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Generation of Biocompatible PCL Foams by Supercritical Foaming

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In this work, polycaprolactone (PCL) foams were generated by a supercritical CO_2 (SC-CO_2) assisted process. These foams can find application in tissue engineering as scaffolds, which require specific biological and morphological properties. SC-CO_2 foaming process was carried out under different pressure and temperature conditions, in order to study the influence of these operating parameters on the final samples morphology. These polymeric foams were then analyzed by scanning electron microscope (FE-SEM) in order to observe their internal structure. The performed analyses showed the influence of pressure and temperature on the external shape and on the morphology of these polymeric foams, in particular on the pore size. Pressures of 100, 150, 200 and 250 bar and temperatures of 40 and 60°C were tested as operating variables. The PCL foams obtained at 40°C and 200 bar presented the lowest value of the average pores diameter (i.e., 85 ± 24 μm); this value was about 7 times lower than that of the foams produced operating at 40°C and 100 bar (622 ± 62 μm). These results confirmed the high versatility of the SC-CO_2 foaming that allowed to generate PCL foams with tunable morphological characteristics.

1. Introduction

Polymer foams are widely used in many engineering applications, such as medical devices, electronics, biotechnology, packaging, etc. (Wang et al., 2015). To obtain the desired polymeric product, numerous studies have been carried out to understand the mechanism and the foaming process: the physical and chemical structure of polymeric foams (biodegradable and non-biodegradable), in fact, can be well regulated by an appropriate selection of materials and by the optimization of the operating parameters. The foaming occurs when free gas molecules are converted into spherical bubbles and this generally happens when the surrounding conditions change rapidly to allow a regular response of the system (Lee et al., 2006).

The most common foaming technique uses a chemical agent that can be an organic or inorganic component, thermally unstable, which decomposes producing gaseous compounds after heating. However, this decomposition can cause the production of polluting gases (Reverchon et al., 2007a). For this reason, ecological techniques have been developed to perform this process, such as the use of supercritical CO_2 (SC-CO_2) (Reverchon et al., 2007b).

A supercritical fluid is defined as a substance for which both temperature and pressure are above the critical values (for CO_2, Tc= 31°C, Pc= 73.8 bar) (Marra et al., 2012; Baldino et al., 2017a; Baldino et al., 2017b; Sarno et al., 2016). The particular combination of the typical viscosity of a gas and the typical density of a liquid makes supercritical fluids excellent solvents for different applications, such as micronization (De Marco et al., 2015b), coprecipitation (Prosapio et al., 2016), aerogel formation (Baldino et al., 2016a). SC-CO_2 has been often used to generate polymeric porous materials by different techniques, such as gel drying (De Marco et al., 2015a), phase inversion (Baldino et al., 2016b), scaffolds formation (Cardea et al., 2014), electrospinning (Baldino et al., 2019), showing interesting advantages with respect to the traditional processes, such as low pollution, short processing times and high versatility.

Among these techniques, one of the most interesting is the supercritical foaming. The supercritical foaming process involves a large number of bubbles that grow near each other in a polymer/gas solution. The initial stage of gas bubble formation in a molten polymer matrix is called nucleation. To describe this phenomenon, the cell model can be used, which assumes that each bubble is surrounded by a viscoelastic fluid envelope.

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To grow, the energy possessed by a bubble must overcome the barrier of free energy. This barrier can be reduced by increasing the supersaturation of the solution, thus increasing the temperature or reducing the pressure, and this leads to a higher nucleation rate. SC-CO_2 assisted foaming process for the production of polymeric foams consists in the diffusion of CO_2 inside the system and the consequent dissolution within the polymeric matrix. The fluid, therefore, plastifies the polymer causing a sharp drop in the glass transition temperature (T_g) and the consequent softening of the material. Subsequently, the system is depressurised leading to a sudden drop in pressure and to a supersaturated state of the solution. At this point, the nucleation of the bubbles takes place and, then, the growth of pores. At the same time, with the CO_2 venting from the polymer, the T_g increases, so that the effect of the plasticization is weakened and the matrix vitrifies and, therefore, the growth of the pores is inhibited. When the vitrified polymer is too rigid to expand, the foaming is completed and the voids occupied by the gas bubbles are preserved, thus producing an expanded porous foam (Chen et al., 2016).

