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Biopolymeric Porous Structures Obtained by Supercritical Fluids Assisted Processes

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In the last years, biolpolymeric porous structures have acquired an increasing importance in different fields of engineering, ranging from chemical engineering to tissue engineering. Until now, various processes have been implemented for the generation of porous structures, but they are all characterized by several limits, such as long processing times, traces of organic solvents in the final products, low versatility, etc. In this work, we tested a green process assisted by supercritical fluids for the generation of biopolymeric porous structures: the supercritical phase inversion process. We processed different biopolymers such as Polysulfone, Polymethylmethacrylate and Polyvinyl alcohol, and analyzed the effect of process parameters (pressure, temperature, polymer concentration, kind of solvents) on the final morphology. The results confirmed the advantages of the supercritical fluids assisted process with respect to the traditional ones: indeed, dry porous structures were obtained in few hours; moreover, changing the parameters, it was possible to control the kind of structures obtained (from cellular one to bicontinuous) and the size of the pores and porosity (from 70 to 90%); finally, the structures were characterized by residual solvents amount lower than 5 ppm.

1. Introduction

In recent years, the attention for biopolymeric polymers is largely increasing for different applications such as pharmaceuticals, tissue engineering, food, biomedical, etc. Indeed, the peculiarities of these polymers make them particularly important and performing. One of the most common way to use biopolymers is as porous structures. Indeed, they can be used in different processes such as filtration, controlled release, impregnation, etc. (Ambekar and Kandasubramanian, 2019).

Various processes have been implemented for the generation of porous structures such as phase inversion, electrospinning, foaming, 3D printing, etc., but they are all characterized by several limits, such as long processing times, traces of organic solvents in the final products, low versatility, etc. (Cardea et al., 2006). For these reasons, supercritical fluids assisted processes have been implemented. Supercritical fluids are fluids operating over their critical point; for example, carbon dioxide, when it is used over about 31°C and 73 bar is at supercritical conditions and presents very interesting peculiarities such as high solvent power, high diffusivity and low viscosity; moreover, carbon dioxide is cheap and not polluting (Prosapio et al., 2016). So, the use of supercritical carbon dioxide for the generation of porous biopolymers has been recently studied and largely developed.

Different processes have been proposed using supercritical carbon dioxide:

- Supercritical foaming (Di Maio and Kiran, 2018)
- Supercritical phase inversion (Cardea et al., 2006)
- Supercritical electrospinning (Baldino et al., 2019)
- Supercritical gel drying (Baldino et al., 2015)
- Supercritical impregnation (Caputo et al. 2010)

Among these techniques, in this work we focused our attention on supercritical phase inversion process. This process consists of the contact between a polymeric solution and supercritical carbon dioxide. During this contact, the supercritical carbon dioxide acts as an anti-solvent with respect to the polymer, a ternary solution is formed, and a phase separation occurs. Depending on the kind and shape of demixing gap of the ternary system (polymer-solvent-supercritical carbon dioxide) and on the process parameters, it is possible to obtain

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different porous morphologies, ranging from dense film, to cellular structures, to bicontinuos structures to microparticles (Cardea et al., 2014). Moreover, the intrinsic advantages of the supercritical phase inversion, with respect to the traditional process, is the high versatility due to the peculiarities of supercritical carbon dioxide that can be modulated by changing the process parameters (Baldino et al., 2017). Moreover, it is also possible to generate loaded porous structures, adding a solute (i.e. a drug, a vitamin, a grow factor, etc.) in the starting polymeric solutions (Cardea et al., 2018).The main process parameters of the supercritical phase inversion process are: polymer concentration, kind of solvent, temperature, pressure and time.

