How high pressure CO₂ impacts PLA film properties

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Abstract. This work investigated the sorption and the diffusion properties of CO₂ under high pressure and the further modifications induced in Poly(lactic acid) (PLA) thin layers. Poly(ethylene terephthalate) (PET) was also considered for comparative purposes. Firstly, from thermodynamic equilibrium, the CO₂ sorption isotherm (two sorption-desorption cycles, up to 25 bar, at 25 °C) gave strong evidence of a physisorption mechanism and of a hysteresis phenomenon. Infrared spectroscopy analysis confirmed that no chemical reaction occurred. Secondly, from the kinetics aspect, the CO₂ diffusion coefficient was found around 10⁻¹³ m²·s⁻¹ and was slightly faster for sorption compared to desorption. Additionally, when CO₂ sorption occurred, the PLA structure and its functional properties were modified due to plasticization and swelling. CO₂ plasticization reduced the glass transition temperature of PLA and accelerated the physical ageing of the polymer. These results are therefore of significant importance in industrial processing and applications which involve close contact between CO₂ and PLA.

Keywords: biodegradable polymers, PLA, carbon dioxide gas, polymer ageing, mass transfer

1. Introduction

Poly(lactic acid) or PLA is a renewable and biodegradable polyester, which holds a strategic place in the bioplastic market. It is considered as one of the most interesting candidates for substituting conventional (non-biodegradable and oil-based) plastics [1–3]. The European Bioplastic Association has reported that the worldwide production of PLA exceeded 207 thousand tons in 2014, and it is expected to double in 2019 [4]. According to that association, the largest consumption of PLA is currently as packaging for foods, beverages and cosmetics, and almost certainly they would remain as the main application of PLA in the near future [4]. PLA is also a competitive material in other market segments, which are believed to have a higher importance in the next years, such as bio-medical devices, textiles, automobile appli-

ances, electrical appliances and 3D printing, thanks to its biocompatibility nature and relative easiness to modify its functional properties.

Poly(ethylene terephthalate) or PET is one of the conventional plastic most frequently used in food packaging. The European production of this polyester exceeded 4 million tons in 2014 and it is largely used as bottles of soft drinks and water, containers for fruits and trays for pre-cooked meals [5]. PLA can be considered as a good candidate for a gradual replacement of PET in food packaging, since both polyesters are similar in appearance, thermal and in mechanical properties [1]. However, substituting PET with PLA is currently a suitable strategy for food packaging applications with only low barrier requirements. PLA indeed displays lower barrier performances to water vapor, oxygen (O₂), carbon dioxide

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(CO₂) and nitrogen (N₂) [1, 2]. This can compromise the quality and the safety of some products such as foods packed in Modified Atmosphere Packaging (MAP) or carbonated beverages. Developing PLA based materials able to compete with PET and with other high performing plastics – such as polyamide (PA), poly (vinylidene chloride) (PVDC) or poly (vinyl alcohol) (PVA) – is thus an ecofriendly challenge for the near future, which could open new application scenarios to PLA.

CO₂ plays a key role in food processing and food packaging. On one hand, food industries largely draw on this gas as an ingredient of carbonated beverages (e.g. soft drinks, sparkling wines or carbonate water) and for extending the shelf life of fresh, dairy and meat products in MAP, by limiting oxidation reactions, color changes and microbial growth [6–8]. On the other hand, due to its technological advantages there is an increasing interest in the use of CO₂ as a supercritical fluid (pressure > 73.8 bar and temperature > 31.1 °C) [9]. Supercritical CO₂ is used for extracting nutraceuticals or functional ingredients (e.g. vitamins, essential oils, antioxidants) from biological materials [10, 11], fractionating and deodorizing lipids [12], decaffeinating green coffee beans, defatting foods, removing ethanol from alcoholic beverages (e.g. beer and wine) [13] and inactivating microorganism and enzymes [14, 15].

Based on those considerations, there is a clear interest in studying the interactions between CO₂ and PLA, and the modifications that such molecule could induce in the PLA material, which is suitable as a substitute of PET. For now, most of the related literature is focused on the effects of supercritical CO₂ (or conditions near to it) on the PLA properties, such as foaming properties [16], thermal behavior [17–19], hydrophobic drug encapsulation [20, 21] or swelling [22, 23]. Nevertheless, there is not enough available information related to the effects of CO₂ at conditions lower than its supercritical point, which are often the conditions encountered in food packaging and food processing.

The main objective of this research was thus to study the sorption properties of PLA regarding CO₂ and the modification induced by CO₂ in PLA thin layer films at high pressures conditions. The CO₂ sorption isotherm (two sorption-desorption cycles) of PLA at 25 °C up to 25 bar was first determined. The related effective diffusion coefficients were then calculated and the modifications on chemical and functional

properties of the material were evaluated. PET films were also used in this study for comparative purpose.

2. Experimental

2.1. Samples

Semicrystalline PLA (Polylactic acid) commercially available for food packing applications was used in this study (thickness = 30 µm, $\bar{M}_w \approx 200\,000\text{ g}\cdot\text{mol}^{-1}$, PDI ≈ 2.2 , D-level $\geq 4.25\%$). These PLA films were subjected to a biaxial orientation and annealing during production and were supplied by Taghleef Industries (commercial name: Nativia NTSS, Udine, Italy). Amorphous PET (Polyethylene terephthalate) films were also used for comparison purposes (thickness = 200 µm). PET films were not subjected to bi-orientation and were purchased from WIPAK Gryspeerdt SAS (commercial name: APET 200, Bousbecque, France).

