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Sorption and diffusion of compressed carbon dioxide in polycaprolactone for the development of porous scaffolds

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ABSTRACT

In this work different phenomena related to sorption of carbon dioxide in polycaprolactone (PCL) have been investigated systematically. The use of compressed carbon dioxide is discussed for obtaining porous scaffolds from this biocompatible polymer. In order to determine the plasticization effect of carbon dioxide on the degree of foaming it is necessary to discuss sorption data with respect to morphological features of the polymer at conditions nearby the melting point. The amount of carbon dioxide dissolved and the kinetics of the sorption process are found to depend strongly on temperature and pressure. The solubility takes values of up to 25 wt.% being favoured by a melting and glass transition temperature depression which can be observed along with an enhanced mass transfer rate. In general, CO₂ sorption in PCL increases linearly with pressure. When decompressing, microfoaming occurs which enhances the rate of gas release. Changes in morphology and crystallinity occur as a consequence of the pressure treatment. Compared to the melting temperature at atmospheric pressure there is a dramatic reduction observed under pressure where melting occurs already at a temperature below 40 °C. Even after pressure-treatment, there is a remaining change in melting temperature and crystallinity observed. Optimum conditions for obtaining adequate porous scaffolds of PCL are a relatively slow decompression after treatment at 17 MPa and 35 °C.

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1. Introduction

In the last decade, significant research effort has been devoted to achieve biodegradable scaffolds with well-defined properties for bone tissue engineering and for drug delivery systems. Diverse design criteria have been specified for an ideal scaffold with potential application in the mentioned areas. However, neither of the developed materials has successfully fulfilled all given requirements. It is well accepted that the ideal porous scaffold should have an interconnected porous structure, sufficient mechanical strength and good cell–scaffold interaction. Pore size, pore morphology and degree of porosity are very important parameters in tissue engineering. It is known that an interconnected pore-structure with pore sizes in the range of 100–500 µm is necessary to promote cell adhesion, proliferation and three-dimensional colonization. Also, the presence of micropores is required for the diffusion of biological fluids [1]. A number of methods have been developed for producing 3D interconnected porous scaffolds, such as fiber bonding, solvent casting, supercritical fluid technology, particulate leaching, melt molding, etc. Among these techniques, foaming with supercritical

carbon dioxide (scCO₂) is superior to other methods for producing solvent-free porous structures. Hence, use of supercritical carbon dioxide is of high interest as an alternative “clean” solvent for processing biodegradable and biocompatible polymers in pharmaceutical and medical applications [2,3].

The high diffusivity of scCO₂ in many solid polymers has a positive influence in polymer modification [4]. It was reported that polymer substrates could be impregnated by swelling of the polymer with a solution of one or more chemical compounds (pharmaceutically or biologically active agents) in CO₂ followed by rapid venting of the supercritical solution. Since the chemical compound has a lower diffusivity than the gaseous CO₂, it can be retained by the polymer. An associated effect of venting is foaming of the polymer. Thus, in the same process it is possible to combine the impregnation and the porous scaffold formation. [3–6].

Actually, polycaprolactone (PCL) is widely used for scaffold assembly. PCL is a semicrystalline and biodegradable polyester with a low melting point of around 60 °C and a glass transition temperature of about –60 °C. Although it is processed by a wide variety of technologies, only few papers are dealing with the morphological changes of PCL under compressed carbon dioxide [7–10]. Carbon dioxide solubility and diffusivity in PCL are influenced by both the molecular structure (the interaction between CO₂ and molecular chains) and the morphology (crystalline or amorphous, related with free volume) of the polymer. In fact, the gas sorption is not a merely physical

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phenomenon, but it also involves specific chemical interactions between CO₂ and polymers. Therefore, the behaviour of the polymer in the presence of CO₂ (swelling, melting point depression, foaming, etc.) is important to be studied for the mentioned applications. Up to now only little work is published on quantitative analysis related with the sorption and desorption kinetics in PCL samples. Duarte et al. [11] used a rudimental gravimetric method to determine the amount of absorbed carbon dioxide by recording desorption kinetics after releasing the pressure and retrieving the polymer sample from the autoclave at defined time intervals. The error caused by the time lag until the sample is placed on a microbalance should be avoided by detecting the weight online under pressure. Leeke et al. [12] used a static method for obtaining solubility data of carbon dioxide in PCL at 40 °C and 60 °C. Cotugno et al. [13] determined sorption isotherms of CO₂ in molten PCL at low pressures and high temperatures representing irrelevant conditions for PCL processing as biomaterial. The melting point depression induced by compressed CO₂ on semicrystalline polymers was studied by Lian et al. [14]. They determined the relation between the CO₂ pressure and the melting temperature of PCL, which was assumed at the point when light transmission was observed through the sample. This effect was exploited by Yoganathan et al. [15]. They assumed that the higher loading of PCL with ibuprofen using CO₂ as a carrier fluid resulted from the melting point depression. Experiments were conducted at temperatures between 35 and 40 °C in the pressure range of 10 to 18 MPa. Further studies performed by Aionicesei et al. [16] do not take into account the different states which the polymer undergoes during sorption and its possible influence on the gas solubility behaviour.

