pressure sampling valve (Rheodyne valve Model 7000). The switching valve was added to allow real-time sampling of the fluid phase in contact with the polymer and to this purpose two ports of the valve are connected with a 6-μL high-pressure sampling loop, whereas the other two ports are connected to the carrier line (H_2) of a Hewlett–Packard Series HP 6890 gas chromatograph.

The GC carrier circuit was modified to use the hydrogen itself, available at 0.5 MPa from the gas generator, to entrain the fluid contained in the sample loop to the chromatographic column (Carboxen™ 1000), which was used to separate the components of the gaseous mixture analyzed by a thermal conductivity detector. Moreover, the loop containing the sorption vessel was equipped with the head of a high-pressure liquid pump (Gilson Model 10SC) whose piston was moved by a custom-made electric motor to ensure mixing of the gas mixture.

The high-pressure part of the experimental apparatus, consisting of the sorption vessel, the Rheodyne valve, the head of the liquid HPLC pump, and the connecting tubing and fittings, is separated by the gas chromatograph and can be inserted as a whole into an electronically controlled oven whose temperature can be kept constant within ±0.3 K (Eurotherm Model 226e).

Determination of solubility

In the following discussion of the method adopted to measure solubility of CO_2 in PVDF we denote with the subscript 1 carbon dioxide and with the subscript 2 the nonabsorbable probe.

The starting point of the calculus is represented by the mass balance equations of the two components, written as

$$M_1^0 = M_1^P + \rho_1^g(V - V_P^0 - V_P^{Sw}) \tag{1}$$

$$M_2^0 = \rho_2^g(V - V_P^0 - V_P^{Sw}) \tag{2}$$

where M_i^0 represents the initial masses of CO_2 and probe delivered in the sorption apparatus, M_1^P is the total amount of CO_2 dissolved in the polymer at equilibrium condition, ρ_i^g represents the weight concentrations of the two components in the gaseous phase at equilibrium condition, V is the total free volume of the experimental apparatus, V_P^0 is the initial volume of the polymer inserted in the sorption cell, and V_P^{Sw} is the volume of dilation of the polymer as a consequence of the sorption of CO_2.

From Eqs. 1 and 2 we obtain the following expressions for the quantity M_1^P:

$$\frac{M_1^0 - M_1^P}{M_2^0} = \frac{\rho_1^g}{\rho_2^g} \tag{3}$$

$$M_1^P = M_1^0 - \frac{\rho_1^g}{\rho_2^g} M_2^0 \tag{4}$$

In this equation the initial total mass of CO_2 and probe added to the system can be measured by weighing the apparatus after each insertion and the weight concentration ratio of the two components in the gas phase can be obtained by the GC analysis of the mixture. By solving the equation it is then possible to obtain the total amount of penetrant dissolved in the polymer.

The mathematical manipulation previously described was selected because it offers several advantages: it implicitly accounts for the effect of the polymer dilation without the need of computing it; makes possible performing of GC calibration in terms of mass ratio of the components, thus avoiding the necessity of determining the total free volume of the experimental apparatus; and, moreover, allows the operator to use the nonabsorbable probe as an internal chromatographic standard to improve the precision of the quantitative analyses because they are unaffected by any density fluctuation in the sampling loop.

Equation 4 can be written in an adimensional form: both members of the equation are divided by the initial mass of the polymer loaded in the apparatus M_P^0

$$\frac{M_1^P}{M_P^0} = \frac{M_1^0}{M_P^0} - \frac{\rho_1^g}{\rho_2^g}\frac{M_2^0}{M_P^0} \tag{5}$$

This equation can be further arranged in terms of an experimentally measured quantity. In fact the direct measured quantity is the ratio X of the chromatographic areas A_1 and A_2 of the two components, which is related to their mass ratio by the equation of the calibration line.

In our case we have seen that calibration points are excellently fitted by a straight line, whose slope F is related to the response factor of the components to the TCD (Figure 2 and Eq. 6):

$$\frac{\rho_1^g}{\rho_2^g} = Y = F\frac{A_1}{A_2} = FX \tag{6}$$

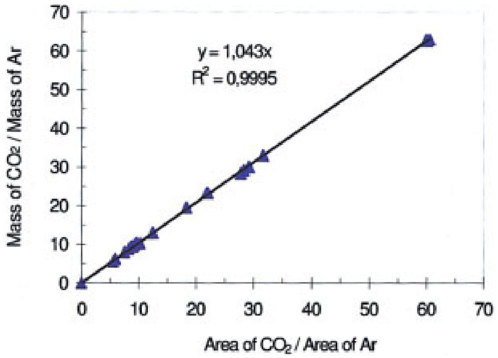

Figure 2. Calibration line of the TCD detector adopted in this study.