2.2. CO₂ sorption properties

The sorption and diffusion properties of CO₂ in PLA and PET were determined by thermogravimetry at 25 °C.

2.2.1. Sorption isotherm

The CO₂ sorption isotherms of PLA and PET films were determined at 25 °C for pressure ranging from 0 to 25 bar, using a magnetic suspension balance (Rubotherm GmbH, Bochum, Germany). Rectangular film samples ($\approx 75\text{ mg}$) were first outgassed under primary vacuum (nXDS Scroll Pumps, Edwards, Czech Republic) at a pressure of about 10^{-5} bar until mass equilibration before being exposed to CO₂ sorption. The CO₂ pressure was then increased step by step waiting for equilibrium before changing the pressure. Equilibrium was considered to be reached when the mass of sample remained constant for at least 12 hours. For each film, 2 cycles of sorption and desorption were performed. The quantity of sorbed CO₂ was calculated according to Equation (1):

$$m_{\text{sorb}} = \frac{m_{\text{Ar}} - m}{m} \cdot 100 \quad (1)$$

where m_{sorb} is the quantity of sorbed CO₂ [wt% of outgassed weight sample] by the material, m_{Ar} is the mass of the sample at equilibrium and after been corrected by the Archimedes buoyancy [g] according to Equation (2), and m is the sample mass after been outgassed [g]:

$$m_{Ar} = m_{app} + d_g (V_p - V_s) - m_p - d_{air} (V_p + V_s) \quad (2)$$

where m_{app} [g] is the sum of apparent mass of the sample and the mass of the empty pan, d_g is the measured density of the gas at the running pressure [$g \cdot cm^{-3}$], V_p is the volume of the pan containing the sample [cm^3], V_s is the sample volume [cm^3], m_p is the mass of the empty pan [g] and d_{air} is the gas density under atmospheric pressure [$g \cdot cm^{-3}$].

2.2.2. Diffusion coefficient

The effective diffusion coefficient of CO_2 in both films was calculated from the previous CO_2 sorption kinetics. The experimental data from each sorption step were modeled using an analytical solution to Fick's second law applied to membrane sorption, or desorption (Equation (3)) [24]. The system was characterized by a uniform gas concentration before the phenomenon took place. When it started, the gas concentration in both surfaces was kept constant while the sorption (or desorption) in both sides of the membrane occurred:

$$\frac{m_t}{m_\infty} = 1 - \sum_{j=0}^{\infty} \frac{8}{(2j+1)^2 \pi^2} \exp \left[\frac{-D_{sorp} (2n+1)^2 \pi^2 t}{4l^2} \right] \quad (3)$$

where m_t and m_∞ are the total amount [g] of sorbed CO_2 (or desorbed CO_2) at time t [s] and at equilibrium, respectively; l is the half thickness of the membrane [m]; D_{sorp} is the effective diffusion coefficient [$m^2 \cdot s^{-1}$].

The effective diffusion coefficient (D_{sorp}) was calculated using the reduction in the sum of squares scores between the model (Equation (3)) and the experimental curve (*fminsearch* function in Matlab R2012a). A maximal value of 10 for j and a mean of the last 50 values for m_∞ were fixed. To determine the confidence interval of diffusion coefficient, the prevision interval of the amount of sorbed CO_2 was calculated based on the sum of squares between the model and experimental curve (Equation (4)):

$$m_t = m_{mod} \pm \sqrt{\frac{\sum_{i=1}^n (m_{mod} - m_{exp})^2}{n-2} \left[1 + \frac{1}{n} + \frac{(\bar{t} - t)^2}{\sum_{i=1}^n (t_i - \bar{t})^2} \right]} \quad (4)$$

Figure 1. Selected example of sorption kinetics of CO_2 on PET (between pressure 4.3 and 9.7 bar). Displayed are experimental data along with modeling according to Equation (3). Also indicated are predictive interval curves and model curves base on confidence intervals at 95%.

where $t_{\alpha/2;n-2}$ is a value of t distribution, α is the confidence level (5%), n is the number of points, m_{mod} and m_{exp} are the modeled and experimental values of the total amount of sorbed (or desorbed) CO_2 , respectively.

Finally, the coefficient of determination (R^2) has been calculated with the total sum of squares (SS_{tot}) calculated according to Equation (5):

$$SS_{tot} = \sum_i^n \left(m_{mod} - t \cdot \frac{m_n}{t_n} \right)^2 \quad (5)$$

For each curve, the diffusion coefficient has been calculated, along with the upper and lower bounds of the confidence interval as reported in the example given in Figure 1.

2.3. Modifications induced by CO_2 sorption

Selected functional properties of PLA and PET films were compared prior to and after CO_2 sorption at 25 °C, under the same high pressure conditions as previously used.