In order to determine the plasticization effect on the degree of foaming during decompression it is necessary to relate sorption data of CO₂ in PCL with morphological features of PCL samples at conditions of temperature and pressure nearby the melting point. Next to transport kinetics of dissolving gas molecules, it is important to learn about structural changes associated to swelling and melting behaviour under pressure in order to develop and design scCO₂ based processes and to select operating conditions for production of PCL scaffolds with adjustable porous structures. To our knowledge, this paper is the first to systematically report data of CO₂ solubility and diffusivity within PCL as well as swelling of PCL at temperatures of 30, 35 and 40 °C and pressures between 10 and 20 MPa associated with morphological and structural characteristics of the obtained porous samples.

2. Materials and methods

Granules of PCL with a molecular weight of 74,000 were purchased from Sigma Aldrich, Germany (PCL80). Pieces of 10 × 4 × 2 mm, that were made by melting PCL at 105 °C, were used for preliminary studies performed between 10 and 20 MPa in a temperature range of 30 to 40 °C. Spheres with diameters of approximately 7 mm were used for quantitative measurements on swelling and sorption.

The investigations on swelling were performed in a high-pressure view chamber (P_{max} = 50 MPa, T_{max} = 120 °C, Eurotechnica, Germany) provided with a CCD camera. A schematic of the experimental set-up is shown in Fig. 1.

Sorption of carbon dioxide in PCL was determined by use of a magnetic suspension balance (P_{max} = 35 MPa, T_{max} = 120 °C, Rubotherm, Germany). The weight of the sample under the actual conditions of pressure is transmitted to a microbalance outside the autoclave by a magnetic suspension coupling. The time dependant weight is recorded by a PC. A schematic of the setup is shown in Fig. 2.

The recorded balance readings must be corrected for the change in buoyancy that occurs due to swelling. The mass gain, M_t , under pressure can be determined from the balance readings at $t = 0$, w_0 and $t > 0$, w_t , by the following equation [17]:

$$M_t = (w_t + V_t \rho_{CO_2}) - w_0 \quad (1)$$

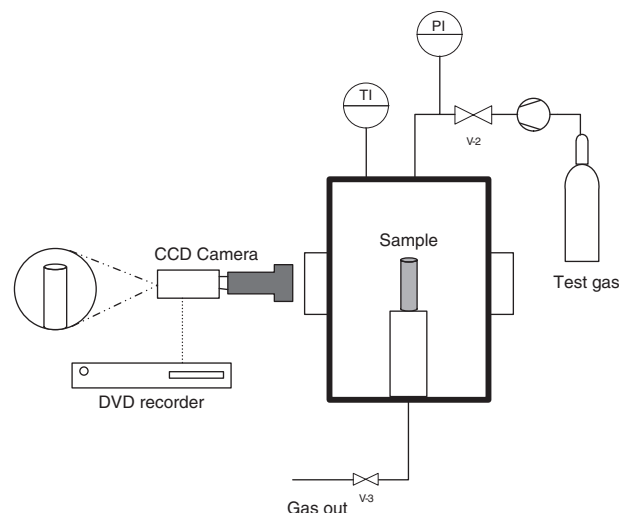


Fig. 1. Experimental set-up of the high-pressure view chamber.

where V_t is the actual volume of the sample and ρ_{CO_2} the density of the surrounding fluid. Gas densities within the relevant pressure and temperature range were obtained from the GERG equation of state [18].

After sorption of CO₂ into PCL samples, gas decompression was performed at different rates: 1, 5, 10 and 20 bar/min. Finally, all PCL samples were characterised by Differential Scanning Calorimetry (DSC), density measurements (Archimedes Method) and Scanning Electron Microscopy (SEM) prior and posterior to the treatment with compressed CO₂. Differential Scanning Calorimetry (DSC) was performed with a Shimadzu DSC-50 thermal analyser under nitrogen atmosphere at a heating rate of 10 °C/min, from room temperature to 120 °C. Density values were calculated by using a Sartorius Balance

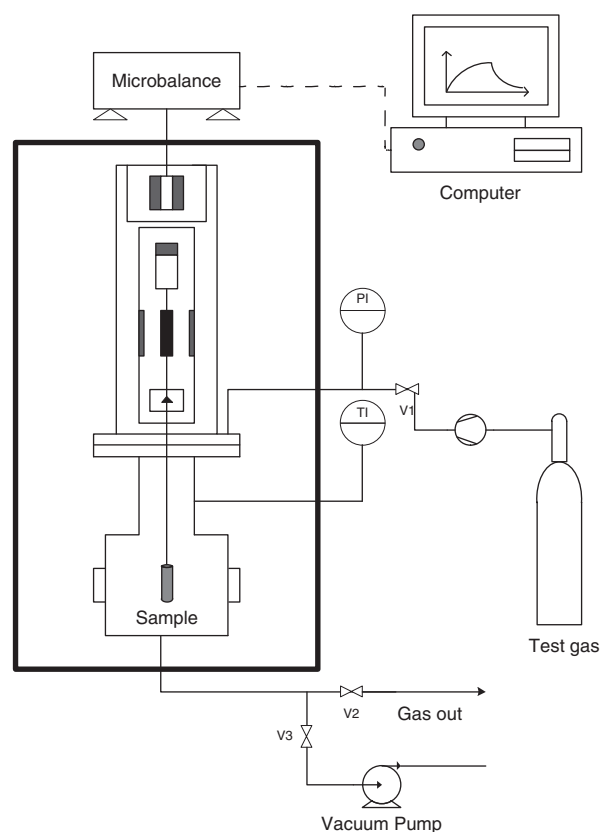


Fig. 2. Experimental set-up of the high-pressure apparatus for sorption measurements.