Total number of experimental points: 86. Each mixture loaded in the experimental apparatus was analyzed by at least four injections before changing the composition to a new value. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

By substituting the previous equation Eq. 5 becomes

$$\xi = \beta - \alpha F X \tag{7}$$

where ξ denotes the mass of sorbed CO_2 per gram of polymer, β denotes the ratio between the initial masses of CO_2 and polymer, and α represents the ratio between the initial masses of Ar and polymer.

It can be observed that an explicit calculation of the polymer dilation could theoretically be obtained directly from the solution of Eq. 2 after insertion of the probe concentration. To use this approach, however, a very accurate estimation of the total free volume V of the apparatus is necessary both because it appears explicitly in the equation and because it must be used to calibrate the GC in term of weight concentration of the probe:

$$V_P^{Sw} = V - V_P^0 - \frac{M_2^0}{\rho_2^g} \tag{8}$$

Selection of the probe

A crucial point for the accuracy and precision of our technique is the selection of the compound that must be used as a probe. An ideal probe should satisfy several preconditions:

(1) It must be absorbed in a negligible way in the polymer phase so that in principle its amount in the fluid phase does not change during the soaking experiment.

(2) It must modify in a negligible way the chemical potential of the other species dissolved in the gas mixture. A close approximation of this condition ensures that the presence of the probe does not alter the equilibrium partitioning between the polymer and the fluid phase of the compounds under investigation.

(3) It must be completely miscible with other components of the fluid phase under adopted experimental conditions and must be detectable by TCD using hydrogen as a carrier.

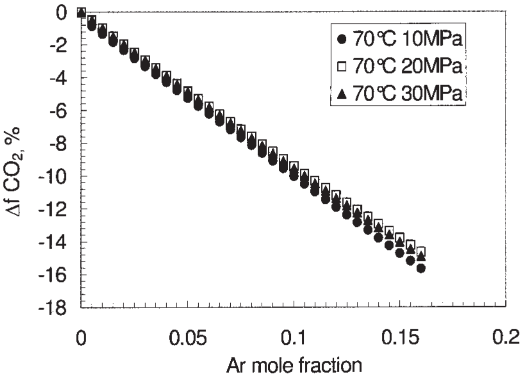

Figure 3. Computed relative variation in the fugacity of CO_2 in mixture with Ar as a function of the inert mole fraction at 70°C and different pressures.

A noble gas should be an ideal candidate as a probe, having weak interactions with the other components of the gas phase and with the polymer segments. Moreover, with the exception of helium and neon, that given their small masses have properties that cannot be described by classical statistical mechanics, the heavier noble gases (argon, krypton, and xenon) can be considered *simple molecules* whose potential energy is determined only by the distance of separation and not by the relative orientation between two molecules. On this basis we decided to test the behavior of argon as a probe.

The effect of the noble gas on the fugacity of carbon dioxide in binary mixtures was estimated using the Peng–Robinson equation of state[19] using literature values[20] for the pure component parameters and considering null interaction parameters in the van der Waals mixing rule. The relative deviations in the fugacity of CO_2, computed as a function of the inert mole fraction at fixed total pressure of the system at 70 and 40°C, are reported in Figures 3 and 4, respectively. It can be observed that if Ar mole fractions < 0.05 are used, the fugacity of carbon dioxide decreases of $<6\%$ with respect to that of the pure component, independently from the value of the total pressure in the range 10–30 MPa.

The solubility of Ar in PMMA was estimated by Rajendran et al.[12] using an empirical correlation, resulting in a value about sevenfold lower than that of CO_2 under similar operative conditions. The adopted correlation assumes that the potential field of the gaseous molecules that are sorbed can be described by Lennard–Jones expression so that specific interactions with the polymer are neglected. In this scenario the amount of sorbed compound per unit mass of amorphous phase of the polymer depends only on the polymer state (rubbery or glassy). On the other hand, it is well known that CO_2 interacts both with the carbonyl moiety of PMMA[21] and with fluorine atoms on the backbone of fluorinated polymers.[22] On this basis it seems reasonable to hypothesize that an even greater difference in the solubility of Ar and CO_2 in the aforementioned polymers should be expected. With this awareness, to estimate the solubility of Ar inside PVDF, we performed a measurement using the gravimetric method proposed by Berens.[23] The experiments were performed at 20.0 MPa and 40°C using a polymer film (purchased from Goodfellow) whose crystallinity was measured by DSC to be comparable with that of PVDF pellets used to carry out the sorption experiments. The room-condition desorption profile, plotted as a function of the square root of time, is substantially linear at low desorption times (Figure 5) so that the amount of dissolved Ar in the matrix was computed by extrapolation of the line at initial time to be 0.17–0.23% w/w. This concentration is about 60 times lower than that computed by Briscoe et al.[16] for sorption of CO_2 inside PVDF at similar *T* and *P* values.