2.3.1. Sorption conditions

PLA films were subjected to primary vacuum before and after gas sorption. In the case of PLA films, gas sorption took place in a chamber saturated with CO_2 at 25 bar for 5 days. PLA films stored in a chamber with N_2 under same conditions, and PLA films stored at 1 bar of CO_2 for 5 days were used as control samples, for non-reactive gas and non-pressurized sample, respectively. In the case of PET films, samples from CO_2 sorption isotherm were analyzed. This sorption condition also involved high pressure treatments at 25 bar. Similarly, PET films stored for 5 months

at room conditions, and PET films stored for 5 days under 1 bar of CO₂ were analyzed as control samples for long time ageing and non-pressurized sample, respectively.

2.3.2. Surface chemistry

Changes in the surface chemistry were evaluated using Attenuated Total Reflectance Fourier Transform Infrared analysis (ATR-FTIR) with a spectrometer (Spectrum 65, PerkinElmer, Waltham, MA, USA) equipped with ZnSe crystal. The wavenumber investigated ranged from 4000 to 650 cm⁻¹, with a resolution of 2 cm⁻¹. 128 scans were collected for each spectrum. Six samples for each films condition were analyzed. Film spectra were normalized according to the height of the peak at 1452 cm⁻¹, corresponding to the bending vibration mode of –CH₃ and –CH₂ of PLA and PET, respectively [25, 26].

2.3.3. Phase transitions

The thermal events of PLA and PET films were determined by Differential Scanning Calorimetry (DSC), using a Q20 calorimeter (TA instruments, New Castle, DE, USA). Films were weighed (around 5 mg) and sealed into aluminum pans (TA instruments) before being subjected to a double heating-cooling cycle at 10 °C·min⁻¹ under N₂ atmosphere (flow rate = 25 mL·min⁻¹). For PLA films the temperature range investigated was from –10 to 200 °C, while for PET films it was from –10 to 300 °C. The thermal events related to glass transition (inflection point of glass transition temperature T_g and variation of specific heat ΔC_p), associated endothermic event (enthalpy of relaxation ΔH_{relax}), cold crystallization (temperature of cold crystallization T_{cc} and enthalpy of cold crystallization ΔH_{cc}) and melting (temperature of melting T_m and enthalpy of melting ΔH_m) were calculated from the first heating cycle, using TA Universal Analysis 2000 software (version 4.5 A, TA instruments). The reversibility of thermal events was assessed from the second heating cycle.

The crystallinity degree (X_c) of films was also calculated, according to Equation (6):

$$X_c = \frac{\Delta H_m - \sum \Delta H_{cc}}{\Delta H_m^0} \cdot 100\% \quad (6)$$

where $\sum \Delta H_{cc}$ [J·g⁻¹] is the sum of cold crystallization peaks and ΔH_m^0 is the enthalpy of melting of the pure polymer (PLA = 93 J·g⁻¹ [27]; PET = 140 J·g⁻¹ [28]).

2.3.4. Mechanical properties

The mechanical behavior of PLA films was assessed by uniaxial tensile testing at room conditions ($T \approx 25$ °C) using a texture analyzer (TA HD plus, Texture Technologies, Hamilton, MA, USA) and according to NF EN ISO 527-1 standard [29]. The initial gauge length was 10 cm, a 100 kg load cell was used and tests were performed with a constant crosshead speed of 1 mm·min⁻¹. 7 to 12 rectangular specimens (dimensions of 15×2.5 cm) were prepared with a precision cutter (JDC, Thwing Albert Instrument Company, West Berlin, NJ, USA) and analyzed for each condition. The transversal direction to process line (TD) of films was considered for this analysis. The Young's modulus (E_{Young} [GPa]), yield strength (σ_y [MPa]), yield elongation (ϵ_y [%]) tensile strength (σ_b [MPa]) and elongation at break (ϵ_b [%]) were determined from the resulting stress – strain curves.

2.3.5. Barrier properties to CO₂

The permeability (P) of PLA films to CO₂ was determined using a manometric method on a GDP-C permeameter apparatus (Brugger Feinmechanik GmbH, Munich, Germany) in dry conditions (0% Relative Humidity, RH) at 25 °C. The system was outgassed under primary vacuum before testing. At time zero one side of the film was flushed with the gas (flow ≈ 100 cm³·min⁻¹) and the pressure increase on the other side was recorded over time. Permeability was determined from the steady state of transfer.

From the lag time, the effective diffusion coefficient (D_{perm}) (Equation (7)) and the solubility coefficient (S_{perm}) were also calculated (Equation (8)):

$$D_{perm} = \frac{l^2}{6\vartheta} \quad (7)$$

$$P = D_{perm} \cdot S_{perm} \quad (8)$$

where D_{perm} is the effective diffusion coefficient [m²·s⁻¹], l is the thickness of the film [m], ϑ is the lag time [s], P is the measured permeability [mol·m⁻¹·s⁻¹·Pa⁻¹] and S_{perm} is the solubility [mol·m⁻³·Pa⁻¹]. The subscript perm of D and S parameters denotes that they were determined from the manometric method, to differentiate them from their counterparts calculated from the CO₂ sorption isotherm (D_{sorp}).

2.4. Statistical analysis

Data were analyzed with Student t-test and, when required (groups > 2), with one-way analysis of vari-

ance (ANOVA) and with Tukey-Kramer multiple comparison test, using GraphPad Prism software (version 5.01, GraphPad Software Inc., La Jolla, CA, USA). The significance level of all statistical tests was fixed at 0.05.

