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Polycaprolactone foams prepared by supercritical CO_2 batch foaming of polymer/organic solvent solutions

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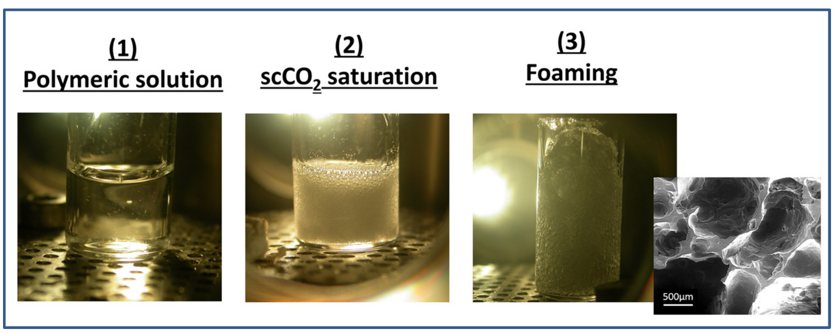
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the batch foaming of polymeric solutions by means of supercritical CO_2 ($scCO_2$) is described. The developed process combines the advantages of processing materials from solution in organic solvents and $scCO_2$ batch foaming to prepare foams with uniform and controllable porosity. Polycaprolactone (PCL) was selected as semi-crystalline polymer as a case study and foams from solutions in different $scCO_2$-miscible organic solvents, namely ethyl acetate, chloroform, dioxane and dimethyl sulfoxide, were prepared.

Obtained results demonstrate that processing PCL solutions by means of $scCO_2$ batch foaming enables preparing solid polymeric foams with solvent residue close to 1 wt. %, density values in the 0.2–0.5 g/cm^3 range, hundreds of microns pore size and pore walls with spherulitic morphology. The advantage of this process is herein demonstrated by the fabrication of composite PCL foams containing 30 w% of either inorganic TiO_2 nanoparticles and 5-fluorouracil chemotherapeutic by processing polymeric solutions in a single step.

1. Introduction

Polymeric foams are essential elements of our life for applications requiring light-weight materials coupled with energy absorption capability and mass transfer control. The widespread use of these materials spans from acoustic and thermal insulation, cushioning and medical devices for cell transplantation and controlled drug delivery [1–3]. Furthermore, composite foams prepared by blending polymers and additives allow manufacturing porous materials with enhanced mechanical strength, thermal degradation stability and biocompatibility [4].

Among the different polymeric foams fabrication processes, those based on supercritical CO_2 ($scCO_2$) are undoubtedly advantageous and were widely investigated in the past decades by several groups [2–11].

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Table 1
Physical-chemical properties of organic solvents used for the preparation of PCL foams.

Compound	Density [g/cm^3]	Boiling point [ºC]	Dielectric constant ε	Hansen solubility parameters [(J cm^{-3})$^{1/2}$]					
				δ_d	δ_p	δ_h	δ_T	Distance-to-PCL	Distance-to-CO_2
Ethyl acetate (EA) [20]	0.902	77.1	6.1	15.8	5.3	7.2	18.1	2.7	1.4
Chloroform (CL) [21]	1.49	61.1	4.1	17.8	3.1	5.7	18.9	3.5	4.9
Dioxane (DX) [21]	1.03	101.1	2.2	17.5	1.8	9	19.8	3.2	6
Dimethyl sulfoxide (DS) [20]	1.1	189	46.7	18.4	16.4	10.2	26.7	12.1	13.3
PCL [20]	1.145	/	/	17	4.8	8.3	20.4	/	/
CO_2 [22]	/			15.6	5.2	5.8	17.4	/	/

δ_d = nonpolar atomic interactions; δ_p = dipole-dipole interactions; δ_h = the hydrogen bonding interactions.

Indeed, CO_2 is eco-friendly and non-flammable, whereas $scCO_2$ is obtainable at moderate critical temperature and pressure. The combination of $scCO_2$ gas-like viscosity and liquid-like density made this compound usable as a solvent, antisolvent or solute, e.g., plasticizer in polymer foaming. Taking advantage of these properties, $scCO_2$ represents, nowadays, the paramount compressed fluid for preparing polymeric foams with nano- and/or micrometric size pores in both batch and continuous processes.

