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Modification of polystyrene properties by CO_2: Experimental study and correlation

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ABSTRACT: The sorption of CO_2 in polymers entails their swelling and plasticization whose study is crucial for the design of processes and further applications. The operating conditions during foaming, purification, or impregnation of polymers in CO_2 are mainly determined by the mentioned binary system. In this work, the modification of polystyrene's physical properties (glass transition temperature and viscosity) has been experimentally studied. Since plasticization phenomena are very valuable for the processing of polymers, the amount of CO_2 absorbed into the polymer is related with the changes in the described properties. Furthermore, interfacial tension is also correlated with the sorption of CO_2 from literature data. The proposed correlation fits pretty well the properties shifts in the studied working conditions. Finally, the influence of pressure and temperature on the diffusivity of the CO_2 in the polystyrene is calculated through the measurement of viscosity along time. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41696.

KEYWORDS: glass transition; polystyrene; viscosity and viscoelasticity

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INTRODUCTION

CO_2 has been used in many different applications, mainly in the field of polymers[1–5] since it is nontoxic, nonflammable, inexpensive, presents a solvent strength adjustable and moderate critical temperature and pressure, which makes it an excellent fluid for polymer processing.[2] Nevertheless, the behavior of polymers and high pressure gases is still nowadays a source of scientific interest and a key issue for new industrial applications.[6] Solubility, diffusivity, density, and permeability data are very important for understanding the systems containing a polymer and $scCO_2$.[4] The small molecule diffuses between the polymer chains more easily than a large molecule and its sorption increases the free volume and the polymer segment mobility. The sorption of CO_2 into polymers results in swelling and consequently promotes changes in the mechanical and physical properties of those polymers. The absorbed gas acts as "*lubricant*," making easier for chain molecules to slip over one another and thus causing polymer softening; by this reason CO_2 is known as plasticizer.[7] An increase in CO_2 concentration promotes changes in the properties of the polymer as a consequence of the swelling and plasticization.[6,8] Plasticization generally causes changes in the thermal and mechanical properties of a polymer system that results in the decrease in rigidity at room temperature, the depression of glass transition temperature (T_g) and toughness and the increase in elongation and flexibility.[9,10]

There are several factors determining the interaction between the plasticizer and the polymers: the chemical nature of the polymer and its physical state, its crystallinity and degree of crosslinking, the intermolecular forces between the polymer and the gas and the molecular size of the diluent (CO_2).[5,11] For the rational design of processes and applications, the study of the behavior of the system polymer/CO_2 and the knowledge of the mechanical and physical property changes is crucial. For instance, nucleation of foams using CO_2 takes place at temperature close to the T_g.[12]

The influence of pressure and temperature on the behavior of the binary systems is crucial to select the most suitable conditions to perform several applications including CO_2 and polymers. The purification and precipitation of polymeric matrix, the foaming of polymers, the formation of powdered polymers or even their fractionation[7] are included among the most useful processes where the modified characteristics of the polymer play a crucial role. The control over the properties and design of functional materials is influenced by the gas sorption into the polymer.[6,13] Also, reliable high pressure rheological data are essential for the application of CO_2 to induce plasticization in the industrial plastics processes.[9,14]

Table I. Property, Models Used in the Correlation, or Prediction, Source of Data and Range of Pressure and Temperature Used

	Model		Source of experimental data	Range of pressure (bar)	Range of temperature (°C)
Sorption	Sánchez – Lacombe EoS	$\tilde{\rho}^2+\tilde{P}+\tilde{T}\cdot[\ln(1-\tilde{\rho})+(1-1/r)\cdot\tilde{\rho}]=0$	This work	1-200	30
Glass transition temperature	Chow	$\ln\left(\frac{T_g}{T_{g,0}}\right)=\beta\cdot[\theta\cdot\ln\theta+(1-\theta)\cdot\ln(1-\theta)]$ $\theta=\frac{M_m}{zM_d}\frac{w_1}{1-w_1}$ $\beta=\frac{zR}{M_m\Delta C_{pp}}$	This work	1-200	30-100
Interfacial Tension	Macleod – Sugden	$\sigma^{1/n}=[P_{PS}]\cdot\rho_L-[P_{CO_2}]\rho_V$	29	1-200	90-120
Diffusion	Fick model	$\frac{n(t)}{n(\infty)}=1-\left\{\sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\cdot\pi^2}\cdot\exp\left[\frac{-D\cdot(2n+1)^2\cdot\pi^2\cdot t}{4\cdot L^2}\right]\right\}\cdot\left\{\sum_{m=0}^{\infty}\frac{8}{(2m+1)^2\cdot\pi^2}\cdot\exp\left[\frac{-D\cdot(2m+1)^2\cdot\pi^2\cdot t}{4\cdot aL^2}\right]\right\}$	This work	20-100	60-100