3. Results and discussion

The results and discussion section is firstly focused on the CO₂ sorption properties of PLA film compared to PET material. Secondly, the modifications induced by the CO₂ sorption on the functional and barrier properties of films are investigated with particular attention paid to PLA.

3.1. Sorption properties for CO₂

3.1.1. CO₂ sorption isotherm

Although several CO₂ sorption studies have been conducted on PLA [19, 22, 30–34], no information concerning the solubility of CO₂ during consecutive sorption/desorption cycles are available in the literature. These steps are crucial because they provide information on the interactions between the sorbent and the polymer. For example, if hysteresis between sorption/desorption steps is detected, it indicates that these interactions modified the polymer. If an increase in the polymer weight is noticeable after outgassing following the first sorption/desorption cycle, it suggests that the polymer chemically fixed the sorbent via covalent bounds (chemisorption). On the contrary, if the polymer returns back to its initial weight, it indicates that only low energy interactions or physical modifications occurred during sorption. Thus, to better understand the type of interactions between CO₂ and PLA, the CO₂ sorption isotherm was determined at 25 °C from 0 to 25 bar involving two sorption/desorption cycles (Figure 2).

During the first sorption, the quantity of CO₂ sorbed by PLA linearly increased with pressure, for the whole range of pressure investigated from 0 to 25 bar. Such Henry's type isotherm was already observed in other studies involving pre-supercritical conditions [19, 30–32]. A plateau (or pseudo plateau) was only reported when supercritical conditions (pressure > 73.8 bar and temperature > 31.1 °C) were exceeded [22, 23, 33]. The quantity sorbed at CO₂ pressure close to 25 bar was rather high, around 7 wt% of the initial mass of the polymer, which represents a molar ratio of 0.11 mol of CO₂ per mol of PLA monomer unit. Similar quantities of CO₂ (≈7 to 10 wt%) were sorbed

Figure 2. Sorption isotherms (2 cycles of sorption and desorption) of CO₂ of PLA at 25 °C

by PLA at ≈25 bar at 40 °C in previous studies [19, 22]. Thus, this suggested a great sorption capacity of PLA polymer for CO₂ molecules, possibly as a consequence of a high amount of sorption sites.

Now looking at the first desorption, the shape of the isotherm exhibited a nonlinear behavior. Sorbed quantities of CO₂ were higher than those for the first sorption, unambiguously indicating hysteresis phenomenon in PLA. At the end of the desorption step, the PLA returned to its initial weight, showing the PLA capability to release all the sorbed CO₂ molecules when the sample is taken back under vacuum. It gave strong evidence that CO₂ molecules were only physically retained, without involving covalent bond formation (chemisorption), and thus suggesting that modifications revealed by the hysteresis concerned only the physical state of PLA like swelling or plasticization. The second sorption did not follow the same way as the first sorption. In this case, a nonlinear increasing trend was observed, with sorbed CO₂ values lying between the first sorption and desorption cycle. The behavior of second desorption was rigorously analogous to the first one. At the end of the second desorption cycle, all CO₂ molecules were also fully desorbed from the PLA polymer when maintained under vacuum at 25 °C. Such hysteresis confirmed modifications in the physical state of the polymer, as a result of physical interactions like plasticization or swelling. PLA, as other polyesters, is known to establish low energy interactions (of Lewis acid-base nature) between CO₂ molecules (electron acceptor) and carbonyl groups of the polymer (electron donor), which leads to plasticization and swelling [22, 34–36]. As a result, PLA chains are becoming more spaced, PLA intermolecular interactions reduce, the system mobility increases and new sorption sites are exposed, favoring therefore CO₂ sorption [22, 33, 37].

The CO₂ sorption isotherm of PET was also determined using the same gravimetric technique (Figure 3).

It is noteworthy that the sorption isotherm trends were analogous to those of PLA. The first CO₂ sorption also followed a linear behavior according to Henry's law, while the successive steps highlighted once again a hysteresis phenomenon. Such similarity can be explained by the chemical nature of both polyesters. PET also has carbonyl groups able to interact with CO₂ molecules, leading to a plasticization effect. No chemisorption was detected, suggesting that modifications induced by CO₂ sorption only concerned the physical state of the polymer, in a similar way than for PLA. The main difference between PLA and PET was in the quantity of sorbed CO₂. Even if they lied in the same order of magnitude, PLA clearly sorbed more CO₂ than PET in the whole range of pressure studied (≈ 7 vs. 4 wt% at ≈ 25 bar). Lower CO₂ solubility in PET compared to PLA was also observed by Champeau *et al.* (2014) [22] in a sorption

Figure 3. Sorption isotherms (2 cycles of sorption and desorption) of CO₂ of PET at 25 °C

study involving supercritical CO₂. This difference is firstly surprising when considering that PET was mainly amorphous contrarily to PLA which was semicrystalline ($X_c = 3.0$ vs. 24.8%, respectively, Table 1). Crystals are known to have a lower free volume and thus reduce the regions swelled due to sorption [30]. Therefore, such a lower CO₂ solubility in PET may come from the lower density of carbonyl groups compared to PLA (approximately one carbonyl group each 96.08 and 72.06 g·mol⁻¹, respectively) and from the presence of phenyl groups, which are less susceptible to interact with CO₂. It is possible thus to infer that the chemical structure of the polymer had a major influence in the sorption properties rather than its physical and morphological structure (*e.g.* crystallinity degree and orientation of chains).