Traditional foaming techniques are based on the high pressure processing of solid polymeric materials in the form of granules, films or disks [2–4,6,7]. In a typical batch foaming experiment, the solid material is placed inside a high pressure vessel and saturated with $scCO_2$ followed by pressure quench, which cause polymer crystallization and pores setting. This preparation approach requires proper combination of saturation temperature, pressure and time. Most importantly, in the case of semi-crystalline polymers, during saturation the temperature-pressure pair of experimental parameters must be sufficiently high to plasticize the polymer and eventually melt the crystalline structure to promote polymer foaming. For example, it was demonstrated that $scCO_2$ processing of polycaprolactone (PCL) at pressure higher than 10 MPa induces the melting temperature depression from about 60 °C down to 35 °C [7,12]. However, there is the evidence that the thermal history and therefore the crystalline structure of PCL affected the final foams properties even at temperature higher than 35 °C [13]. Furthermore, the incorporation of additives and fillers into the final foams often requires an additional melt compounding step before foaming process with the consequent increase of production times [4,8,9,13].

$ScCO_2$ has also been used as antisolvent for membranes formation by means of phase inversion and solvent extraction [14–16]. In a typical process, the polymer was dissolved in a CO_2-miscible organic solvent and the solution was subsequently put in contact with a $scCO_2$ stream to progressively induce solvent extraction, polymer precipitation and membrane drying. The $scCO_2$-antisolvent approach allowed overcoming limitations related to liquid-vapour interface and pore collapse during drying, as well as the need of using high operating temperatures. This process was very useful for preparing flat membranes. However, the attempt of increasing sample thickness, up to a millimetre or more, was detrimental due to the formation of $scCO_2$ concentration gradients that may lead to inhomogeneous foams [17]. Another limitation of $scCO_2$ antisolvent precipitation was related to the difficulty of achieving large pores, several hundreds of microns in size, and the fine control of pores interconnectivity. These issues were solved in part by adding a solid porogen to the polymeric solution or by controlling the depressurization rate after drying [14,18,19].

Herein, the batch foaming of polymeric solutions by means of $scCO_2$ as a blowing agent is presented as a possible alternative approach to solid-state foaming of semi-crystalline polymers. The approach developed in this work is novel, as it involves the preparation of polymeric solutions in organic solvents followed by $scCO_2$ batch processing and foaming in a single step. As shown in this work, the final foams properties can the tuned by the proper combination of polymeric solution formulation and $scCO_2$ operating conditions. Furthermore, the incorporation of additives can be optimized by the hydrophilic/hydrophobic nature of the organic solvent chosen or by the anti-solvent precipitation from solution, making also the process more versatile and less time consuming if compared to tradition melt-compounding processes.

The polymer used is PCL, which is a biodegradable polyester characterized by a high crystalline fraction (60%) and, for this reason, the processing of PCL in the solid form and at temperatures below melting is strongly affected by the crystalline structure [4,12,13]. Solvents used were ethyl acetate, chloroform, dioxane and dimethyl sulfoxide and the effect of $scCO_2$/solvent/polymer interactions and operating conditions on PCL foams formation was investigated. The chosen organic solvents are able to dissolve PCL and, concomitantly, are characterized by different chemical and physical properties, such as boiling point, dielectric constant and toxicity/sustainability. These aspects are very important to demonstrate the versatility of the developed foaming approach also for the fabrication of composite foams. This aspect was finally evidenced in this work by the fabrication of composite PCL foams loaded with silanized TiO_2 nanoparticles starting from solution in chloroform, as this solvent enabled an appropriate particles dispersion, as well as loading the foams with 5-fluorouracil from solution in dimethyl sulfoxide, as this solvent enabled the dissolution of high drug concentration.

2. Experimental

2.1. Materials

Polycaprolactone (PCL, Mn = 45 KDa), chloroform (CL), dioxane (DX), dimethyl sulfoxide (DS) and 5-fluorouracil were provided by Sigma-Aldrich (Madrid, Spain). Ethyl acetate (EA) was provided by Panreac (Barcelona, Spain). The used solvents and their main properties are listed in Table 1. Silanized titanium dioxide (Aeroxide® TiO_2 T805 coated with octylsilane) spheroidal nanoparticles, with an average