The gas solubility in the polymer can be generally described by Henry's law[15–17]:

$$c=H\cdot P \tag{1}$$

where c is the concentration of the gas in the polymer, H is the Henry's law constant, and P is the equilibrium gas pressure. Henry's law is only valid on the ideal solution state and in the case of diluted solutions because it does not consider the interactions between the gas and the polymer. Although, it is not recommended its application at high pressure, it has been widely used due to its simplicity. As an alternative, CO_2 sorption in amorphous polymers can be described using the dual-mode model.[6,18] Dual-Mode sorption model is composed of Henry's law dissolution in the equilibrium region (low pressures) and Langmuir-type sorption in a nonequilibrium region.[16,17,19,20] The nonequilibrium region is related to the excess free volume or unrelaxed free volume in a glassy polymer resulting from the presence of microcavities capable of retaining solute molecules.[21] The Dual-Mode sorption model describes the solubility in the isotherm according to the expression shown below:

$$S=k_H P+\frac{C_H bP}{1+bP} \tag{2}$$

where S is the sorption of CO_2 in the polymer, k_H is the analogs to Henry's law constant, P is the pressure, C'_H is the saturation of the cavities, and b represents the affinity between the solute molecules, and the Langmuir sites present in the polymeric matrix.

Sánchez-Lacombe Equation of State (SL-EoS) is also used to correlate the sorption of CO_2 in PS[22–26] (Table I). The characteristic parameters for carbon dioxide and the polymer are shown in the Refs. 27,28 but the binary interaction parameter should be correlated from experimental data.

In this work, the sorption and the modification of properties because of the plasticizing effect of CO_2 in polystyrene (PS) has been studied due to the versatility offered by this system in a wide purposes field. The shift of the glass transition temperature, interfacial tension, and viscosity as a consequence of the plasticizing effect of CO_2 is correlated to generalize and make easier the application of these results in different processes. Also, from the decrease in viscosity along time, the diffusion coefficients of CO_2 in PS are determined.

MATERIALS AND METHODS

Materials

Polystyrene (average weight molecular weight 280,000 g/mol) in pellets was supplied by Sigma–Aldrich (Spain). The polymer pellets were milled before use to enhance the sorption. Carbon dioxide with a purity of 99.8% was supplied by Carburos Metálicos S.A. (Spain) and used as received.

Sorption of CO_2 in PS

There is a wide variety of CO_2 sorption data in PS due to the different methods and experimental conditions used. Aubert[30] and Zhang *et al.*[31] measured the solubility using gravimetric methods by means of a quartz crystal microbalance while Sato *et al.* determined the sorption by the pressure-decay method[28]

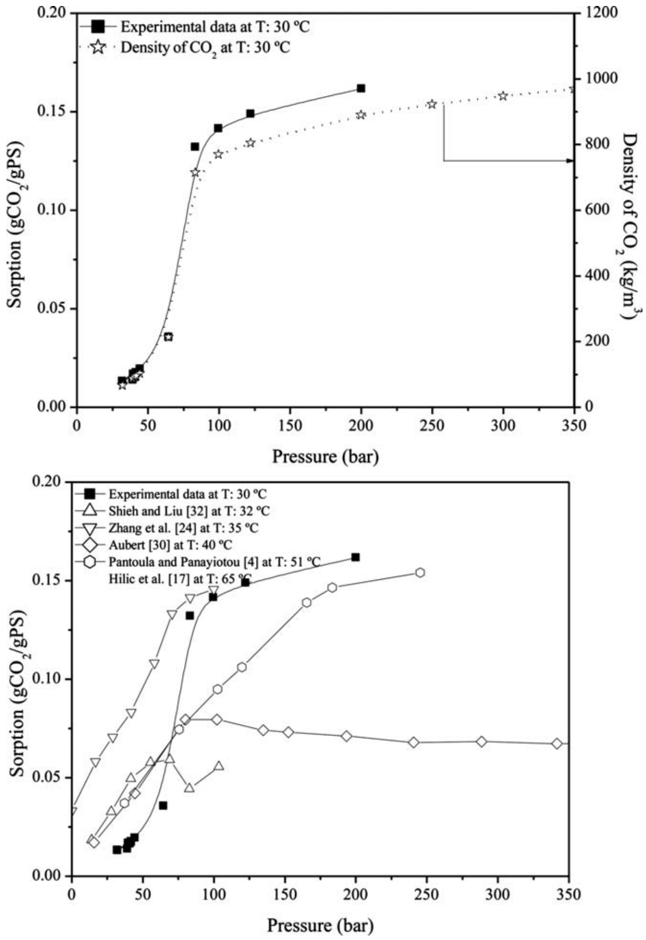

Figure 1. (Upper Figure) CO_2 sorption in PS as a function of pressure at 30°C. The relationship between the sorption of CO_2 and density can be observed in the right axis. (Bottom Figure) Comparison between the experimental data (■) obtained in this work and those from the literature as it is indicated by the markers: (○) Shieh and Liu[40]; (Δ) Zhang *et al.*[31]; (▽) Aubert[30]; (◇) Pantoula and Panayitou,[4] and () Hilic *et al.*[21]

or by the magnetic suspension balance.[32] Also, some authors employed combination of two methods to be more accurate due to changes in the volume of the polymer. Thus, Hilic *et al.*[21] combined the magnetic suspension balance with the pressure-decay method.