3.1.2. Diffusion properties

The time for equilibration for each sorption and desorption steps during thermogravimetric analysis ranged from 1 to 3 days. To go deeper in this analysis and to better understand if these differences were due to CO₂ sorption, and to consider the different thickness of both materials, the effective CO₂ diffusion coefficient (D_{sorp}) of PLA and PET was calculated from each of the sorption and desorption steps (Figure 4). As displayed in Figure 4, there was no significant effect of the pressure of CO₂ on D_{sorp} in PLA. They oscillated around 10⁻¹³ m²·s⁻¹ for all sorption experiments. The same order of magnitude for D_{sorp} values were also observed in other studies [38, 39]. However, when successive sorption cycles were considered significant differences were noticeable. Firstly, the

Table 1. Thermal events of PLA and PET prior to and after gas sorption under various conditions

Film	Condition	Glass transition		Endothermic event	Cold crystallization		Melting		Crystallinity
		T_g [°C]	ΔC_p [J·g ⁻¹ ·°C ⁻¹]	ΔH_{relax} [J·g ⁻¹]	T_{cc} [°C]	ΔH_{cc} [J·g ⁻¹]	T_m [°C]	ΔH_m [J·g ⁻¹]	
PLA	Initial	64.4±0.9 ^a	0.13±0.03 ^a	0.47±0.14 ^a	§	§	155.1±0.9 ^a	23.0±2.0 ^a	24.8±2.1 ^a
	N ₂ (25 bar)	63.7±0.4 ^a	0.18±0.01 ^b	0.60±0.06 ^a	§	§	154.7±0.4 ^a	26.2±0.1 ^b	28.1±0.2 ^b
	CO ₂ (1 bar)	64.1±0.7 ^a	0.15±0.01 ^{a,b}	0.75±0.11 ^a	§	§	154.0±0.5 ^a	25.1±0.8 ^{ab}	27.0±0.9 ^{a,b}
	CO ₂ (25 bar)	58.9±0.8 ^b	0.13±0.01 ^a	3.24±0.14 ^b	§	§	154.5±0.2 ^a	25.0±0.4 ^{a,b}	26.9±0.4 ^{a,b}
PET	Initial	74.2±0.4 ^x	0.44±0.03 ^{x,y}	0.40±0.03 ^x	136.4±0.1 ^x	32.0±0.6 ^x	250.1±0.2 ^x	36.2±1.0 ^x	3.0±0.4 ^x
	5 months	75.4±0.1 ^y	0.43±0.02 ^{x,y}	0.73±0.21 ^x	135.9±0.3 ^x	31.5±1.0 ^x	248.8±0.4 ^x	37.3±1.0 ^{xy}	4.1±0.1 ^y
	CO ₂ (1 bar)	74.0±0.2 ^x	0.49±0.02 ^y	0.42±0.13 ^x	135.9±0.2 ^x	33.2±0.6 ^x	249.1±0.5 ^x	39.0±0.8 ^y	4.2±0.3 ^y
	CO ₂ (isotherm)	76.4±0.2 ^z	0.48±0.02 ^{x,y}	2.55±0.15 ^y	136.1±0.3 ^x	31.9±0.3 ^x	249.0±0.8 ^x	38.4±0.4 ^y	4.7±0.5 ^y

§Transition not detectable.

Values are reported as mean ± S.D. Significant differences (p -value < 0.05) are indicated with different letters in the same column. For each parameter, two independent ANOVA tests were carried out, one for PLA (subscripts a, b) and one for PET (subscripts x, y, z). T_g – glass transition temperature, ΔC_p – specific heat variation, ΔH_{relax} – enthalpy of endothermic event associated to glass transition, T_{cc} – cold crystallization temperature, ΔH_{cc} – cold crystallization enthalpy, T_m – melting temperature, ΔH_m – melting enthalpy and X_c – crystallinity degree.

Figure 4. Effective diffusion coefficients calculated from sorption isotherms kinetics of PLA (a) and PET (b). Error bars are the predictive intervals.

first sorption cycle was characterized by a high variability, while the variability of other cycles was smaller and rather constant. This was possibly because the initial structure of PLA was highly modified during the first sorption. Secondly, if the mean of all D_{sorp} values for each sorption and desorption cycles are considered, a slight but significant (p -value = 0.03) increase in D_{sorp} values during desorption steps is observed. This could be due to formation of CO_2 clusters in the polymer structure or to CO_2 – CO_2 interactions that appeared to be easily removed.

The D_{sorp} values of PET followed a similar trend to PLA and same considerations thus applied in this case. More precisely, no significant difference was noticed between PLA and PET. Both D_{sorp} values were around $10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$. For PET Similar D_{sorp} values were also observed in other studies [40–42]. The variability of first sorption was higher than the others cycles, and for desorption steps, the equilibrium was reached faster than for sorption.

3.2. Modifications of polymer film induced by CO_2 sorption

The modifications induced by CO_2 sorption at high pressure on the chemical properties, thermal events and functional properties (*i.e.* mechanical and barrier) of films were assessed.

3.2.1. Chemical modifications

Findings of ATR-FTIR analyses were in line with previous sorption isotherm observations, and gave

strong evidence that modification in films functional properties was a consequence of physical reorganization, occurring in the polymer structure.