The specific interaction between SC-CO_2 and polymer molecules is an important parameter to determine the foaming behavior and, finally, the characteristics of the porous structure, such as porosity, average diameter, pore shape, interconnection between of them. For semi-crystalline polymers, the heterogeneous distribution of the polymer chains within the molecular structure, which ranges from a random conformation of chains in the amorphous region to a perfectly ordered structure in the crystalline region, significantly influences the interaction between the SC-CO_2 and the polymer. It has been shown, for example, that depending on the operating conditions (temperature, pressure, etc.), the melting temperature of a semi-crystalline polymer can be lowered to a value below the operating saturation temperature (Lian et al., 2006). This reduction in the melting temperature has a positive effect on the foaming process, since it allows a more uniform absorption inside the polymeric material (Salerno et al., 2014).

In this study, polycaprolactone (PCL) foaming process assisted by SC-CO_2 was performed, studying the effect of process parameters (pressure and temperature) on the final morphology of the samples. PCL is a semi-crystalline hydrophobic polyester with a low glass transition temperature (T_g), around -60°C, and melting temperature between 59 and 64°C. Thanks to its biocompatibility and biodegradability, it is widely used in the biomedical field, such as for scaffolds in tissue engineering applications.

2. Materials and methods

PCL was bought from Sigma-Aldrich (USA) with the following characteristics: pellet of about 3 mm with a Mn of 80000 g/mol. CO_2 (purity 99.9%) was bought by Morlando Group S.R.L. (Sant'Antimo, NA, Italy).

2.1 Foams production by SC-CO_2

Foams were prepared in a home-made laboratory apparatus already used for SC-CO_2 assisted processes (Reverchon et al., 2008), equipped with a 316 stainless steel high-pressure vessel (80 mL) where CO_2 contacted the sample in a single pass bed. The pellets of polymer were placed in the vessel that was then heated and filled with SC-CO_2 up to the desired pressure using a high pressure pump (Milton Roy – Milroyal B, France). The vessel was maintained at the desired temperature and pressure for the time of the experiment (4 h). At the end of this time, the vessel was depressurized in about 20 s opening a fast discharge valve.

Different pressures and temperatures were tested; in particular, pressures of 100, 150, 200 and 250 bar and temperatures of 40 and 60°C were selected as operating variables.

2.2 Foams characterizations

Foam samples were cryofractured using liquid nitrogen and subsequently coated with gold at 30 mA for 150 s (Auto Sputter Coater mod. 108 A, Stansted, UK). After this preparation procedure, samples were morphologically characterized using a scanning electron microscope (SEM mod. LEO420, Assing, Italy).

3. Results and discussion

The PCL foams obtained by the experiments performed in this work using a SC-CO_2 assisted foaming process, at different pressure and temperature conditions, were compared in terms of morphological characteristics. In particular, it was observed how the variation of pressure and temperature influenced the final internal structure and morphology of these polymeric foams.

The effect of the pressure on the foams morphology was studied keeping the other process variables constant (temperature, time of experiment, time of depressurization).

Comparing the PCL foams obtained by SC-CO_2 foaming, performed at 40°C (figure 1), it was observed that the pressure increase caused an evident decrease in the average diameter of the pores characterizing the polymeric foams; these results are shown in figure 2. Moreover, working at larger pressures, the pores appeared to be more regular and regularly distributed within the structure.

The lowest value of the average pores diameter was obtained using a pressure of 200 bar as the operating variable and it was equal to 85 ± 24 μm (figure 1c). This value of the average pores diameter was about 7 times lower than that obtained for the samples processed at 100 bar (figure 1a), equal to 622 ± 62 μm. However, the samples processed at 250 bar were characterized by pores with a more regular shape within the polymeric structure.