Polymer concentration is the most important parameters because affects the solution viscosity and the entry point in the ternary diagram during the phase inversion. The kind of solvent used for the generation of polymeric solution influences the final structure because has effect on the demixing gap (size and shape) in the ternary system. Temperature and pressure affect the supercritical carbon dioxide density and diffusivities; moreover, density is directly proportional to solvent power. So, increasing pressure and decreasing temperature, it is possible to increase the supercritical carbon dioxide solvent power and decrease its diffusivity. On the other hand, increasing temperature and decreasing pressure, it is possible to increase the diffusivity and decrease the solvent power. The diffusivity and the solvent power of the non-solvent (i.e, supercritical carbon dioxide) in the supercritical phase inversion process largely affect the final morphology of the porous structures. Indeed, they influence the phase separation rate, the mechanism of demixing occurring and also the shape and the size of the demixing gap in the ternary system. The time of the experiments mainly affects the residual solvent amount: usually, 5 hours are sufficient for completely eliminate the solvents.

In this paper, we focused our attention on three different polymers processed by supercritical phase inversion:

- Polysulfone (PSU)
- Polymethylmethacrylate (PMMA)
- Polyvinyl alcohol (PVA).

Polysulfones are a family of high-performance thermoplastics. These polymers are known for their toughness and stability at high temperatures. Due to the high cost of raw materials and processing, polysulfones are used in specialty applications and often are a superior replacement for polycarbonates, for example in processes of dialysis.

Polymethylmethacrylate is a transparent thermoplastic often used in sheet form as a lightweight or shatter-resistant alternative to glass. The same material can be used as a casting resin or in inks and coatings, among many other uses. It is an economical alternative to polycarbonate when tensile strength, flexural strength, transparency and UV tolerance are more important than impact strength, chemical resistance, and heat resistance. Additionally, it does not contain the potentially harmful bisphenol-A. It is often preferred because of its moderate properties, easy handling and processing, and low cost.

Polyvinyl alcohol is a water-soluble synthetic polymer. It is used in papermaking, textile warp sizing, as a thickener and emulsion stabilizer in adhesive formulations and a variety of coatings. It is colourless and odorless. It is commonly supplied as beads or as solutions in water. It is used in a variety of medical applications because of its biocompatibility, low tendency for protein adhesion, and low toxicity. Specific uses include cartilage replacements, contact lenses and eye drops.

Supercritical phase inversion process has been tested on these polymers; in this study a selection of the effect of some the process parameters on the final morphology of the porous structures has been reported.

2. Materials and Methods

2.1 Materials

Polysulfone, Polymethylmethacrylate and Polyvinyl alcohol and the different solvents used (Acetone, N-Methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO)) were bought by Sigma-Aldrich. CO_2 (99.9% purity) was purchased from Morlando Group s.r.l. (Sant'Antimo NA, Italy).

2.2 Porous structures preparation

Supercritical phase inversion apparatus and methodology were already described elsewhere (Reverchon et al., 2007). Basically, solutions of polymer at different polymer concentration (ranging from 5 to 50% w/w) in different solvents were prepared. The prepared solutions were subsequently placed in a cap that was put inside a home-made high pressure vessel, that was filled with CO_2 up to a pressure ranging between 100 and 250 bar by a high-pressure pump (Milton Roy – France). After that, the vessel was heated up to a temperature ranging between 35 and 55 °C. These conditions were kept for 5 hours and then the system was slowly depressurized. Finally, the vessel was opened and the cap with the processed material was recovered (Reverchon et al., 2008).

2.3 Porous structures characterization

Porous structures were fractured in liquid nitrogen and coated with gold using a sputter coater (Agar Auto Sputter Coater mod. 108 A, Stansted, UK) at 40 mA for 120 s; then, structures morphology was observed by a field emission scanning electron microscope, FESEM (mod. LEO 1525, Carl Zeiss SMT AG, Oberkochen, Germany).

Mean diameter, standard deviation and pore size distributions (PSDs) were measured by an image analysis software (Sigma Scan Pro 5.0, Aspire Software International Ashburn, VA) using FESEM images. The elaboration of PSDs was carried out using Microcal Origin Software (release 8.0, Microcal Software, Inc., Northampton, MA) on about 300 pores.