(YDK01) with a density kit. Morphologies of all samples were observed by scanning electron microscopy (SEM), employing a Jeol JXA-8600 microscope after coating the samples with a thin gold layer. The obtained images were analysed by means of a commercially available imaging software tool in order to describe polymer morphology and pore diameter. In general, measurements were carried out at least in duplicate at 30, 35 and 40 °C in the range of 10–20 MPa.

3. Results

3.1. Preliminary studies

The shape and size of rectangular PCL samples were recorded as a function of time at constant pressure and temperature by means of a CCD camera as mentioned above. Some representative images are shown in Fig. 3. When PCL samples are contacted by compressed CO₂ at 35 °C, a profile of plasticization propagates throughout the sample. Fig. 3a shows that PCL is not completely plasticized at 35 °C and 15 MPa after 30 min of treatment. However, when the pressure is increased to 17 MPa the sample is completely plasticized after 30 min (Fig. 3b). If the pressure is increased to 20 MPa, the shape is totally changed within only 20 min. (Fig. 3c).

Fig. 3a and d shows the influence of temperature on plasticizing at pressure of 15 MPa. When the temperature is raised to 40 °C (Fig. 3d) the sample is completely deformed after 20 min.

3.2. Swelling measurements

The behaviour of spherical shaped samples was investigated to evaluate the volume change under pressure exposure. In this case the diameter of the samples was used to calculate the time dependant volume change. Fig. 4a shows the swelling behaviour of samples treated at 30 °C and different pressures. The overall change in volume of these samples increases as the pressure is raised. After 50 min, the volume has increased approx. 10% in all cases. At this point a first plateau is reached after which the volume further increases. After about 250 min an equilibrium is achieved with clear differences in the volume change among the different pressures with the strongest swelling at the highest pressure. Fig. 4b shows the swelling behaviour of samples treated at 35 °C and different pressures. At this temperature a melting point depression is observed, i.e. during the course of the sorption the samples are partially or completely melted. At 10 MPa it is still possible to evaluate the volume change even after 50 min. At higher pressures (>13 MPa) the melting process occurs faster and after 20 min the melted regions have already deformed the sample inhibiting further evaluation of the volume through the calculation of the sample diameter. Therefore, equilibrium values of swelling at these conditions cannot be given. Up to 20 min of treatment, a significant difference in the volume change was observed for the samples treated at 13 MPa and 35 °C with respect to the samples treated at 15 MPa and 18 MPa at the same temperature. Instead of increasing, as expected, the volume change at 15 MPa and 18 MPa is lower because of the enhanced melting

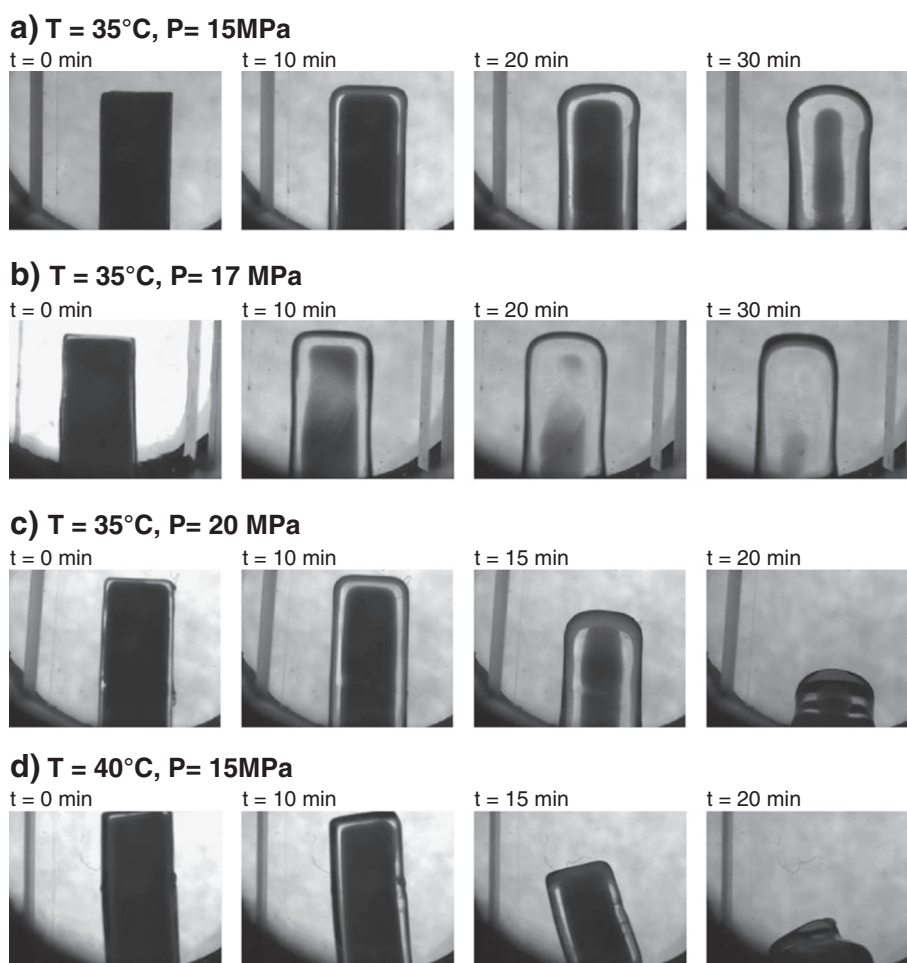


Fig. 3. Features of PCL samples under different P conditions at T = 35 °C and at different treatment times.