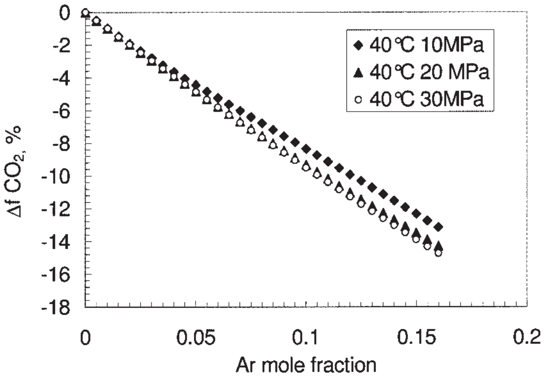

Figure 4. Computed relative variation in the fugacity of CO_2 in mixture with Ar as a function of the inert mole fraction at 40°C and different pressures.

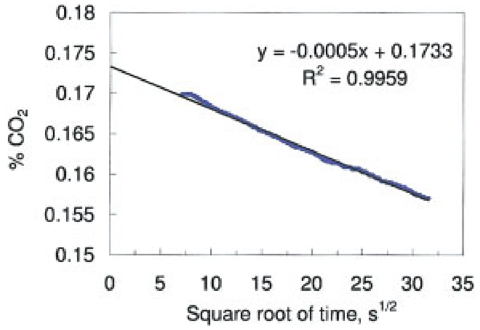

Figure 5. Desorption profile at room conditions of Ar from a PVDF film exposed to the noble gas at 40°C and 20 MPa for 18 h.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

On the basis of these experimental results it seems reasonable to adopt Ar as a probe for the measurement of sorption of carbon dioxide into PVDF, provided that the concentration of the inert is kept <0.1 mole fraction.

Table 1. Sorption of CO_2 in PMMA at 50°C*

y_2	P (MPa)	ξ	Uncertainty $+\Delta\xi$	$-\Delta\xi$
0.0949	6.6	0.106	0.004	0.001
0.0511	9.5	0.166	0.008	0.003
0.0317	11.6	0.156	0.015	0.004
0.0280	14.1	0.230	0.019	0.006
0.0245	15.7	0.239	0.020	0.006
0.0232	17.1	0.244	0.022	0.006

*y_2, initial mole fraction of Ar in fluid phase; ξ, mass of sorbed CO_2 (g/g of PMMA).

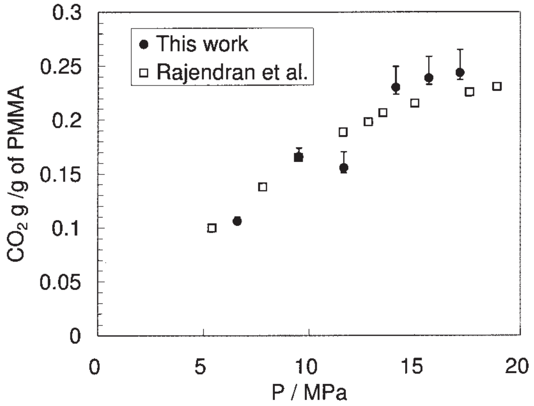

Figure 6. Comparison between our results of sorption of CO_2 in PMMA and those obtained by Rajendran et al.[12] at 50°C.

Sorption of carbon dioxide in PMMA

The reliability of the proposed technique was first verified by measuring the sorption of carbon dioxide in PMMA. The solubility of CO_2 in this polymer has already been measured at low and moderate pressures (up to 150 bar), with good agreement with literature data, by a purely gravimetric technique based on two sequential weightings of the polymer sample: the first in the presence of CO_2 alone and the second after addition of Ar that was used as a nonabsorbable compound with the function of modifying the density of the fluid phase in contact with the polymer. From a comparison of the two balance signals—assuming that the noble gas neither changes the volume of the polymer nor dissolves in the polymer nor displaces the sorbed carbon dioxide—it is possible to calculate both the volume of the swollen polymer and the mass of sorbed CO_2.[12] Our experiments were performed using the GC-based technique at 50°C, changing the pressure from 6.6 to 17.1 MPa and using in all cases about 1 g of Ar as a nonabsorbable probe. The measured solubilities are summarized in Table 1 and plotted in Figure 6 as a function of pressure together with the results of error estimation (see appendix). Our results are in good agreement with those reported by Rajendran et al.,[12] who used both a conventional technique based on the simultaneous utilization of mass suspension balance and visual determination of polymer swelling and the aforementioned Ar-based pure gravimetric technique.