3. Results and discussion

The first polymer on which we focused our attention is the PMMA. We prepared solution of PMMA in Aceton at different polymer concentration (from 5 to 50% w/w) and analysed the effect of polymer concentration on porous structures surface and internal section.

The experiments were carried out at 200 bar and 35°C. Regarding the surface, the sample with a polymer concentration of 5% w/w (Figure 1a) partially precipitated forming a thin interconnected structure; this phenomenon is probably due to the fact that, at low polymer concentrations in the initial solution, the carbon dioxide-driven process is very fast, and the low quantity of polymer present is not sufficient to form a solid and compact structure. For the samples with a percentage of polymer higher than 5% w/w (Figure 1b, 1c, 1d), completely smooth surfaces were generated.

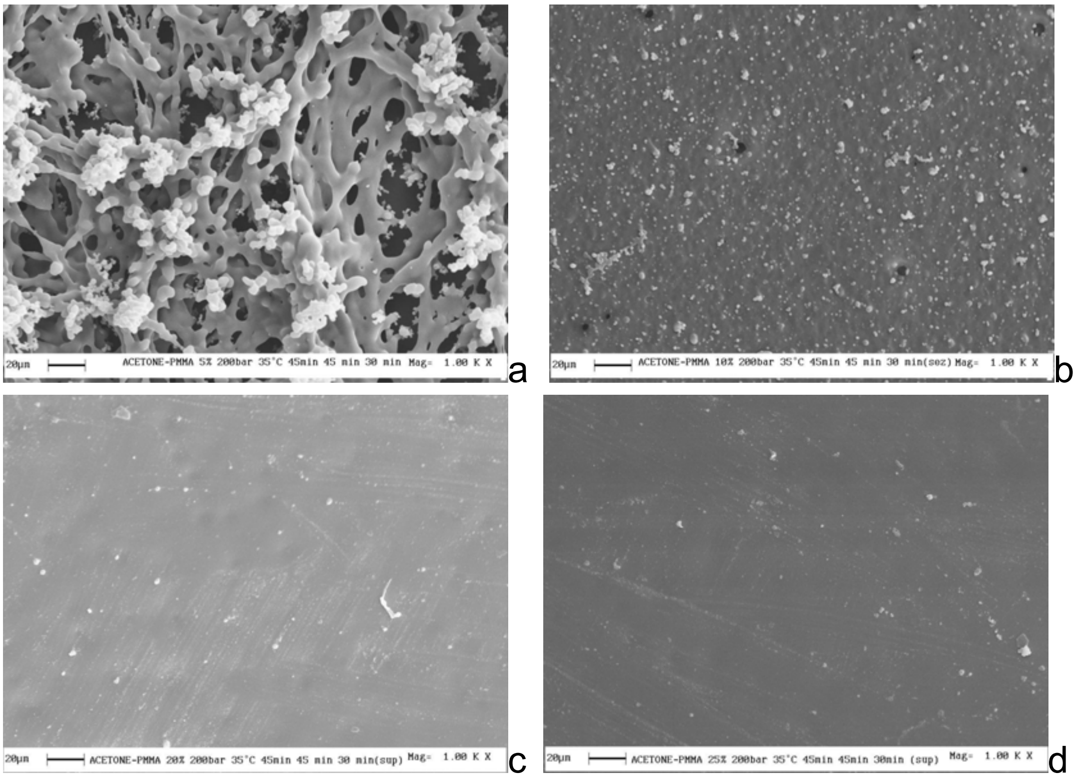

Figure 1. SEM images of PMMA surfaces obtained at 200 bar and 35°C, at different polymer concentration: a) 5% w/w, b) 10% w/w, c) 25% w/w, d) 50% w/w (scale bars = 20 μm*).*

Regarding the internal section, except for the sample at 5% w/w, porous and homogeneous cellular structures were produced. The pore size distribution varied according to the polymer concentration in the initial solution as shown in the images in Figure 2 and by the distribution in Figure 3: increasing the polymer concentration, the pores size increases too.