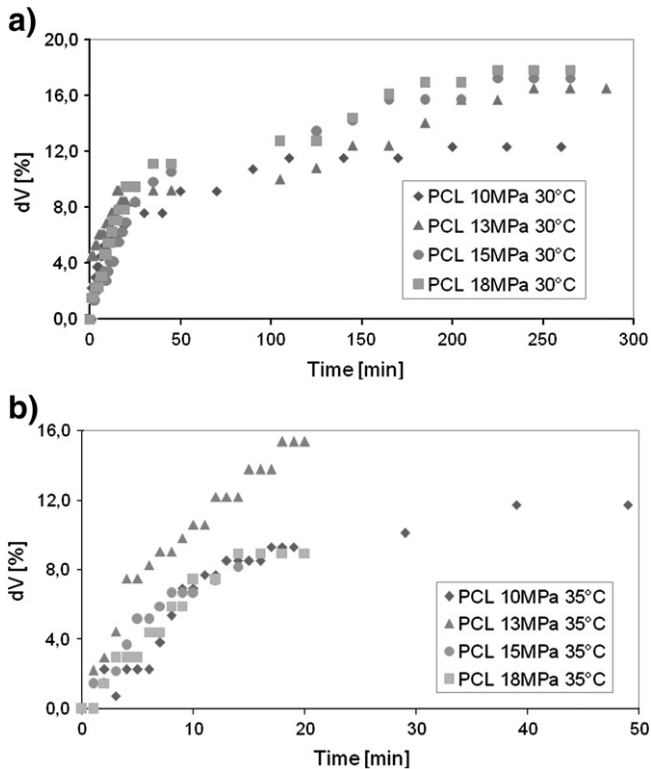


Fig. 4. a) Measured swelling kinetics of CO₂ in PCL at 30 °C and different pressures. b) Measured swelling kinetics of CO₂ in PCL at 35 °C and different pressures.

point depression. The samples start to melt after 20 min already, apparently leading to less increase in volume at the changing aggregate state.

3.3. Sorption kinetics

Spheres of the same diameter as used in the swelling tests were used in the sorption experiments. The samples were placed in a cage within the high-pressure balance described above. Constant temperature and pressure were applied until the sorption equilibrium was achieved. From the weight change, the amount of CO₂ entering the PCL sphere was determined. Therefore, the change in volume also needs to be accounted for since it affects the buoyancy by the surrounding compressed CO₂ which on its turn would give misleading results. Swelling values from the previous section were used to correct the balance readings for the buoyancy effect.

Fig. 5 shows the amount of gas absorbed by a sphere of PCL as a function of time at 13 MPa and 30 °C. As expected, the gas sorption increases rapidly during the first hours of the experiment and then it levels off. All treated samples present the same qualitative behaviour. Further, the difference is pointed out in the same diagram between the sorption omitting and including the buoyancy correction. After reaching the equilibrium sorption, the gas pressure is released and desorption of the gas from the PCL sample starts. Ideally, the signal decreases until reaching zero mass uptake.

In order to quantify the mass transfer of the gas within the polymer, the apparent diffusion coefficient was determined by adapting a theoretical approach to the experimental values. Applying the Fick's law of non-stationary diffusion, which was analytically solved for spherical particles by Crank [19], the following equation is obtained:

$$\left(\frac{M_t}{M_\infty}\right) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2t/a^2) \quad (2)$$

assuming that the weight change in Fig. 5 originates from sorption of the carbon dioxide. M_t/M_∞ is the mass uptake of CO₂ as a function of

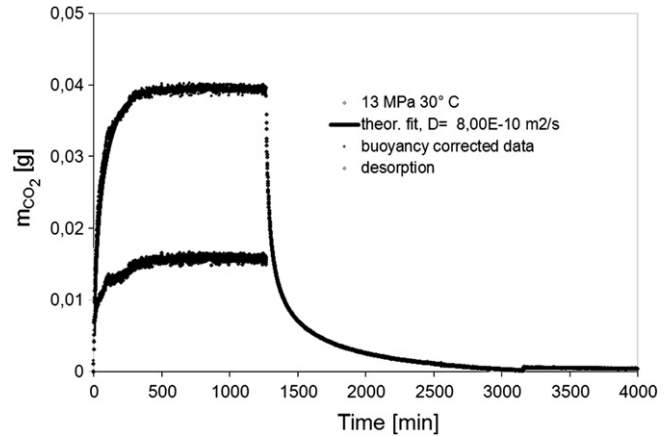


Fig. 5. Experimental and theoretical sorption kinetics applying Eq. (2).

time, t , related to the equilibrium value. a is the radius of the sphere, D is the diffusivity and n the running index of the series. The diffusion coefficient in Eq. (2) is adjusted until the theoretical and experimental curves coincide as also shown in Fig. 5.

In Table 1 results of swelling, sorption equilibrium and diffusivity of CO₂ within PCL are listed at the conditions of interest within the frame of this work.

3.4. Characterization of CO₂-treated PCL samples

The pore morphology was investigated using scanning electron microscopy (SEM). Fig. 6 shows the effect of the temperature on the microstructure of the PCL samples treated at different conditions. Pore formation was detected in the bulk of the sample processed at 40 °C but little pore formation was detected at 30 °C. Fig. 7 shows the development of microstructures in case of samples treated at $T > 30$ °C at different conditions of pressure and decompression rate, dP/dt . In all cases a porous microstructure was observed. However, the developed pore diameter depends strongly on the decompression rate.