The ATR-FTIR spectra of PLA and PET films displayed the typical vibrations bands of these materials in accordance with other studies (Figure 5 and 6) [25, 26, 43, 44]. For PLA, $-\text{C}=\text{O}$ stretching (1720 cm^{-1}), $-\text{CH}_3$ bending (1452 cm^{-1}), $-\text{C}=\text{O}$ bending (1270 cm^{-1}), $-\text{C}-\text{O}-\text{C}$ stretching (1185 cm^{-1}), $-\text{C}-\text{O}-\text{C}$ stretching (1130 and 1088 cm^{-1}), $-\text{OH}$ bending (1046 cm^{-1}) and $-\text{C}-\text{C}-$ stretching attributed to amorphous and crystalline phases (863 and 758 cm^{-1} , respectively) [25, 44]. For PET, $-\text{C}=\text{O}$ stretching (1752 cm^{-1}), $-\text{CH}_2$ bending (1452 cm^{-1}), $-\text{C}=\text{O}$ bending (1260 and 1246 cm^{-1}), $\text{O}-\text{C}$ stretching (1118 and 1098 cm^{-1}) and the vibration modes associated to the aromatic ring (1578 , 1506 , 1018 , 874 and 726 cm^{-1}) [26, 43].

When the properties of polymer materials are modified by chemical reactions such as degradation, polymerization or chemical bonds creation, formation of new bands or chemical shifts are expected in the ATR-spectra. Neither PLA nor PET displayed shifts or new bands after the two cycles of CO_2 sorption and desorption, indicating that no chemical reaction occurred during this CO_2 sorption in isothermal conditions. However, significant changes in the relative intensity of peaks related to vibration of carbonyl groups (PLA) as well as groups associated to carbonyls (PLA and PET) and aromatic cycle (PET) were observed. These modifications can be attributed

Figure 5. ATR-FTIR spectra of PLA before and after been subjected to CO₂ sorption isotherm analysis. Significant differences are evidenced with stars.

Figure 6. ATR-FTIR spectra of PET before and after been subjected to CO₂ sorption isotherm determination. Significant differences are evidenced with stars.

to structural rearrangements induced by plasticization and swelling of polymer chains during CO₂ sorption. The sorption sites (carbonyls) and the chemical groups near to them were the most affected in both materials. Furthermore, it appeared that the impact of such modifications were more pronounced in PLA, probably as a consequence of the higher CO₂ sorbed quantity and interactions with carbonyls groups as previously displayed by sorption isotherms.

3.2.2. Physical modifications

The thermal events of PLA and PET films stored under various sorption conditions were determined using DSC analysis, after pressure release from the samples. Only the first heating scan was considered in order to take into account the physical modifications induced by interactions with the CO₂. The related DSC curves for PLA and thermal parameters are reported in Figure 7 and Table 1, respectively.

Figure 7. DSC curves (First heating) of PLA films: starting material and following different treatments (previously equilibrated at 25 °C with CO₂ at 1 and 25 bar, or with N₂ at 25 bar)

All PLA film samples displayed the typical thermal events of semicrystalline materials, namely glass transition, endothermic event associated to glass transition and melting of crystals, which are characteristic of the coexistence of amorphous and crystalline phases in the PLA structure. As previously reported, the multi peak around glass transition was most likely due to bi-orientation process, which induced an organized structure of the PLA chains and crystals [45]. The initial PLA material was compared with a sample subjected to CO₂ sorption at 25 bar, which corresponds to the higher pressure step of the previous sorption isotherm (Figure 2). For the latter, the T_g decreased of $\approx 6^\circ\text{C}$ when compared to the initial material, and the enthalpy of the associated endothermic event increased around 5 times. However, when PLA was placed in contact with N₂ at the same pressure of 25 bar, no change was noticeable. This clearly meant that those modifications could not be attributed only to high pressure treatments, but were unambiguously related to CO₂ sorption at this pressure. Similarly, when CO₂ pressure was only 1 bar, no modification appeared. Therefore, this suggested that two conditions were required to induce changes in the amorphous phase of PLA: sorption of CO₂ molecules and at high pressure conditions. When relatively high quantity of CO₂ were sorbed under high pressure ($\approx 7\%$ at 25 bar, Figure 2), it induced structural changes in the PLA polymer which were not totally recovered even when the pressure was released, and notwith-

standing the fact that the CO₂ only interacted by low energy interactions.

Nofar and coworkers [46, 47] have observed a clear T_g depletion in PLA as a consequence of solubilizing CO₂ in the polymer matrix. They reported a T_g decrease from ≈ 55 to 35°C for different types of PLA (e.g. branched, linear, amorphous, and semicrystalline) under CO₂ at 25 bar using high pressure differential scanning calorimetry. Based on these considerations, it can be hypothesized that the increase of the endothermic event associated to glass transition was a consequence of an accelerated physical ageing favored by T_g depletion, which came close to operative temperature (25 °C) for the highest pressure steps of the sorption isotherm. Physical ageing could be defined as the slow molecular rearrangements occurring in amorphous polymers, when stored at lower temperatures than T_g , which tend to reduce its free-energy and free volume [48, 49]. As consequence of these molecular rearrangements, the polymer structure get continuously denser and becomes more glass-like and less rubber-like [48].