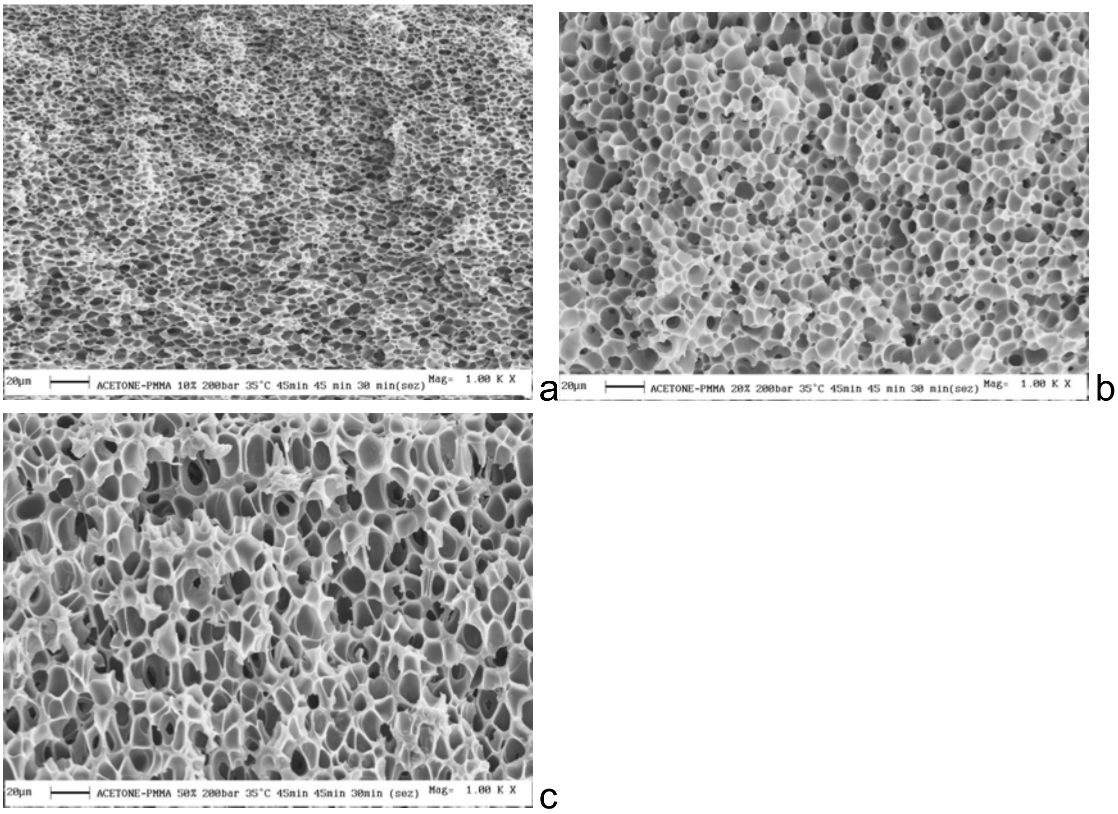

Figure 2. SEM images of PMMA internal section obtained at 200 bar and 35°C, at different polymer concentration: a) 10% w/w, b) 20% w/w, c) 50% w/w (scale bars = 20 µm).