In Table 2 the temperature and pressure, the depressurization rate dP/dt , the solubility of CO₂ in PCL (S) and several characteristics of scCO₂ processed PCL samples (Density (δ), pore diameter (d_{pore}), melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity (X_c)) are listed. For comparison, the density, T_m , ΔH_m , X_c of untreated scCO₂ PCL samples are also shown. The crystallinity of PCL samples (X_c) was determined using a heat of fusion value (ΔH_{100}) of 135.31 J/g [20] for 100% crystalline PCL according to Eq. (3):

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (3)$$

Fig. 8 shows the DSC analysis of samples processed according to the conditions listed in Table 2. Fig. 9 is included for illustrating the microstructures of the scCO₂ samples from which the pore diameters

Table 1
Swelling (dV), solubility (S) and diffusivity (D) of CO₂ within PCL.

P [MPa]	T [°C]	dV [%]	S [wt.%]	D [10^{-9} m ² /s]
10	30	14.5	13.6	1.5
13	30	16.5	20.2	1.0
18	30	17.8	21.0	1.0
10	35	11.7	12.6	3.0
13	35	15.4	22.0	3.0
15	35	9.2	20.0	4.0
15	40	8.0	40.0	10

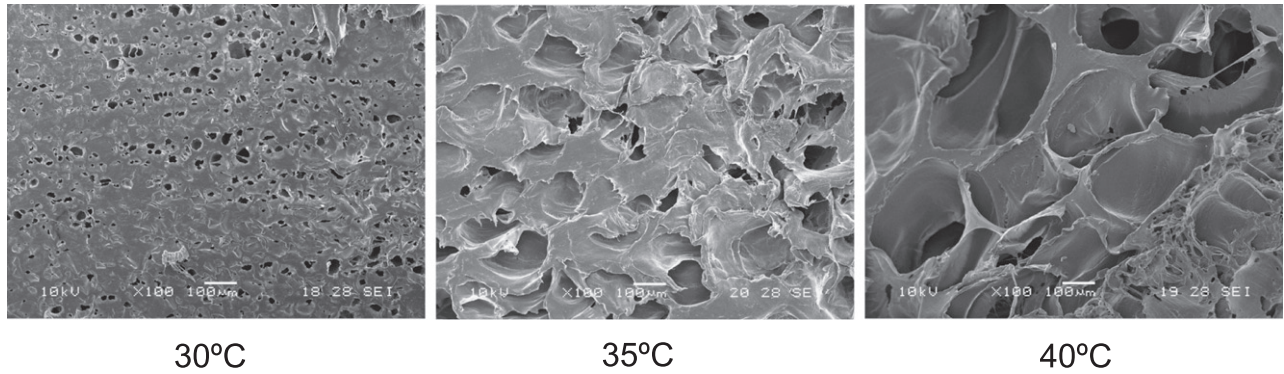


Fig. 6. Effect of temperature on developed microstructure for PCL samples processed at 15 MPa and 20 bar/min of dP/dt.

were determined. Both, homogeneous and rather heterogeneous structures can be observed, the pore diameters taking values of up to 360 μm .

4. Discussion

From the visual observations (Fig. 3), it was possible to confirm the capability of CO_2 to reduce the polymer melting point and therefore to act as a plasticizer. Also, a change in volume of the PCL became evident due to the absorption of the CO_2 into the polymer. At high pressures the gas uptake is larger, the plasticizing effect of the gas on the polymer is enhanced and as a result an increase of the polymer swelling is observed. A boundary propagating inside the polymer samples is clearly distinguished from the pictures in Fig. 3 which corresponds to the diffusion front of the compressed CO_2 and represents an interface between the molten and still semicrystalline regions. Further, the melting point is observed decreasing from 62 $^\circ\text{C}$ at ambient pressure to 35 $^\circ\text{C}$ at 20 MPa. After 20 min of exposure at 35 $^\circ\text{C}$ and 20 MPa the sample is completely deformed whereas at 15 MPa the sample basically preserves

its original shape. At 15 MPa though, the sample of PCL melts at 40 $^\circ\text{C}$. At 30 $^\circ\text{C}$ none of the samples changed to a completely molten state.

From these observations it is possible to state that at 35 $^\circ\text{C}$ and 15 MPa PCL melts after 50 min of CO_2 treatment. These conditions are in accordance with the results obtained by Lian et al. [14]. However, the results reported by Shieh et al stated that a higher pressure (30.4 MPa) is necessary for melting PCL at 35 $^\circ\text{C}$. The higher pressure indicates that less severe conditions might not have been investigated extensively enough.

The effect of the temperature on the polymer swelling can be analysed from Fig. 4. The volume change of the samples treated at 30 $^\circ\text{C}$ increases as the pressure is raised (Fig. 4a). At higher pressures the concentration of the gas increases along with the swelling of the sample. At 10 MPa swelling appears to increase with temperature although the equilibrium in case of 35 $^\circ\text{C}$ is not reached (Fig. 4b). This phenomenon can be explained by the fact that the elastic modulus of the polymer decreases when temperature is raised. It means that at high temperatures the dilatation capacity of the polymer considerably increases facilitating swelling of the polymer structure.