In this work, experimental sorption measurements were performed by two methods. *Ex situ* gravimetric measurements promulgated by Berens *et al.*[33] involves the saturation of the polymeric sample with supercritical CO_2 until the equilibrium conditions are achieved. Next, the gas is removed from the sample to atmospheric pressure quickly and the weight loss over time is plotted. Samples are weighted before and after equilibrium in a precision analytical balance with 0.0001 g accuracy. The equilibrium solubility is obtained from the extrapolation backwards from the time of the first measurement. These data are checked by volumetric measurements, which consist on the saturation of the PS sample in a previously calibrated crucible. When the equilibrium is reached (at least 24 h) the crucible is vented quickly and the volume of CO_2 is measured through a turbine flowmeter. The difference between the vented CO_2 and the amount of CO_2 inside the crucible belongs to the sorption in the polymer. The average standard deviation between the two methods is 0.00536 g CO_2/g PS.

High-Pressure Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was the selected technique to study the influence of CO_2 on the glass transition temperature of PS. A schematic diagram of the experimental setup is shown elsewhere.[12] The experiments were performed in a SENSYS evo DSC (Setaram, Madrid) equipped with two high pressure Inconel crucibles enabled measurements up to 400 bar. The samples of PS are placed in the crucibles, weighted and filled with CO_2. CO_2 is cooled and pressurized to the desired by means of a positive-displacement pump and a syringe pump, which controls the amount of gas fed. The samples are annealed at the desired pressure for 24 h to ensure the total CO_2 sorption. DSC scans are made using an initial heating at 25°C/min up to 120°C to release thermal and absorption history and to provide a better fit of the polymer in the crucible. The samples are then cooled at the same rate and annealing for 30 min. T_g measurements were carried out during the second heating, and it was identified from the change in heat flow resulting from a change in heat capacity at the transition temperature during each scan. Then, the vessel is vented by opening a discharge valve and the amount of CO_2 is also measured by a turbine flow meter.

The accuracy of the experimentally determined T_g has been calculated from the comparison of two different runs carried out under identical conditions. In these experiments the T_g presented a deviation of 0.4546°C, indicating that reproducibility of the data is good. Nevertheless, to minimize experimental errors each run is replicated twice.

Determination of the Viscosity

A Physica MCR 301 rheometer (Anton Paar, Hertfor, UK) was used to determine the effect of pressure and temperature on the viscosity of PS. The PS is milled to fill the surface of the cell

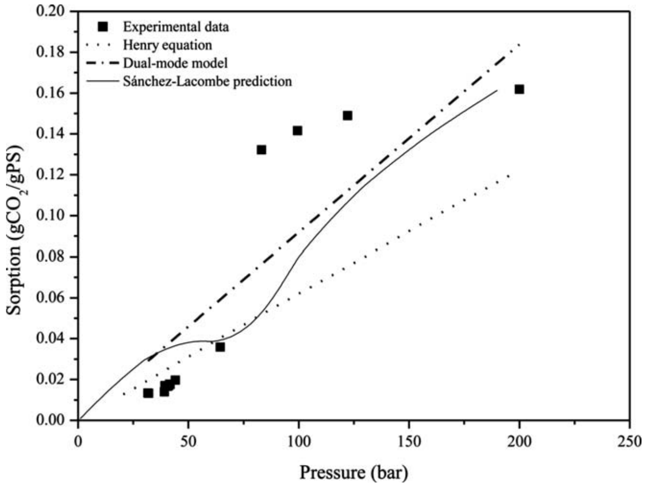

Figure 2. Correlation of sorption experimental data (■) using different models: Henry's law (. . .), Dual-mode model (-----) and Sánchez-Lacombe Equation of State (—). The good agreement between the experimental data and Sánchez-Lacombe EoS can be checked.

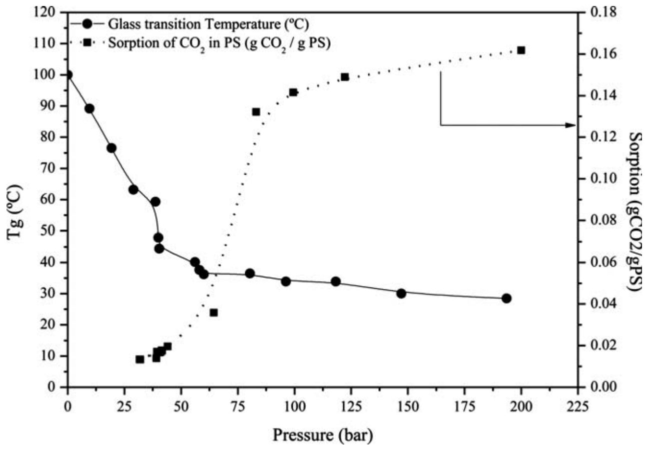

Figure 3. Influence of pressure on the glass transition temperature of PS (●-left axis) and the sorption of CO_2 (■- right axis). The decrease of T_g is related with the increase of CO_2 sorption.

that is sealed and charged with CO_2 using a syringe pump (Teledyne, Thousand Oaks, CA). The samples are left for 30 min to allow the diffusion of CO_2 into the samples. The shear rate is ranged from 0.001 to 1000 min^{-1} over 5 min and data points are recorded every 3 s. At least three analyses are run for the different conditions.