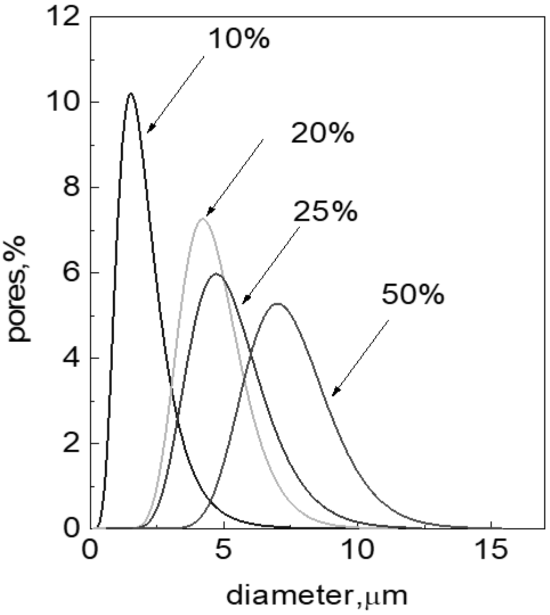

Figure 3. Pore size distribution of PMMA porous structures obtained at 200 bar and 35°C and at different polymer concentration.

The decrease of mean pore size from about 7.5 to about 2 µm, when the polymer concentration decreases from 50 to 10% w/w, can be explained considering that, an increase of polymer concentration leads to an increase of system viscosity during the phase separation. For this reason, when the viscosity is higher, the process is slower (the supercritical carbon dioxide diffuses inside the solution in a more difficult way), and the pores have more time to grow.

Similar results were obtained in the case of Polysulfone. In particular, increasing the polymer concentration from 5 to 30% w/w, cellular structures were obtained and mean pores size increased from about 4 to 25 µm.

Subsequently, we focused our attention on PVA structures. In particular, we analyzed the effect of solvent used for the formulation of the polymeric solution. We tested PVA solutions prepared with DMSO and NMP. The comparison between experiments carried out in DMSO and in NMP with a solution of 15% w/w of polymer at 100 bar and 35°C is reported below (Figure 4).

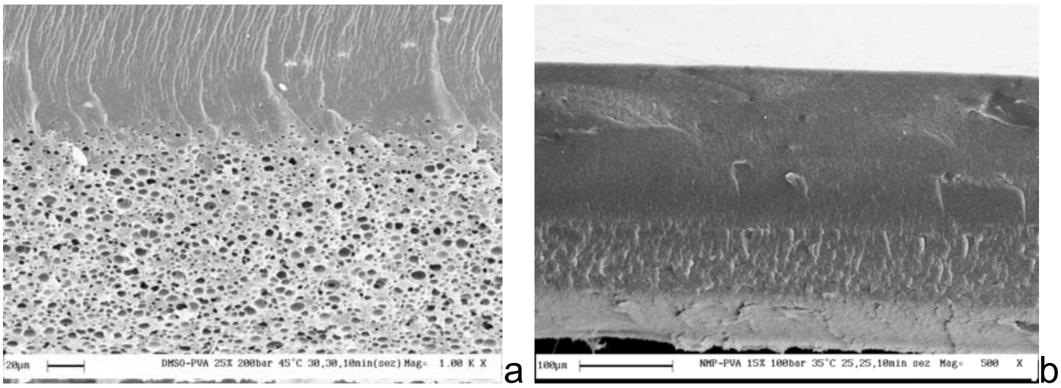

Figure 4: SEM images of sample sections at 15% w/w in polymer at 100 bar and 35°C: a) PVA-DMSO (scale bars = 20 µm), b) PVA-NMP (scale bars = 100 µm).

The PVA structures obtained starting from PVA-DMSO were characterized by porous cellular structure with dense skin (Figure 4a). On the other hand, starting from PVA solutions in NPM, structures without pores were generated (Figure 4b), i.e., dense film; this is an indication of the fact that the ternary solution did not entered in the miscibility gap during the process. Probably, during the diffusion of carbon dioxide, a direct accumulation of polymer occurred. This also happened with the other concentrations and with the other experimental conditions tested, excluding the 5% w/w concentration in NMP, for which a spinodal structure was obtained. This result is shown in the qualitative ternary diagram reported in Figure 5. For solutions more concentrated than 5% w/w in NMP, with the diffusion of carbon dioxide into the solution, the ternary system concentration does not enter in the binodal curve, but goes towards a "gelation/vetrification" zone where the direct accumulation of the polymer occurs; i.e., dense film formation.