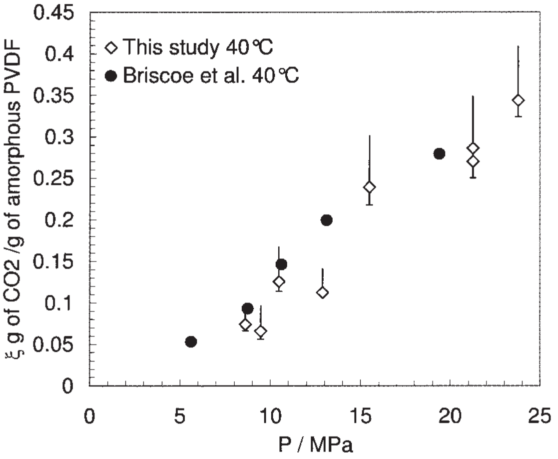

Figure 7. Solubility of CO_2 in PVDF at 40°C as a function of pressure.

Comparison between the results obtained with our technique and those obtained by Briscoe and Mahgerefteh.[15]

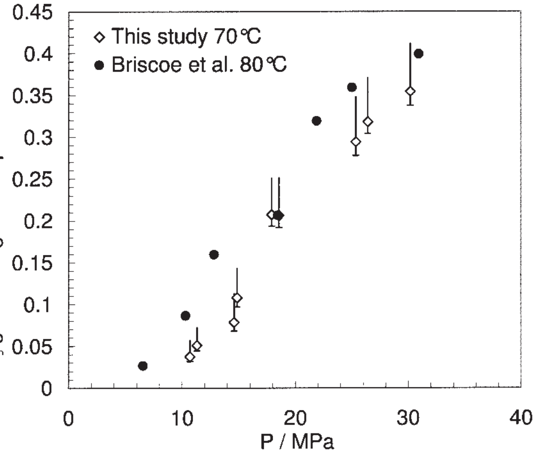

Figure 8. Solubility of CO_2 in PVDF at 70°C as a function of pressure.

Comparison between the results obtained with our technique and those obtained by Briscoe and Mahgerefteh[16] at 80°C.

Sorption of carbon dioxide in PVDF

The sorption of carbon dioxide in PVDF was studied at 40 and 70°C using Ar as a probe. The sorption isotherms are presented in Figures 7 and 8, whereas measured solubilities are summarized in Tables 2 and 3 together with the results of error estimation performed with the procedure described in the appendix.

Most of the experiments were performed by adding about 1 g of the probe to the fluid phase. Sorption data are reported with reference to the mass of amorphous polymer because it is commonly accepted that, in the case of semicrystalline polymers, the absorption of gaseous molecules occurs only in the amorphous domains, whereas crystallites constitute a nonsorbing, nonpermeable phase.[24] In the case of semicrystalline polyethylenes[25,26] it has been proposed that the solubility of gaseous molecules inside polymers having different degrees of crystallinity can be expressed by

Table 2. Sorption of CO_2 in PVDF at 40°C*

y_2	P (MPa)	ξ	Uncertainty $+\Delta\xi$	$-\Delta\xi$
0.050	8.6	0.074	0.023	0.008
0.038	9.5	0.066	0.031	0.010
0.029	10.5	0.126	0.042	0.012
0.022	12.9	0.112	0.029	0.002
0.037	15.5	0.239	0.062	0.021
0.016	21.3	0.270	0.067	0.020
0.017	21.3	0.286	0.063	0.020
0.018	23.8	0.344	0.065	0.020

*y_2, initial mole fraction of Ar in fluid phase; ξ, mass of sorbed CO_2 expressed in g/g of amorphous PVDF considering a 55% crystallinity of the polymer.

Table 3. Sorption of CO_2 in PVDF at 70°C*

y_2	P (MPa)	ξ	Uncertainty $+\Delta\xi$	$-\Delta\xi$
0.061	10.7	0.038	0.019	0.006
0.055	11.3	0.051	0.021	0.006
0.034	14.6	0.078	0.034	0.011
0.033	14.8	0.108	0.035	0.011
0.026	17.9	0.207	0.044	0.014
0.025	18.5	0.206	0.045	0.014
0.021	25.3	0.294	0.054	0.016
0.022	26.4	0.318	0.053	0.014
0.020	30.2	0.354	0.057	0.017

*y_2, initial mole fraction of Ar in fluid phase; ξ, mass of sorbed CO_2 expressed in g/g of amorphous PVDF considering a 55% crystallinity of the polymer.

$$S = S^*\alpha \tag{9}$$

where α is the volume fraction of the amorphous polymer phase and S^* is the solubility of the gas in a completely amorphous polymer.