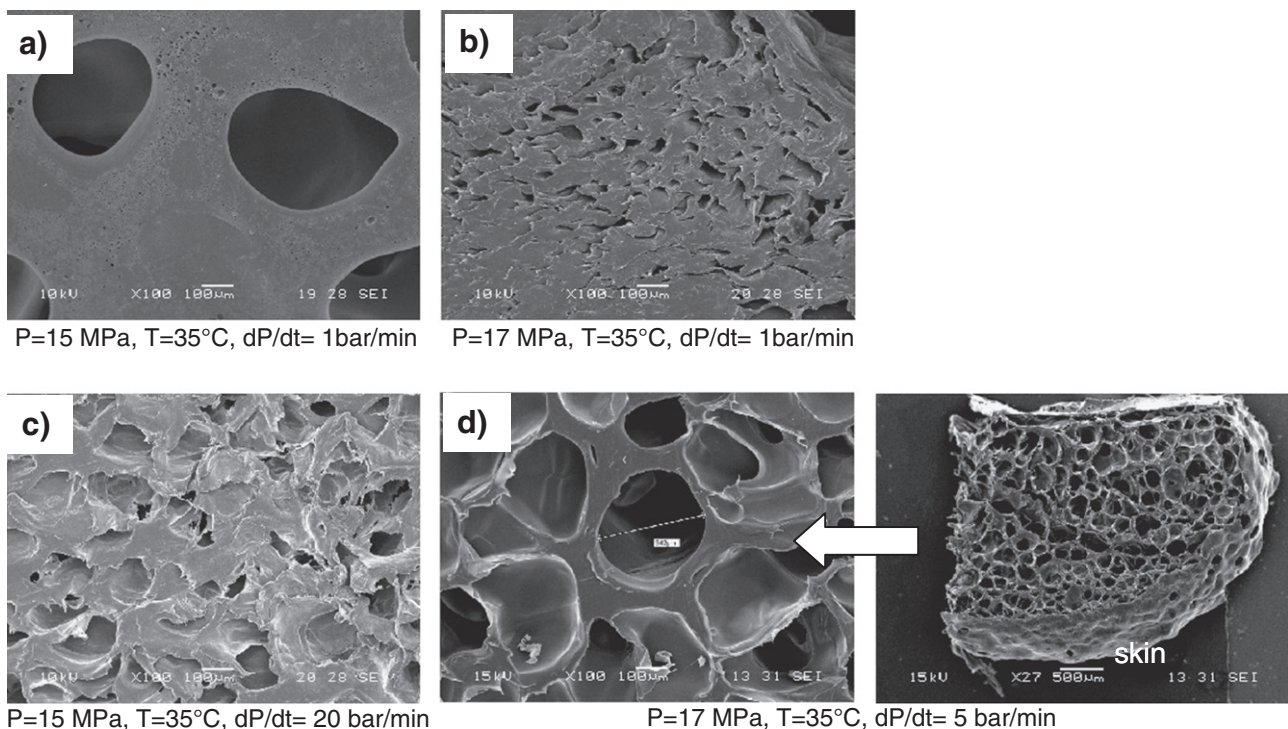


Fig. 7. Microstructure of the PCL samples treated at different conditions of T and P.

Table 2
Density (δ), depressurization rate (dP/dt), solubility (S), pore diameter (d_{pore}) indicated as one mean value, a range (“–”) or shown as double modal (“/”), melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity (X_c) of scCO₂ processed PCL samples.

Sample	P [MPa]	T [°C]	dP/dt (bar/min)	S [wt.%]	δ [g cm ⁻³]	d_{pore} [μm]	T_m [°C]	ΔH_m [J/g]	X_c [%]
PCL	Non treated	–	–	–	1.14	–	65.1	97.2	71.8
PCL sphere	P_{atm}	105	–	–	1.12	–	63.5	83.6	61.8
PCL10/35/10	10	35	10	14.0	0.55	130–180	63.2	94.9	70.2
PCL15/30/10	15	30	10	19.3	1.02	–	67.2	90.1	66.6
PCL15/35/10	15	35	10	19.2	0.44	110/230	63.9	96.0	71.0
PCL15/40/5	15	40	5	40.0	0.35	360	64.6	77.0	56.9
PCL15/40/10	15	40	10	40.0	0.32	290/1.5 mm	64.4	90.4	66.8
PCL17/35/5	17	35	5	*	0.34	340	63.6	85.7	63.3
PCL18/30/10	18	30	10	24.9	1.10	–	65.9	97.0	71.8
PCL18/35/10	18	35	10	*	0.50	200	65.0	95.12	70.2

*Samples were decomposed by melting before obtaining saturation during sorption.

The sorption measurements (Table 1) show that a higher amount of gas is absorbed when pressure is increased, while this amount usually decreases when the temperature is raised as seen for 13 MPa and also found by Aionicesei et al. in poly(L-lactide) and poly(D,L-lactide-co-glycolide) materials [16]. The most important factors influencing the solubility, and thus the swelling, are the free volume and crystallinity. At higher pressures the concentration of CO₂ within the polymer increases due to the gas molecules are forced between polymer chains and consequently the plasticizing effect of the gas on the polymer structure becomes stronger. As a result, the enhanced chain mobility allows

easier diffusion of the gas. For a given pressure, the temperature rise causes a decrease in gas density, and this is associated with lower solubility of CO₂ in the polymer [16]. When rising the temperature above 35 °C in PCL samples gas sorption is considerably increased which is due to the fact that the aggregate state of the polymer changes. At 15 MPa and 35 °C the polymer is clearly above the T_g , but not yet above the T_m , whereas the sample treated at 40 °C has exceeded the melting temperature. At this point the availability of free volume within the system has increased and higher amounts of gas enter into the polymer.