RESULTS

Results have been divided in two main blocks. Initially, the sorption of CO_2 is determined experimentally and correlated using Henry, Dual-mode model and Sánchez-Lacombe Equation of State. Next, the influence of the CO_2 sorption on the modification of the PS properties is studied. The sorption of CO_2 in Polystyrene produces polymer swelling,[31,34,35] large depression in glass transition temperature,[12,36,37] interfacial tension,[29,38] and viscosity.[39] Experimental measurements of the glass transition temperature and viscosity and interfacial tension data summarized from the literature are related with the experimental sorption of the gas molecule in the polymer.

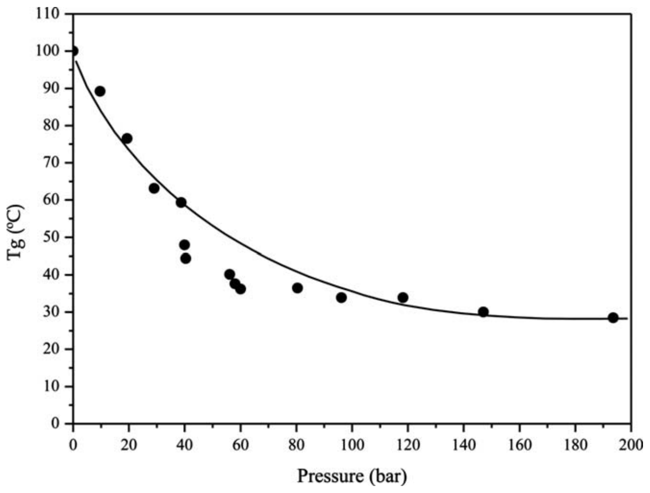

Figure 4. Prediction of the decrease of T_g of PS (●) using the Chow model. The perfect agreement between the experimental data and the prediction is observed.

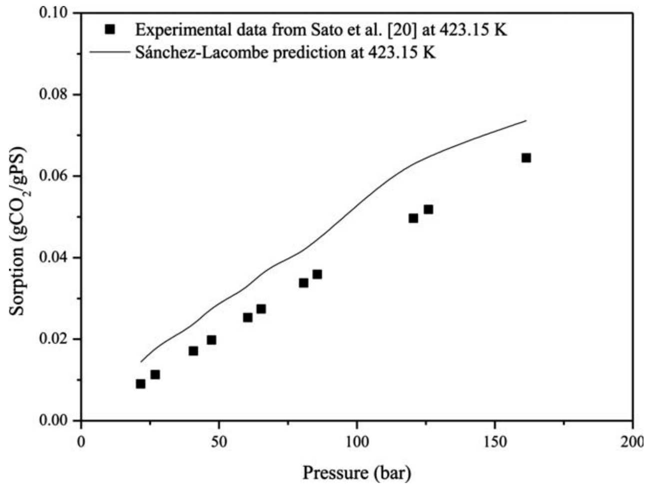

Figure 5. Prediction and comparison of the sorption of CO_2 in PS at 423.15 K to validate the S-L EoS at higher temperature. Experimental data were obtained from Sato *et al.*[28]

Sorption of CO_2 in PS Plasticization

The experimental data of CO_2 sorption in Polystyrene at 30°C are depicted in Figure 1. Although high temperature are generally used to melt the polymer ($T_g \approx 373$ K) and determine the sorption, the plasticizing effect of CO_2 decreases dramatically the T_g and low operating temperatures can be used to perform the experiments. For this reason, in this work the sorption of CO_2 in PS at 30°C is determined.

Figure 1 shows that sorption of CO_2 increases almost linearly with pressure up to 100 bar where it reaches a constant value close to 0.16 g CO_2/g PS. The sharp rise observed in our experimental data can be explained due to the proximity of the critical point of CO_2 (P: 73.8 bar; T: 31°C), where the density of the gas molecule changes dramatically (right axis).

According to the literature, when temperature increases, solubility of CO_2 decreases due to the density decrease.[41] This trend has been generally observed in many gas/polymer systems, where the highest values of sorption could be reached at high pressure and low temperature. By this reason, the sorption of CO_2 is commonly related with its density, thus, when density increases higher amount of CO_2 are absorbed into the polymer.