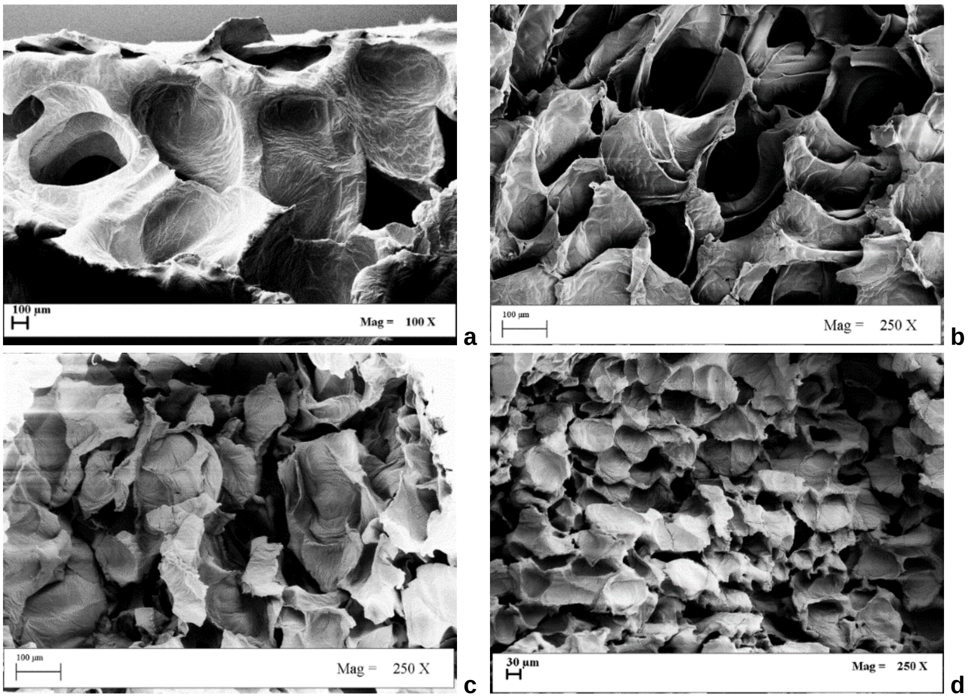

Figure 1: SEM images of PCL foams obtained at 40°C and a) 100 bar, b) 150 bar, c) 200 bar, d) 250 bar.

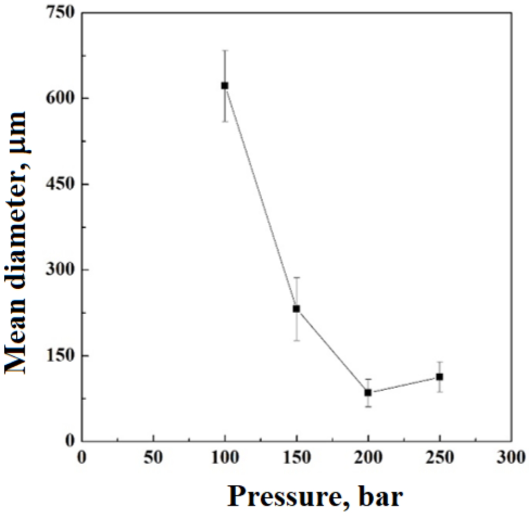

Figure 2: Effect of operative pressure on pore size of PCL foams produced at 40°C.

Comparing the samples obtained by SC-CO_2 foaming performed at a temperature of 60°C (figure 3), it was observed that also in this case the pressure had a high influence on the final morphology of the polymeric foam. The smaller average pores diameter was obtained by carrying out the process at 250 bar (figure 3d), and was equal to 131 ± 36 μm (figure 4). Therefore, also in this case, the pressure increase led to the production of foams characterized by pores with a lower average diameter, which also were more regular than the one observed in the samples produced at lower pressure. Furthermore, the PCL samples processed at larger pressures also presented an improved pores distribution within the internal structure.