A relevant finding from the present work is the T_g reduction observed for the PLA film sample placed in CO₂ environment at 25 °C and 25 bar, but for which all CO₂ molecules were desorbed at the time of analysis. Such result indicated that structural modifications were induced by CO₂ physisorption. There was no complete return of PLA to its initial physical state when removing CO₂. It probably led to a less com-

pact network with increased free volume. This result is of particular interest, because it revealed that bulk properties of PLA films can be modified by CO₂ sorption/desorption cycles at conditions lower than the supercritical point and have to be considered for development of PLA-based materials.

The CO₂ sorption at high pressure did not influence the crystallinity degree of PLA films (Table 1), probably because the T_g depletion during sorption conditions still remained higher than operative conditions (25 °C). Indeed, lower T_g temperatures could induce transitions from glassy to rubbery state, favoring crystallization. However, a small but statistical significant increase in crystallinity degree was observed in PLA after N₂ sorption at high pressures (28.1 vs. 24.8 %). This increase was unexpected, since no modifications in the amorphous phase were observed and only very low interactions (and therefore no-plasticization) between PLA and N₂ were suggested in the corresponding literature [39, 50, 51]. Indeed, N₂ solubility in PLA was reported to be around 1–2 magnitude lower than the corresponding CO₂ values [39, 50, 51].

In the case of PET, the effects of CO₂ sorption at high pressure were evaluated by analyzing outgassed samples from CO₂ sorption isotherm (Figure 3). Since determining CO₂ sorption isotherm involved ≈2.5 months, samples stored at room conditions (close to 25 °C) for 5 months were used as control specimens to evaluate if physical ageing occurred.

Films subjected to CO₂ sorption at 1 bar were also considered to evaluate the modifications induced by sorption of CO₂ at low pressure. The related DSC curves and thermal parameters are reported in Figure 8 and Table 1.

PET films displayed the typical thermal events of purely amorphous materials: glass transition, endothermic event associated to glass transition, and equivalent exothermic and endothermic transitions related to cold crystallization and melting of PET crystals, respectively. When the melting enthalpy was subtracted to the cold crystallization enthalpy, a small percentage of crystals (3%) were found in PET.

A significant increase (p -value < 0.001) of the endothermic event related to glass transition was noteworthy for PET sample placed under high CO₂ pressure (up to 25 bar) during the sorption isotherm experiment. No significance increase (p -value > 0.05) in such thermal event was observed in control samples neither consecutively to long time storage (5 months) nor following sorption of CO₂ at low pressure (1 bar), suggesting an acceleration of physical ageing when in contact with high pressure of CO₂, in an analogous way to PLA. Several studies have already reported a decrease of T_g in PET films when CO₂ molecules are solubilized in the polymer [52–55], with values ranging between 40 and 60 °C at ≈20–25 bar using high pressure differential scanning calorimetry [52, 53].

Figure 8. DSC curves (First heating) of PET films: starting material and PET following different treatments and storage conditions (storage for 5 months at room conditions, previously equilibrated with CO₂ at 1 bar and previously submitted to CO₂ sorption isotherm determination up to 25 bar)

Although a T_g decrease is observed in the above-mentioned studies, a small increase in T_g of PET samples after CO₂ sorption at high pressure was observed in this study. Such an increase can be considered in line with the effects of physical ageing, since no CO₂ molecules remained in the polymer matrix during the DSC analysis. In fact, the molecular rearrangements in physical ageing involve a densification of the polymer structure, which can decrease the free volume [48, 49]. In contrast to PLA, it seems that swelling induced by CO₂ sorption was less pronounced in PET, probably due to the lower CO₂ sorption level. Lastly, a small increase in the crystallinity degree (from 3 to $\approx 4.5\%$) was observed in samples used for CO₂ sorption determination and on samples stored for 5 months at room conditions, which could result from relaxation phenomena during ageing, which led to the formation of crystallites.

3.2.3. Impact on the functional properties

In order to investigate if the modifications induced in the physical state of PLA also influenced its main functional properties, the mechanical behavior under tensile stress and the barrier properties to CO₂ of PLA prior to and after CO₂ sorption at 25 bar were measured.

Mechanical properties

Table 2 reports the Young's modulus (E_{Young}), yield strength (σ_y), yield elongation (ε_y), tensile strength (σ_b) and elongation at break (ε_b) of PLA.

The mechanical behavior of films was influenced by the previous sorption of CO₂ at high pressure. However, a not clear effect of CO₂ plasticization was observed, since a significant decrease (p -value = <0.0001) of strength at the yield point (σ_y), followed by a significant increase (p -value = 0.014) of strength at the break point (σ_b) and no change in elongation at break (ε_b) were noticed in PLA samples after CO₂

sorption. This ambiguous result could be explained by the two phenomena occurring consecutively to CO₂ sorption. The plasticization effect of CO₂, which tended to swell PLA chains, could generate the decrease of σ_y , while the acceleration of physical ageing could induce the increase of σ_b , due to a densification of the PLA structure. If p -values related to the significance of difference for both parameters are compared, a much lower value is found in σ_y compared to σ_b , suggesting a weak domination of CO₂ plasticization over PLA structure densification.

Barrier properties

The permeability (P), the diffusion coefficient (D_{perm}) and the solubility coefficient (S_{perm}) of PLA films to CO₂, determined by manometric method are reported in Table 2.