A comparison between our experimental data and those reported in the literature at temperature between 32 and 65°C are shown in Figure 1 (right). Data could be divided in two groups attending to the maximum sorption values. Shieh and Liu,[40] Zhang *et al.*,[31] and Pantoula and Panayiotou[4] data reached values of sorption around 0.06 g CO_2/g PS at 32, 35, and 51°C, respectively. On the other hand, Aubert[30] and Hilic *et al.*[21] showed an increase on sorption reaching 0.16 g CO_2/g PS at 40 and 65°C, respectively. The last cited references present similarities with regard to the experimental data shown in this work.

The sorption of CO_2 in polystyrene is correlated using Henry, Dual-Mode model equations and Sánchez-Lacombe EoS (Figure 2) for its application in further processes design. The easiest model to correlate the sorption of CO_2 into the PS follows the law of Henry [eq. (1)], where the sorption of CO_2 is

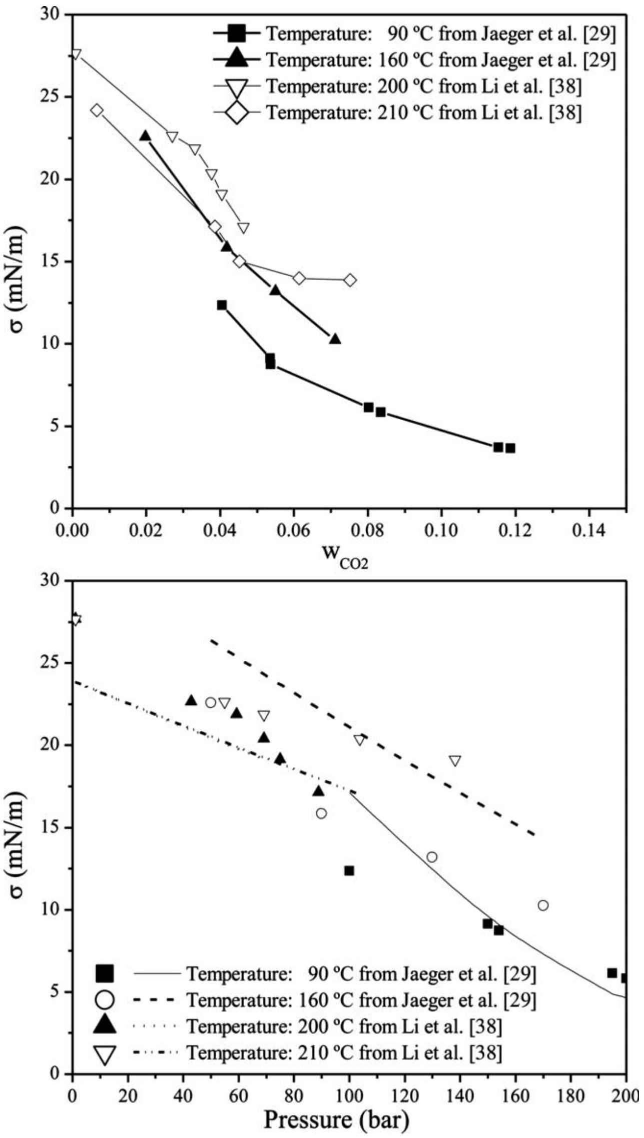

Figure 6. Influence of sorption (upper figure) and pressure (figure below) on the decrease of the interfacial tension of PS. Experimental data are from Jaeger *et al.*[29] and Li *et al.*[38] The influence of molecular weight distribution and crystallinity makes difficult the accurate prediction of the decrease of IFT.

proportional to the pressure. It is especially suitable to fit the sorption of CO_2 at low pressures.

Figure 2 compares the model prediction and correlation and the experimental data for the systems. It is observed that SL-EoS correlates the experimental data with reasonable accuracy and improves the results shown by the Dual-Mode model. At low pressure ($\leq$75 bar) Henry's law correlates pretty well the experimental results, while the Dual-Mode model and the SL-EoS overestimates the values of sorption. Nevertheless, when pressure increases Dual-Mode model and the SL-EoS enhance the correlation of the sorption of CO_2 in PS. At pressure higher than 75 bar, the experimental values are higher than the correlated, it can be explained considering that glassy polymers have nonequilibrium excess free volume and the CO_2 could be absorbed into these microcavities achieving an increase in sorption.[19]

Glass Transition Temperature

The influence of pressure on the CO_2 sorption and on the glass transition temperature of PS is shown in Figure 3.

Figure 3 shows two trends, at low pressure there is an almost linear decrease of T_g following the opposite trend of the sorption of CO_2. Thus, the T_g of PS decreases with increasing the mass of CO_2. At higher pressure, when the critical pressure of CO_2 is reached, T_g remains approximately constant around 30°C due to the saturation of PS as sorption values confirm. The plasticization of PS with compressed CO_2 depends on many factors, such as the free volume of the polymer under pressure, the polymeric chains flexibility, the critical temperature and in particular, the sorption of CO_2 in PS.[10] In this case, the effect of the sorption is exclusively studied.