It must be emphasized that Eq. 9 cannot be considered rigorously valid for all semicrystalline polymers because a sorption of penetrants has been shown in the crystals of the δ-form of syndiotactic polystyrene.[27] In spite of this we have used the model with an a priori approach to correct our solubility data, taking into account the crystallinity of the PVDF used in the measurements. To this purpose polymer samples randomly chosen from PVDF (received from Solvay) were analyzed by DCS. Calorimetric measurements were performed on the virgin polymer, on thermally treated PVDF, and on specimens obtained after CO_2 desorption. We computed a crystallinity of about 55%, substantially unaffected by either thermal treatment or sorption process. The experimental data obtained in this study have been compared with those measured by Briscoe and Mahgerefteh[15] with a different experimental technique using a PVDF sample with a crystallinity of 53%; good agreement was obtained at 40°C, whereas the mass sorption measured by the GC method is somewhat lower than that determined using the vibrating-arm technique at 70°C.

From the error analysis reported in the appendix we have found that our experimental methods tend to underestimate the sorption for the effect of probe absorption inside the polymer. In the case of low critical temperature gases an increase in the solubility in polymers when the temperature is increased was sometimes observed.[2] On this basis it could be hypothesized that the larger difference between the two sets of data at 70°C could be partially attributable to a more relevant sorption of Ar inside the polymer.

On the other hand, in comparing our data with those reported by Briscoe, we are aware that Shenoy et al.[17] measured—using a linear variable differential transformer—a linear swelling of PVDF significantly higher than that reported by Briscoe and coworkers (3.9% at 75°C and 27.6 MPa vs. 1.2% at 80°C and 30.0 MPa). As mentioned earlier, the vibrating-beam technique requires a correction of the measurement for the mass of entrained gas that depends on the swelling of the polymer. An underestimation of the swelling leads to an overestimation of the amount of gas sorbed in the polymer because the effect of the higher mass of entrained gas is erroneously attributed to higher sorption in the polymer. This swelling underestimation could then contribute to creation of differences between the two families of experimental points.

To obtain a simple quantitative description of the sorption isotherms we used a thermodynamic approach already adopted by Shim and Johnston[28] to describe the distribution of toluene between a polymer and a CO_2-based supercritical (SC) phase. Thus we used the Flory equation to express the activity of carbon dioxide inside the amorphous domains of the polymer and the Peng–Robinson equation of state to determine the fugacity of the supercritical solvent in the gaseous phase. In this approach the phase equilibria may be described by choosing an ideal gas reference state for the SC solvent and a hypothetical pure liquid standard state for the solvent in the polymer. The equilibrium condition for the partitioning of CO_2 between the gaseous phase and the polymer at fixed temperature T and pressure P is defined by

$$a_1 = \frac{y_1 f_1}{P_1^{sat}\varphi_1^{sat}\exp\left[\dfrac{v_1^P(P - P_1^{sat})}{RT}\right]} \tag{10}$$

where a_1 is the activity of CO_2 in the polymer phase; y_1 is the mole fraction of CO_2 in the gaseous phase (unity for a one-component phase); f_1 is the fugacity of CO_2 in the fluid phase; P_1^{sat} is the vapor pressure of CO_2 that can be extrapolated above the critical point, if necessary; φ_1^{sat} is the fugacity coefficient at the vapor pressure; and v_1^P is the partial molar volume of CO_2 in the polymer phase.

To describe the polymer phase we adopted Flory's theory for the free energy of mixing of the amorphous portions of the polymer with the solvent so that the activity of the solvent in the polymer is given by

$$\ln a_1 = \ln \Phi_1 + \left(1 - \frac{1}{r}\right)(1 - \Phi_1) + \chi(1 - \Phi_1)^2 \tag{11}$$

where Φ_1 is the volume fraction of CO_2 inside the amorphous domain of the polymer; r is the ratio of molar volume of polymer to solvent ($r \to \infty$ for high molar mass polymers); and χ is the Flory interaction parameter.