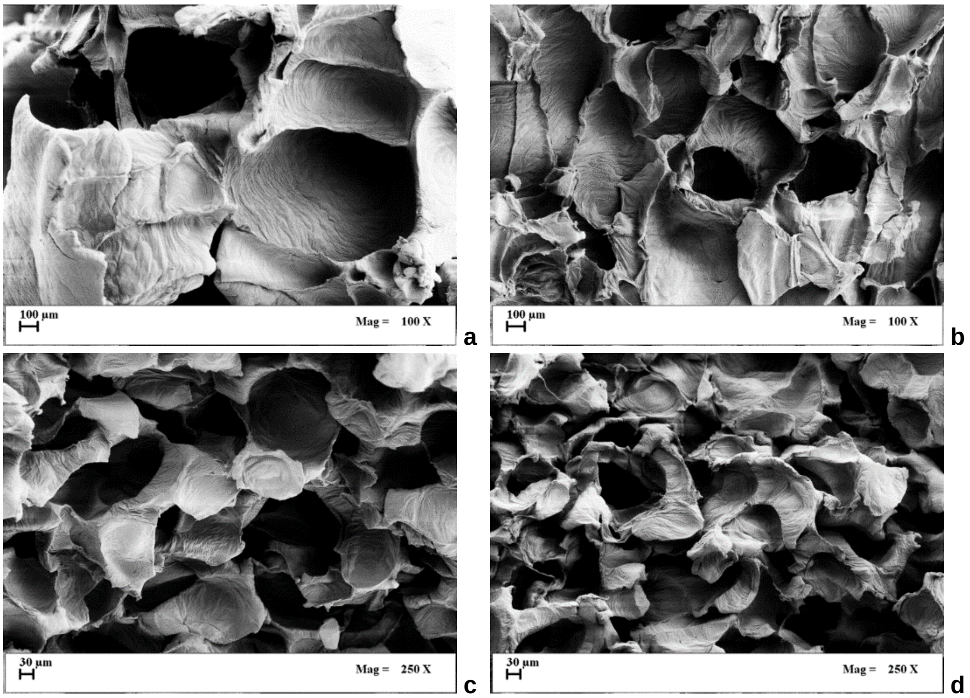

Figure 3: SEM images of PCL foams obtained at 60°C and a) 100 bar, b) 150 bar, c) 200 bar, d) 250 bar.

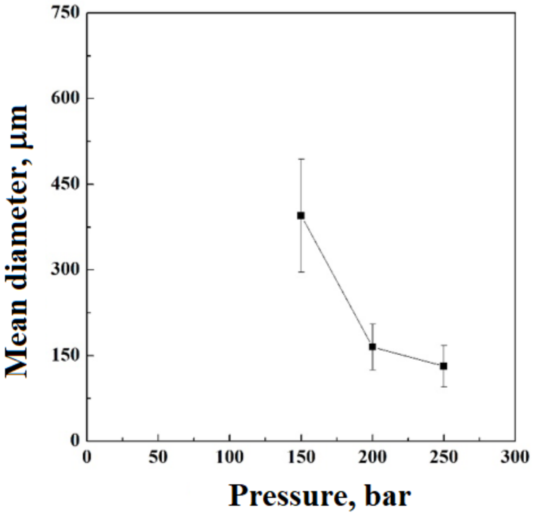

Figure 4: Effect of operative pressure on pore size of PCL foams obtained at 60°C.

Subsequently, the effect of temperature on the final morphology of the polymeric foams obtained by SC-CO_2 process was analysed. Various tests were carried out varying temperature and maintaining the other operating parameters constant. For example, comparing the samples obtained at a pressure of 250 bar (figure 5), the increase in temperature (from 40 to 60°C) led to a considerable increase in the average diameter of the pores of the produced foams. This trend is well evidenced in figure 6 and was found for each pressure tested (100, 150 and 200 bar). In particular, increasing the temperature from 40 to 60°C, the pore size increase from 113 ± 26 µm to 131 ± 36 µm.