The CO_2 sorption into the PS is the responsible of the subsequent plasticization of the polymer. These molecular level phenomena are observed macroscopically by the decrease in the glass transition temperature (T_g) of the polymer.[7] Polymers in glassy state present a fixed free volume and any polymeric chain, but when temperature increases or a plasticizer is added, the free volume is expanded and the energy of molecular thermodynamic movement is enlarged promoting the movement of the polymeric chains.[42]

Sorption of CO_2 in PS lowers its T_g significantly below that observed at atmospheric pressure ($T_g \approx 373$ K). It is confirmed that the solubilization of CO_2 into the polymer induces the plasticization of the plastic which is noticeable in a reduction of T_g.[43,44] This effect could be predicted according to Chow's equation[45] (Table I).

In Chow's equation, T_g is the glass transition temperature of the polymer under pressure; $T_{g,0}$ is the glass transition temperature of the pure polymer at atmospheric pressure; β is the nondimensional parameter; M_m is the molar mass of the monomeric unit, which makes up the polymer (104.15 g/mol for PS); M_d is the molar mass of the dissolved gas (44.01 g/mol for CO_2); R is the gas constant (8.3145 J/K·mol); ΔC_{pp} is the excess transition

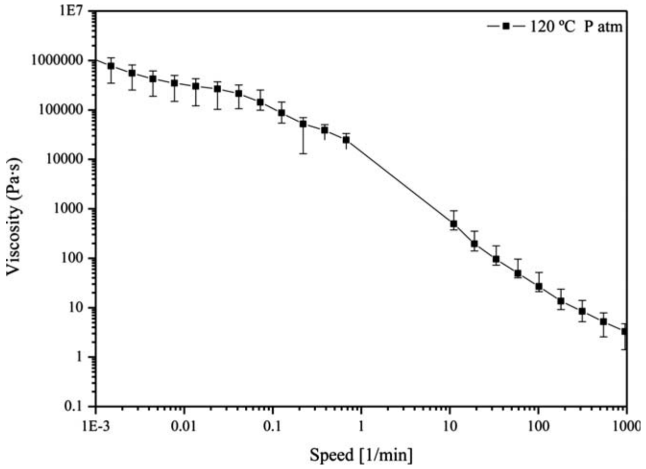

Figure 7. Determination of the linear viscoelastic region of PS at 120°C and atmospheric pressure. The polymer shows Newtonian behavior between 0.001 and 0.01 min^{-1}. The error bars represent the standard deviation of the measurements from the mean.

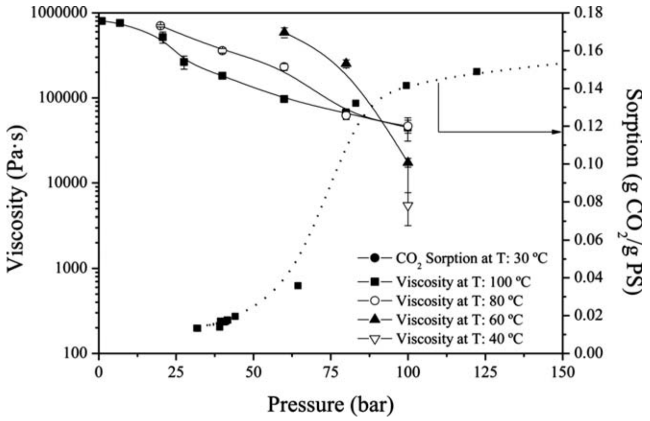

Figure 8. Effect of pressure and temperature on the decrease of viscosity of PS in CO$_2$. The relationship between the drop of viscosity (left axis) and the sorption of CO$_2$ (right axis) can be observed.

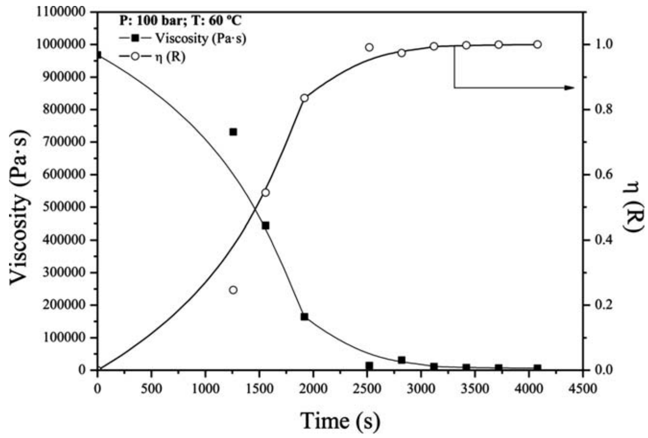

Figure 9. Evolution of viscosity of PS as a function of time till saturation of polymer is reached, at 60°C and 100 bar.

isobaric specific heat of the pure polymer (0.2593 J/g·K), and z is the lattice coordination number which can be either 1 or 2. Generally for polymer with small repeat units, z is the equal to 1,[24] but Chow proposed z =2 in the case of PS.[45] The use of Chow's model becomes complicated due to the uncertainty of the estimation of z-values. When z is 2 or greater, retrograde vitrification of PS is predicted, nevertheless, in the range of working conditions this phenomenon was not observed experimentally. Furthermore, Liu *et al.*[46]concluded that optimization of z is also dependant of the excess transition isobaric specific heat of the polymer. For the explained reasons, in this work $z=1$ is selected.[24]