The volume fraction of CO_2 in the polymer phase can be expressed in terms of experimentally measured sorption data by

$$\Phi_1 = \frac{\dfrac{\xi_1}{(1 - X_c)}}{\dfrac{\xi_1}{(1 - X_c)} + \dfrac{PM_1}{v_1^P}\dfrac{1}{\rho_2^a}} \tag{12}$$

where ξ_1 represents the CO_2 sorbed in the polymer (g CO_2/g polymer); X_c is the crystallinity of the polymer (determined by DSC); PM_1 = molecular weight of CO_2; and ρ_2^a is the density of amorphous PVDF.

The partial molar volume of CO_2 inside PVDF was computed at 42 and 80°C by Briscoe and Mahgerefteh[15] using volume swelling data. Considering that the thermodynamic function varies moderately with T and P, in the pressure

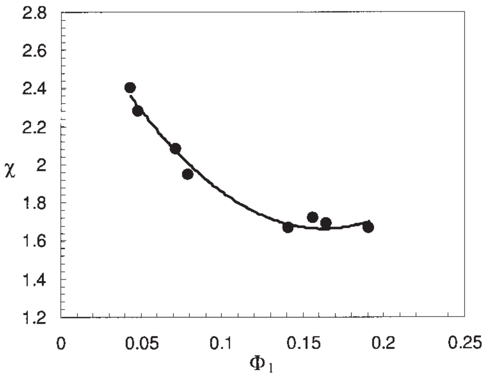

Figure 9. Polymer–CO_2 Flory interaction parameters as a function of carbon dioxide volume fraction at 40°C.

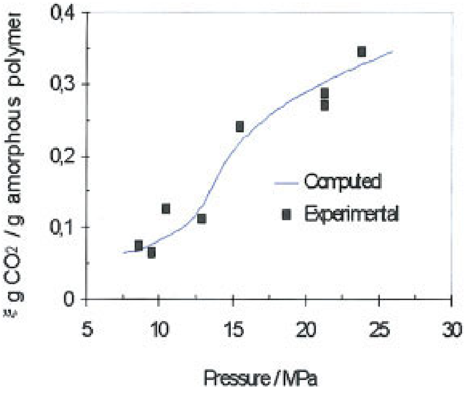

Figure 11. Experimental and calculated sorption isotherms at 40°C.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

domain from 10 to 30 MPa, it can be approximated by a constant value of 18 cm^3/mol.

The value of f_1 at different pressures was computed using the Peng–Robinson equation of state,[18] neglecting the amount of Ar added as a probe

$$\ln\frac{f}{P} = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}\,B}\ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right) \quad (13)$$

where

$$A = \frac{aP}{R^2T^2} \qquad B = \frac{bP}{RT} \qquad Z = \frac{Pv}{RT} \quad (14)$$

The pure component parameters a and b are expressed in terms of the critical parameters and acentric factor of the considered compound using equations reported in the literature.[19]

The hypothetical vapor pressure of CO_2 above the critical temperature was extrapolated by the equation

$$\ln P^{sat}(\text{bar}) = 10.860 - \frac{1996.12}{T} \quad (15)$$

obtained by fitting the vapor pressure data[29] from −18.9 to 31.1°C.

The Flory interaction dimensionless parameter χ was regressed from experimental data and can be expressed by quadratic functions (Figures 9 and 10) of the solvent volume fraction, as previously reported by other researchers[5,28]:

$$\chi\,(40°\text{C}) = 48.71\Phi_1^2 - 15.88\Phi_1 + 2.96 \quad (16)$$

$$\chi\,(70°\text{C}) = 64.45\Phi_1^2 - 19.63\Phi_1 + 3.07 \quad (17)$$

Using these equations to express the activity of carbon dioxide in PVDF we obtained the continuous curves reported in Figures 11 and 12.

Briscoe et al.[16] previously tried to quantitatively describe the sorption isotherms of carbon dioxide in PVDF using the Sanchez–Lacombe equation of state. DeSimone[30] commented on this attempt observing that, by this approach, it is not possible to attain a good description of the experimentally measured trend, probably because the adopted EOS does not properly describe the chemical potential of the solvent inside the polymer because of its semicrystalline nature. In fact it is observed that the sorption is overpredicted at lower pressures

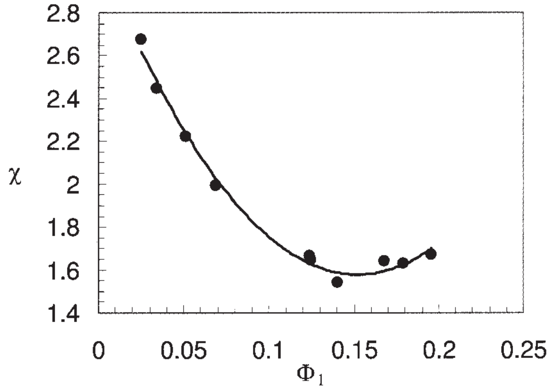

Figure 10. Polymer–CO_2 Flory interaction parameters as a function of carbon dioxide volume fraction at 70°C.