As expected at 30 °C the diffusion coefficient decreases as the pressure is raised. However, at 35 °C instead of decreasing, an increment of the diffusion coefficient with pressure is observed. This phenomenon is due to the increased availability of free volume in the samples once they reach the molten state, which promotes the diffusivity of the gas within the system.

When the pressure is suddenly released the gas escapes from the polymer causing the nucleation and growth of bubbles within the polymer matrix leading to the formation of a polymeric foam. It only occurs when the operating conditions are considerably above T_g . Below T_g foaming will not occur, because the polymer matrix is too rigid to allow the nucleation and growth of the bubbles [21]. In this work it is known that all the experimental conditions are above the glass transition temperature. Polymer foaming processes are influenced by many parameters, such as temperature, pressure and depressurization rate. The effect of all these parameters on the final porous structure was analysed through the SEM images obtained.

The effect of the temperature was evaluated from Fig. 6. At higher temperatures two effects can be considered. First, since the viscosity of the system is lower at higher temperatures there is less resistance for the bubbles to grow and to coalesce, hence increasing the size of the bubbles as the temperature increases.

The effect of the pressure is shown in Fig. 7a and b. When pressure is enhanced the amount of gas absorbed increases as well. It will lead to the formation of more nucleation sites and therefore the bubble density increases and their size decreases when the pressure is raised.

Finally, the effect of the depressurization rate can be observed from Fig. 7. As the depressurization rate decreases there is more time available for the diffusion of CO₂ from the polymer matrix into the bubbles, leading to bigger sizes. Therefore, one can expect that as the decompression rate decreases the size of the pore will increase while the specific number of pores decreases. These results are in accordance with the analysis carried out by Jenkins et al. [10] that report the effect of venting time on the microstructure development from molten PCL samples at 65 °C and 170 bar. As the vent time increased the average pore size also increased.

Skin formation at the surface was found in all foamed samples. Fig. 7d shows two pictures of the same sample, the first was obtained from the inside and the second shows the surface of the sample. The formation of a skin at the surface of the foamed samples was already reported. The main reason for skin formation may be the rapid diffusion

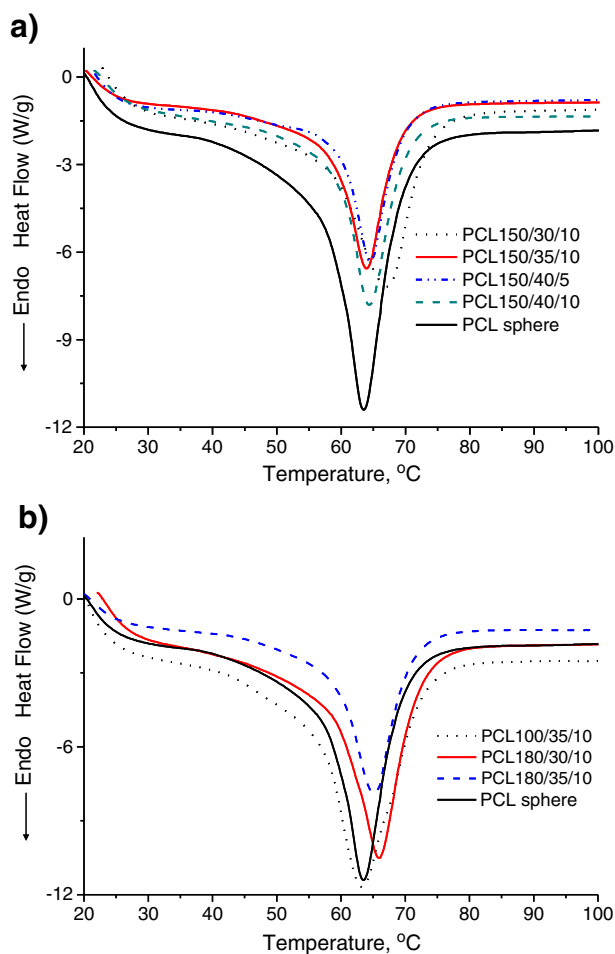


Fig. 8. DSC analysis of samples processed according to the conditions listed in Table 2. a) Samples treated at 15 MPa, b) Samples treated at 10 and 18 MPa. (PCL sphere: pretreated at P_{atm} and 105 °C).