The concentration of CO$_2$ in PS is required in order to predict the Chow's curve of T_g versus pressure. Sánchez-Lacombe EoS is applied to obtain the sorption of CO$_2$ in the polymer as a function of pressure. Those theoretical data obtained from the application of SL-EoS and Chow's equation are compared with the values of T_g obtained experimentally (Figure 4). The predicted data (solid curve) shown in Figure 4 fits accurately the experimental values of the glass transition temperature of PS under CO$_2$ pressure, and small deviation is observed in the range of pressure studied.

Interfacial Tension

The influence of CO$_2$ on the interfacial tension (IFT) of PS is studied theoretically and results are compared with the Refs. 29,38,47. It should be outlined that the molecular weight and crystallinity of PS plays a crucial role on the IFT and for this reason, important dispersion of data is shown in the literature. On a regular basis, IFT of PS decreases at rising pressure in CO$_2$ atmosphere and the slope of the IFT-curve decreases at elevated pressure. The decrease of IFT is attributed to two phenomena: when pressure increases, the free energy density of CO$_2$ becomes closer to that of the polymer phase and the second effect is related with the amount of CO$_2$ absorbed in the PS, which plasticizes the polymer.[48] The relationship between the sorption of

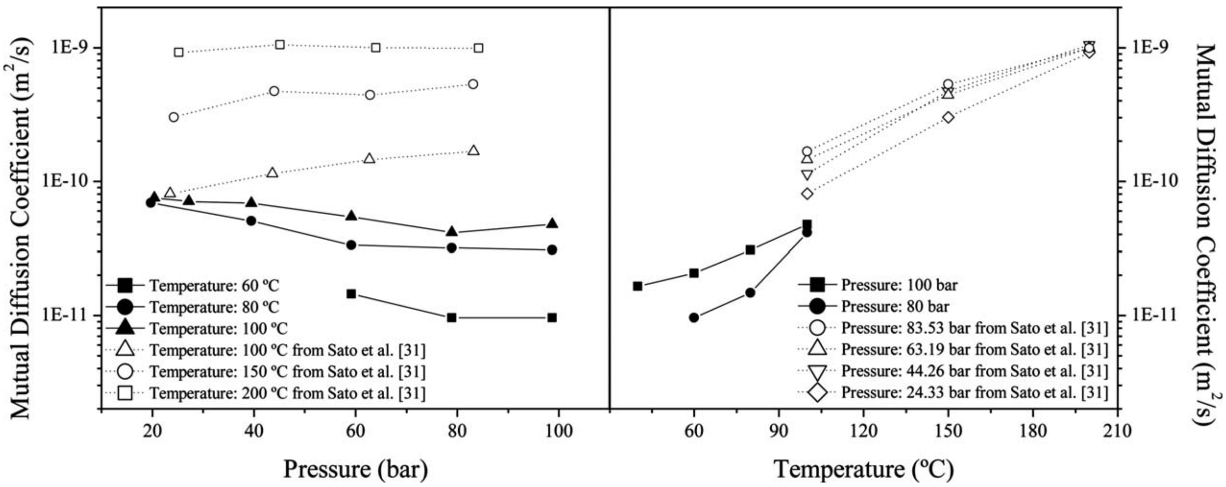

Figure 10. Influence of pressure (left figure) and temperature (right figure) on the mutual diffusion coefficients of CO$_2$ in PS in a range of pressure from 20 to 100 bar and temperature from 40 to 100°C. Our experimental data were compared with the Ref. 32 and a good agreement between them was observed.

CO_2 and the IFT was described by Pastore Carbone *et al.*[48] using the empirical expression shown below:

$$\sigma_{\text{sol}} = (1 - w_{\text{co}_2})\sigma_{\text{Pol}}^{1/r} \tag{3}$$

where σ_{sol} is the interfacial tension of the mixture PS/CO_2, w_{co_2} is the weight fraction of the dissolved CO_2, σ_{pol} is the interfacial tension of the polymer, and r is the fitting parameter. The estimation of w_{co_2} in the range where the IFT was measured experimentally is predicted according to S-L EoS. Initially, the agreement between the predicted w_{co_2} and the values shown in Ref. 32 in a wider range of temperature are depicted in Figure 5.

The average standard deviation between experimental and predicted data is 0.006 g CO_2/g PS, which means that sorption of CO_2 in PS could be successfully predicted using S-L EoS for the entire range of temperature and pressure. Thus, the predicted values concerning the concentration of CO_2 in PS (w_{co_2}) are used to correlate the IFT of the mixture according to eq. (3).