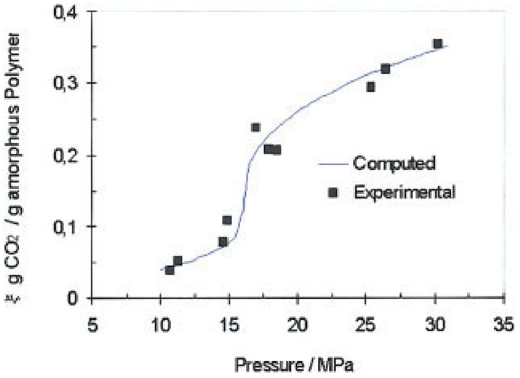

Figure 12. Experimental and calculated sorption isotherms at 70°C.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and underestimated at higher density of the SC phase. The heuristic approach adopted in this work attributes the duty of describing polymer–solvent interactions to the quadratic expressions (Eqs. 16 and 17), obtained from the experimental points measured. With this approach it is possible to compute sorption isotherms that exhibit a sigmoidal shape, which seems close to the experimental trend observed in this work.

Conclusions

A novel experimental method to measure sorption of gaseous molecules inside a polymer was used to measure solubility of dense carbon dioxide in polymers. The technique is based on the use of a gas chromatograph to determine the equilibrium composition of the fluid phase in contact with the polymer. These data are used to solve the algebraic system of mass balance equations of the components that partition between the two phases. To consider the effect of polymer swelling on the measurements, Ar was added to the fluid phase to be used as a probe that is not absorbable by the polymer. The technique was validated by measuring the sorption of carbon dioxide in poly(methylmethacrylate) and was then used to determine the solubility of high-pressure CO_2 in PVDF at 40 and 70°C. Error analyses performed on the experimental points obtained with the GC-based technique gave an estimation of the uncertainty in the measurements within 30% of the computed value for most of the experiments.

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Appendix: Error Analysis of the Experimental Technique

A preliminary step in the evaluation of the suitability of an experimental technique is to assess the effect of the main potential source of errors intrinsically involved in the technique that can affect the reliability of the measurement.[31]

To this purpose we have rewritten the mass balance equation of the probe without the constraint of zero sorption inside the polymer:

$$M_2^0 = \gamma M_2^0 + \rho_2^g[V - V_P^0 - V_P^{Sw}] \tag{A1}$$

where γ is the fraction of the probe initially loaded in the system that has been dissolved in the polymer under equilibrium condition.

Using Eq. A1 the fraction of the carbon dioxide sorbed in the polymer initially loaded in the experimental apparatus is computed from the following equation:

$$\xi = \beta - \alpha FX(1 - \gamma) \tag{A2}$$

In our technique we have considered as main sources of random errors the uncertainty in the value of the slope F of the calibration curve, the imprecision in the value of the ratio X of chromatographic areas, the uncertainty in the values of the mass of the polymer, the CO_2, and the probe, all evaluated by electronic scales. A further contribution to the experimental error in the measured quantities can be attributed to the sorption of the probe inside the polymer matrix. This error, as easily inferred from Eq. A2, always has the same algebraic sign and leads to an underestimation of the amount of carbon dioxide dissolved in the polymer and can be considered a systematic error. To quantify the effect of each single parameter on the uncertainty of the measurements we have used the theory of propagation of the error.

Let us assume that a derived property u is related to several mathematical variables X_j by a regular functional relation with respect to continuity and derivability:

$$u = u(X_j) \qquad j = 1, \ldots, n \tag{A3}$$

Let us denote with x_j^i (in lowercase) the values for the variables measured in the ith experiment and with $\overline{x_j}$ the mean value of the jth measured variable.

Then the mean value of the desired property can be approximated by

$$\bar{u} = u(\overline{x_j}) \tag{A4}$$

and its standard deviation (also termed standard error) as a consequence of random errors is given by the error propagation law[32]

$$S_{\bar{u}} = \left\{ \sum_{j=1}^{n} \left[\frac{\partial u}{\partial x_j} \right]^2 S_{\bar{xj}}^2 \right\}^{1/2} \tag{A5}$$

All derivatives appearing in square brackets must be evaluated at the mean value of each x_j and thus must be considered constants.