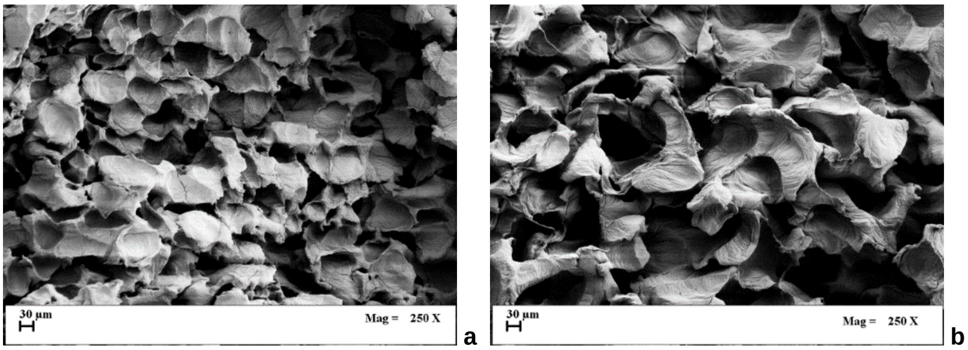

Figure 5: SEM images of PCL foams obtained at 250 bar and a) 40°C, b) 60°C.

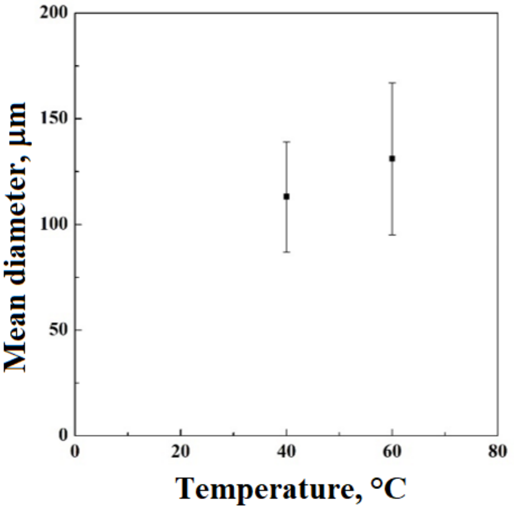

Figure 6: Effect of operative temperature on pore size of PCL foams obtained at 250 bar.

These results can be explained referring to the theory of bubble nucleation within a polymeric matrix. This theory concerns the formation of a dispersed phase within a metastable phase. In the case of the SC-CO_2 assisted foaming process, nucleation is homogeneous, since the cells are generated within a single phase. This nucleation is closely linked to energy activation and leads to the formation of nuclei, which can grow to their critical size, becoming pores, or collapsing. In SC-CO_2 assisted foaming, nucleation is caused by depressurization, which leads to a thermodynamic instability in the system. The number of pores that are formed and their size depend on the activation energy of the nucleation: the lower is the energy, the greater is the amount of CO_2 absorbed, and, consequently, the greater is the density of the formed pores.

The effect of pressure on the SC-CO_2 foaming process also depends on the solubility of CO_2 inside the polymer: at higher pressures, the solubility is greater, therefore a larger amount of CO_2 is absorbed. As the pressure increases, there will be an increase in the number of pores inside the produced foam. Furthermore, the increase in pressure causes a decrease in the diffusivity of CO_2 within the polymeric matrix and this leads to the formation of smaller pores.

The temperature increase, on the other hand, causes an increase in the diffusivity of CO_2 inside the polymer and a decrease in the viscosity of the material, hence a greater mobility of the polymer chains. Both phenomena cause an increase in the nuclei growth rate and, consequently, the formation of larger pores.

4. Conclusions

In this work, PCL foams were produced by a foaming process assisted by SC-CO_2. SEM analyses allowed to observe the internal structure of these foams. The comparison between the results obtained highlighted the influence of the process variables on the final polymeric samples morphology. Firstly, it was observed that the pressure had a high influence on the pores shape and size: the larger was the pressure used, the lower was the average pores diameter. The temperature increase caused the formation of larger and more irregular pores inside the structure. Therefore, to obtain samples having a lower value of the average pores diameter, the process was carried out using a temperature of 40°C and a pressure of 200 bar. Operating in this manner, the produced PCL foams had pores with an average diameter equal to 85 ± 24 μm.

Finally, thanks to these results, it can be concluded that, by varying the operative parameters, the SC-CO_2 foaming process can be optimized in order to obtain polymeric foams with the desired morphological characteristics.

In the future, tests will be carried out at different depressurization time, in order to assess the influence of this operative variable on the final foam structure. Furthermore, other analyses will be performed to verify the interconnection among pores and also mechanical properties of these foams will be determined, in order to ascertain if these samples are suitable for specific biomedical applications.

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