The permeability of PLA films to CO₂ increased of $\approx 11\%$ consecutively to CO₂ sorption at high pressure, in agreement with the T_g decrease detected by DSC. The solubility coefficient increased by around 50%, which was in line with CO₂ sorption isotherm, which displayed a similar increase during the second sorption step (Figure 2). These results confirmed that CO₂ acted as plasticizer and physically intercalated between polymer chains, which in turn expose new sorption sites. These sites would be still available for the next sorption step once the CO₂ molecules were desorbed.

In contrast, a small decrease in the effective diffusion coefficient D_{perm} was noticeable for films after CO₂ sorption. Some studies showed a decrease in water and oxygen permeability for different types of PLA (e.g. totally amorphous, semicrystalline, with/without plasticizers) as a result of PLA structure densification during physical ageing [56–58]. Based on these considerations, it could be hypothesized that such decrease in the diffusion properties originated from the acceleration of physical ageing during CO₂ sorption.

Table 2. Mechanical and barrier properties to CO₂ of PLA prior to and after CO₂ sorption at 25 bar for 5 days at 25 °C

Film	Mechanical properties					Barrier properties to CO ₂		
	E_{Young} [GPa]	Yield point		Break point		P [$10^{-16} \cdot \text{mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$]	D_{perm} [$10^{-13} \cdot \text{m}^2 \cdot \text{s}^{-1}$]	S_{perm} [$10^{-4} \cdot \text{mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$]
		σ_y [MPa]	ε_y [%]	σ_b [MPa]	ε_b [%]			
Initial PLA	4.0 $\pm$ 0.1 ^a	78.8 $\pm$ 1.0 ^a	2.7 $\pm$ 0.2 ^a	98.8 $\pm$ 5.4 ^a	66.9 $\pm$ 10.9 ^a	2.83 $\pm$ 0.03 ^a	10.3 $\pm$ 0.9 ^a	2.8 $\pm$ 0.2 ^a
PLA after CO ₂ sorption at 25 bar	4.1 $\pm$ 0.2 ^a	70.3 $\pm$ 1.3 ^b	2.5 $\pm$ 0.2 ^a	105.8 $\pm$ 3.4 ^b	67.7 $\pm$ 4.3 ^a	3.13 $\pm$ 0.04 ^b	7.8 $\pm$ 0.7 ^b	4.0 $\pm$ 0.3 ^b

Values are reported as mean $\pm$ S.D. Significant differences (p -value < 0.05) are indicated with different letters in the same column (subscripts a, b). E_{Young} – Young's modulus, σ_y – yield strength, ε_y – yield elongation, σ_b – tensile strength, ε_b – elongation at break, P – permeability, D_{perm} – diffusion coefficient from manometric method, S_{perm} – solubility coefficient from manometric method.

Lastly, the diffusion coefficient obtained by the permeability measurement were slightly different from the values obtained during the sorption isotherm experiment ($D_{\text{perm}} \approx 10 \cdot 10^{-13} \cdot \text{m}^2 \cdot \text{s}^{-1}$ vs. $D_{\text{sorp}} \approx 2 \cdot 10^{-13} \cdot \text{m}^2 \cdot \text{s}^{-1}$), possibly because the experimental conditions for calculating such values were not the same. In particular, the former determination (D_{perm}) involves a dynamic system with continuous gas flow; while the latter (D_{sorp}) involves a static system and establishes a boundary layer, which acts as an additional resistance to mass transfer. Nevertheless, the values could be considered very similar between them, since they remained in the same order of magnitude.

4. Conclusions

The CO₂ sorption isotherm (two sorption/desorption cycles) gave evidence of physisorption and hysteresis phenomena in PLA. These results were in line with ATR-FTIR analysis, which did not reveal any chemical differences in the samples before and after been subjected to CO₂ sorption. The effective CO₂ diffusion coefficients of PLA (D_{sorp}) oscillated around $10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ and no effect of CO₂ pressure was found, however the D_{sorp} associated to desorption steps were faster than the sorption steps, probably due to formation of CO₂ clusters or CO₂–CO₂ interactions in the polymer matrix.

The thermal properties revealed physical modifications in the amorphous structure of PLA after CO₂ sorption at high pressure of 25 bar. CO₂ solubilization in PLA induced a T_g depletion, which accelerated the physical ageing of PLA. Two phenomena with opposite effects occurred. On one hand, CO₂ plasticization tended to swell PLA chains, increasing its free volume. On the other hand, the physical ageing tended to get denser the PLA structure. As a result of these bulk modifications, the functional properties of PLA changed. The results of this study are of particular interest because they provide evidence to the capacity of CO₂ to physically modify the bulk properties of PLA even at lower conditions than its supercritical point, which could be considered when materials based on PLA are developed.

Lastly, the behavior of PET after CO₂ sorption was very similar to PLA. All the analyses displayed (sorption isotherm, diffusion coefficient, ATR-FTIR and thermal event) that the PET structure was physically modified by CO₂ sorption in a similar way to PLA.

But as a consequence of its lower CO₂ solubility, the impact of such modifications was of minor intensity. Therefore, the results of this study contribute in giving new evidences of the PLA feasibility as starting material able to substitute PET in packaging applications involving CO₂.

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