With respect to the uncertainty in the desired quantity as a consequence of systematic error in the x_j, it can be estimated, provided that the individual uncertainty of the measured variables is small compared with their average value, by expanding the function into a Taylor series around the point $\overline{x_j}$, neglecting all terms of order two and higher:

$$\Delta u = \sum_{j=1}^{n} \left[\frac{\partial u}{\partial x_j} \right] \Delta x_j \tag{A6}$$

The total error on the measured quantity can be estimated by summing the two quantities so that it can be expressed as

$$-S_{\bar{u}} + \Delta u < (\Delta u)_{\text{total}} < S_{\bar{u}} + \Delta u \tag{A7}$$

Evaluation of imprecision arising from random errors has been estimated by applying Eq. A5 to the functional form in Eq. 7:

$$S_{\bar{\xi}} = [S_{\bar{\beta}}^2 + (\bar{F}\bar{X})^2 S_{\bar{\alpha}}^2 + (\bar{\alpha}\bar{X})^2 S_{\bar{F}}^2 + (\bar{\alpha}\bar{F})^2 S_{\bar{x}}^2]^{1/2} \tag{A8}$$

where the equation is evaluated using the average values for the different quantities.

The standard errors in the adimensional quantities α and β were estimated using the propagation of error formula for the following ratios:

$$\bar{\alpha} = \frac{\overline{M_2^0}}{\overline{M_P^0}} \qquad S_{\bar{\alpha}} = \left\{ \left(\frac{\overline{M_2^0}}{\overline{M_P^0}} \right)^2 \left(\frac{S_{\overline{M_2^0}}^2}{(\overline{M_2^0})^2} + \frac{S_{\overline{M_P^0}}^2}{(\overline{M_P^0})^2} \right) \right\}^{1/2} \tag{A9}$$

$$\bar{\beta} = \frac{\overline{M_1^0}}{\overline{M_P^0}} \qquad S_{\bar{\beta}} = \left\{ \left(\frac{\overline{M_1^0}}{\overline{M_P^0}} \right)^2 \left(\frac{S_{\overline{M_1^0}}^2}{(\overline{M_1^0})^2} + \frac{S_{\overline{M_P^0}}^2}{(\overline{M_P^0})^2} \right) \right\}^{1/2} \tag{A10}$$

In the case of the calibration line, the standard error $S_{\bar{F}}$ in the slope determined by fitting experimental data using the least-squares method was assumed to be coincident with its standard deviation S_F computed from the N experimental data plotted to fit the line according to the equation

$$S_F = \left(\frac{N}{N \sum X_i^2 - (\sum X_i)^2} \right)^{1/2} \left(\frac{\sum (Y_i - \bar{F}X_i)^2}{N} \right)^{1/2} \tag{A11}$$

It must be emphasized that the calibration reported in Figure 2 was obtained from the fitting of 86 experimental points collected at different periods randomly distributed during the experimental campaign of measurements described herein. With obtained experimental data the standard error S_F was estimated to be ± 0.0025.

With respect to the ratio between the chromatographic areas of the carbon dioxide and the probe the mean values and the standard errors were estimated for each equilibrium measurement from $n = 4$ independent GC injections.

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n} \qquad S_{\bar{X}} = \frac{1}{\sqrt{n}} \left[\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n} \right]^{1/2} \tag{A12}$$

The standard errors in the mean values of the masses were assumed to be coincident with the precision of the electronic scales adopted (±0.1 mg for the polymer and ±0.01 g for the gaseous components). It must be mentioned that, under conditions adopted in this study, the main source of error in Eq. A8 is constituted by the second term inside the square brackets.

To estimate the effect of the systematic error arising from the sorption of the probe inside the polymer matrix, Eq. A2 was derived with respect to the adimensional variable γ by applying Eq. A6

$$\Delta\xi = \bar{\alpha}\bar{F}\bar{X}\Delta\gamma \tag{A13}$$

To obtain an estimate of the value of $\Delta\gamma$ we used the results of the sorption experiment performed with Ar and PVDF using the Berens method, mentioned when the selection of the probe was discussed. In that case 5.2 g of polymer were combined with 7.14 g of Ar at 20 MPa and 40°C (the amount of gas was estimated from the free volume of the extractor computed on the basis of the polymer density[33] and using a dedicated equation of state for the noble gas[34]), leading to a sorption of about 2 mg of Ar per g of PVDF. This led to a total amount of sorbed gas of 11 mg, which is about 0.16% of the initial amount loaded in the system. The value of $\Delta\gamma$ was then fixed to 0.005 to be more conservative in the evaluation of the error. This value was also used to estimate the systematic error in the measurements carried out with PMMA. It seems interesting to observe that the sorption of the probe in the polymer is the second more relevant source of error in the experimental measurements under the adopted conditions.

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