The IFT of PS (σ_{pol}) is calculated following the Macleod-Sugden equation[49] and the effect of temperature and pressure on its volume is estimated according to the Tait-relation.[50] The fitted parameter r ranged between 0.34 and 0.37; nevertheless, the correlated values and the experimental data reported in the literature do not fit well, although the predicted values of sorption are reliable. This fact highlights the importance of the experimental measurement of the IFT of polymers at high pressure. This property is affected by the molecular weight or the crystallinity of the polymer, which implies huge uncertainty for its estimation.

The relationship between the sorption of CO_2 in PS and the decrease in the IFT is observed in Figure 6(a). Although a general trend is observed, the references studied different types of PS, which complicates the design of a general fitting independently of the kind of polymer used. The best agreement between experimental and predicted data was achieved using the general Macleod-Sugden[51] correlation for mixtures (Table I). The exponential factor (n) was fitted using the cited references and the optimum value was between 3.4 and 3.7 [Figure 6(b)].

Viscosity

The determination of viscosity at high pressure is still nowadays a challenge since the diluents must be retained in solution under working conditions of pressure and temperature.[52] CO_2 has lower density and higher compressibility than pure polymer, so its dissolution into the PS results in swelling of the polymer. Consequently, an increase in free volume is produced and the transport properties such as viscosity can be enhanced.[53] Figure 7 shows a typical curve obtained from the rheometer measurements at 120°C and atmospheric pressure. There are three different regions: a linear viscoelastic region (shear rate $\leq 0.01\ \text{min}^{-1}$), a depression of viscosity (above the critical shear rate) and finally the stabilization of the viscosity. During the initial stage, the viscosity is independent of shear rate and PS behaves as a Newtonian fluid. In the second stage the viscosity decrease suggests that the polymeric chains are disentangled in the direction of the shear. Finally, when the viscosity is kept constant at high shear rate implies the alienation of the chains.[54] PS exhibited a viscosity of 313.38 kPa s at 120°C and 0.1 MPa, similar to the values showed in the literature by Wingert *et al.*[52] at 140°C.

The effect of pressure and temperature on the viscosity of PS at a constant shear rate (0.01 min^{-1}) was studied (Figure 8). Viscosity decreases significantly when CO_2 is absorbed in the polymer and an increase in the sorption entails a higher decrease of viscosity. The presence of CO_2 (right axis) is the responsible of the viscosity reduction in the PS due to its plasticizing effect. In general, in the standard systems, when pressure increases, viscosity raises; but in this case, the viscosity is decreased by the presence of CO_2. This small molecule is absorbed among the chains of the PS increasing the free volume and their mobility, which causes the reduction in the viscosity.

To obtain reliable results, experiments are carried out when the sample is saturated with CO_2. The changes in the viscosity along time allow the determination of the diffusion of CO_2 in the PS. The sorption of CO_2 in the polymer causes a decrease in viscosity, till the PS is saturated (Figure 9). The initial point (left axis) is the viscosity of the polymer without CO_2 at 100 bar and 60°C and the points shown in the right axis represent the relative viscosity every 5 min. Relative viscosity $\eta_{\text{R}}(t)$ is defined as:

$$\eta_R(t) = \frac{\eta(t) - \eta(0)}{\eta(\infty) - \eta(0)} \tag{4}$$

where $\eta(t)$ is the viscosity at time t, $\eta(0)$ is the viscosity at atmospheric pressure, it means, when the concentration of CO_2 is zero, and $\eta(\infty)$ is the viscosity at saturation. From experimental data shown in Figure 9, the diffusion coefficient of CO_2 in PS was determined assuming that the gas is diffused into the sample through the upper side of the polymer disk, the diffusion coefficient is constant at each value of pressure and temperature and Fickian diffusion is accomplished[55] (Table I). The effect of pressure and temperature on the diffusion coefficient of CO_2 in PS is shown in Figure 10.[32]

According to Figure 10, when pressure and temperature increase, the mutual diffusion coefficient increases, meaning that CO_2 is diffuses faster at those conditions. The effect of temperature on the diffusion coefficients has been generally described attending Arrhenius or Williams-Landel-Ferry model,[56] but due to the lack of experimental data, this behavior could not be checked. The diffusion coefficient of CO_2 in rubbery PS (above its T_g) is around 10^{-10} m^2/s, typical value exhibited by high molecular weight polymers.[36,57] From the comparison of the diffusion coefficient obtained in this work and the data from Sato *et al.*,[32] the feasibility of the viscosity measurements to determine the diffusivity is confirmed.

CONCLUSIONS

The sorption of CO_2 in polystyrene is the responsible of the swelling and plasticization of the polymer, which changes its glass transition temperature, its interfacial tension and its viscosity. The inclusion of a small molecule, as CO_2 is, among the polymeric chains causes an increase of the free volume and enlarges the movement of the polymer chains. By this reason, the decrease of T_g, IFT and viscosity can be related with the sorption. Table I summarizes the model or correlation used to study the modification of PS properties as a consequence of the sorption of CO_2. Finally, the evolution of viscosity along time is a powerful tool to estimate the diffusion coefficients of CO_2 in PS in a wide range of pressure and temperature.

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