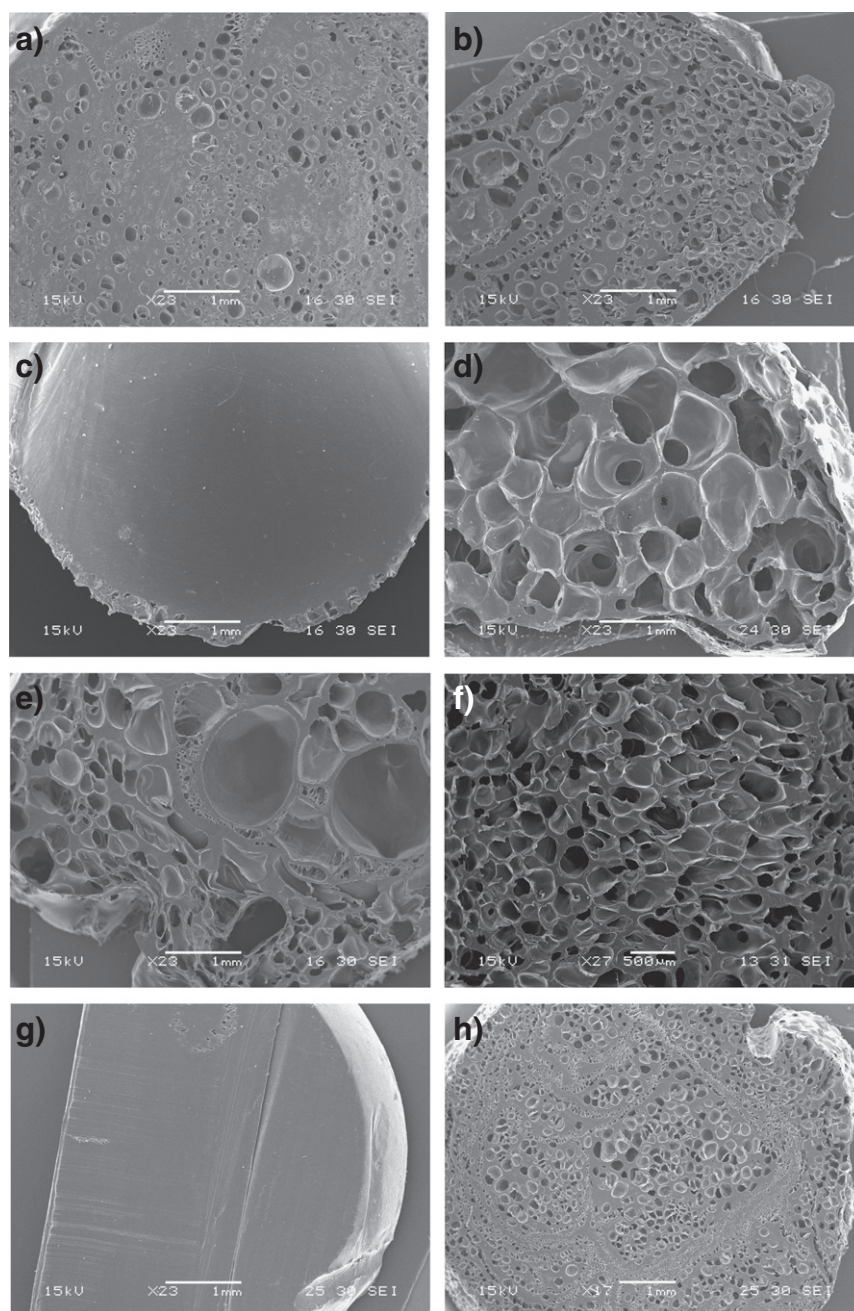


Fig. 9. SEM microscope images of the cross-sections of the SC-CO₂ processed samples: a) PCL10/35/10; b) PCL15/35/10; c) PCL15/30/10; d) PCL15/40/5; e) PCL15/40/10; f) PCL17/35/5; g) PCL18/30/10; h) PCL18/35/10.

of CO₂ from the surface of the sample upon depressurization [21] followed by shrinking and gas enclosure inside the bulk.

From Fig. 8a and b only slight changes in T_m can be observed with respect to the PCL sphere (pretreated at 105 °C). In some cases the melting temperature returns to the original value before pretreatment. A similar behaviour occurs for the crystallinity. In the first place a pretreatment at 105 °C results in decreasing crystallinity. Jenkins et al. [10] reported that an increased degree of crystallinity can be explained in terms of the increased segmental mobility associated with the plasticisation effect of scCO₂. However, explaining the influence of the rate of decompression will need further effort in future investigations.

Finally, Fig. 9 summarizes those cases that were analysed regarding crystallinity and foam properties for illustrating the obtained foam

morphologies which are referred to in Table 2. First of all, it becomes clear that treatment at 30 °C does not result in a foamy structure in spite of the high amount of scCO₂ dissolved in the polymer matrix. Bubble diameters in all other cases are within the scope of the envisaged scaffolds. Nevertheless, strong differences appear especially with respect to the size distribution. In case of a rapid expansion (10 bar/min) a wide size distribution appears that may even come out as bimodal. In the extreme case for very high gas loads (PCL15/40/10) bubbles in the order of mm appear next to the typical ones in the range of 300 µm. The high gas load and the explosive like expansion lead to coalescence of adjacent bubbles. The most homogeneous foams are obtained by expansion at moderate rates that are also reflected by the lowest material densities within the order of

0.35 g/cm³. The melting point of the material after treatment returns to its original value after obviously having been decreased during pressure exposure, thus being a reversible change.

5. Conclusions

In general, CO₂ sorption in PCL increases steadily with pressure whereas the diffusivity is merely a function of temperature. Swelling depends not only on the applied pressure but also on the state of the polymer. Having passed the melting point, the swelling effect of the applied scCO₂ appears to diminish. When decompressing, microfoaming occurs which enhances the rate of gas release compared to the sorption procedure. Changes in morphology and crystallinity occur as a consequence of the pressure treatment. Compared to the melting temperature at atmospheric pressure there is a dramatic reduction observed under pressure where melting occurs already at a temperature of 40 °C at 15 MPa. The objective of obtaining a homogeneous foam of bubble sizes in the range of several hundreds of microns is best obtained decompressing relatively slowly from conditions just above melting. This work forms the base for development of new functionalized materials by quantifying the effect of promising treatment methods on material properties as a function of operating conditions and will be continued in terms of impregnation of composites.

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