For all the polymers tested, residual solvents amount was lower than 5 ppm.

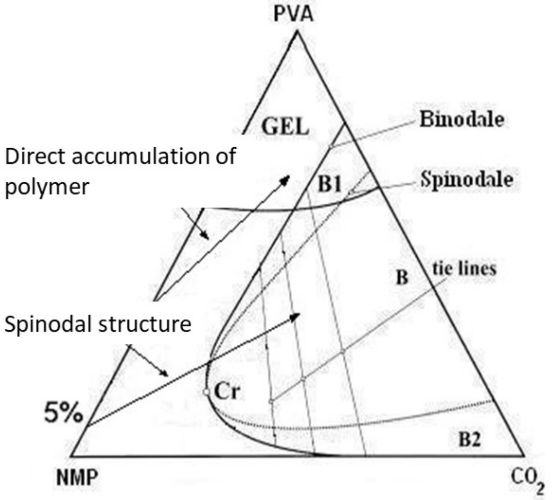

Figure 5: Qualitative ternary diagram: PVA-NMP-CO_2.

4. Conclusions

The supercritical phase inversion process confirmed to be a valid alternative for the generation of biopolymeric porous structures. Moreover, it showed a high versatility by changing the main process parameters; in this way it is possible to generate structures with different morphologies.

References

Ambekar R.S., Kandasubramanian B., 2019, Progress in the Advancement of Porous Biopolymer Scaffold: Tissue Engineering Application, Ind. Eng. Chem. Res., 58, 16, 6163–6194.

Baldino L., Cardea S., Reverchon E. 2015, Natural aerogels production by supercritical gel drying. Chemical Engineering Transactions, 43, pp. 739–744.

Baldino L., Cardea S., Reverchon E. 2017, Biodegradable membranes loaded with curcumin to be used as engineered independent devices in active packaging. Journal of the Taiwan Institute of Chemical Engineers, 71, 518–526.

Baldino L., Cardea S., Reverchon E. 2019, A supercritical CO_2 assisted electrohydrodynamic process used to produce microparticles and microfibers of a model polymer. Journal of CO2 Utilization, , 33, pp. 532–540.

Caputo G., De Marco I., Reverchon E., 2010, Silica aerogel-metal composites produced by supercritical adsorption, Journal of Supercritical Fluids, 54(2), 243-249.

Cardea S., Gugliuzza A., Schiavo Rappo E., Aceto M., Drioli E., Reverchon E., 2006, Generation of PEEK-WC membranes by supercritical fluids, Desalination, 200(1-3), 58-60.

Cardea S., Baldino L., Scognamiglio M., Reverchon E., 2014, 3D PLLA/Ibuprofen composite scaffolds obtained by a supercritical fluids assisted process, Journal of Materials Science: Materials in Medicine, 25(4), 989-998.

Cardea S., Baldino L., Reverchon E. 2018, Comparative study of PVDF-HFP-curcumin porous structures produced by supercritical assisted processes. Journal of Supercritical Fluids, 133, 270–277.

Di Maio E., Kiran E., 2018, Foaming of polymers with supercritical fluids and perspectives on the current knowledge gaps and challenges, Journal of Supercritical Fluids, 134, 157-166

Prosapio V., Reverchon E., De Marco, I., 2016, Formation of PVP/nimesulide microspheres by supercritical antisolvent coprecipitation, Journal of Supercritical Fluids, 118, 19-26.

Reverchon E., Cardea S., Rapuano, C., 2007, Formation of poly-vinyl-alcohol structures by supercritical CO_2, Journal of Applied Polymer Science, 104, 3151-3160.

Reverchon E., Cardea S., Schiavo Rappo, E., 2008, Membranes formation of a hydrosoluble biopolymer (PVA) using a supercritical CO_2-expanded liquid, Journal of Supercritical Fluids, 45, 356-364.