Preparation of Porous Poly(L-Lactic acid)-co-(Trimethylene-Carbonate) Structures using Supercritical CO2 as Antisolvent and as Foaming Agent

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ABSTRACT SUMMARY:

Porous structures of poly(L-Lactic acid)-*co*-(Tri-Methylene-Carbonate) -PLLA-*co*-TMC- were successfully fabricated using two experimental methods, i.e. using supercritical CO_2 as antisolvent and as foaming agent through the pressure induced phase separation technique. Considering the phase inversion method, the effect of the initial polymer concentration of the solution, pressure and temperature on the morphology of the final porous structure (pore size, porosity and cell density) was investigated. The L-L demixing process was suggested as the dominant mechanism for the phase separation and pore production. The temperature window, for which PLLA-*co*-TMC porous structures are successfully produced using the pressure induced phase separation technique, was determined at 150 bar and 210 bar. The effect of temperature on the final porous structure was investigated.

INTRODUCTION:

There are many techniques for the production of polymer porous structures and foams [1-2]. Two techniques using supercritical fluids are mainly used. In the first one CO_2 is used as a non-solvent (antisolvent), while in the second one as a foaming agent in temperature or pressure induced phase separation processes. Biopolymer based foams is an interesting class of cellular materials with many important applications. These include: packaging and insulation materials, controlled drug delivery applications and tissue engineering [3-4].

The production of porous structures consisting of flexible PLLA copolymers, by using CO_2 as antisolvent and as a foaming agent has not been thoroughly investigated. Most literature studies investigate the production of homopolymer PLLA porous structures using supercritical CO_2 as antisolvent or as a foaming agent.

In this work, porous structures consisting of poly(L-Lactic acid)-co-(Tri-Methylene-Carbonate) -PLLA-co-TMC- were prepared with two techniques, i.e. using supercritical CO_2 as antisolvent and as foaming agent. Regarding the former one, dichloromethane (DCM) was selected as solvent, since it is completely miscible with CO_2 at pressures higher than 100 bar at temperatures up to 55 ^oC. Additionally, the solubility of PLLA-co-TMC in CO_2 at these conditions is negligible, making the CO_2 an appropriate antisolvent for this system.

EXPERIMENTAL METHODS:

PLLA-*co*-TMC (Resomer LT 706) was obtained from Boehringer Ingelheim Pharma GmbH. & *Co*. KG. Dichloromethane (>99.9% purity) was purchased from Fluka Chemie GmbH and CO_2 from Air Liquide Mediterranee (>99.98% purity). All materials were used as received.

For the Scanning Electron Microscopy (SEM) observation, uniform cross-sections were produced by fracturing the porous samples in liquid nitrogen. Prior to morphological characterization with SEM (JEOL 6610 LV), the cross-sections were coated with gold (Quorum 150R S). The obtained SEM images were processed using image analysis software (ImageJ v1.48)

RESULTS AND DISCUSSION:

The effect of the initial polymer concentration (varying from 10 to 30% w/v) on the pore diameter was investigated at constant temperature (45 ^oC) and at various pressures from 130 to 210 bar. In Fig. 1 SEM photos of the porous samples derived from polymer solutions with initial polymer concentration a) 10%, b) 15%, c) 22%, d) 30% w/v, at 45 ^oC and 180 bar are illustrated. The porous structures that were produced starting from initial polymer concentration higher than 10% w/v exhibited relatively uniform porous structures. On the other hand, the samples that were produced from solutions with initial polymer concentration equal to 10 % w/v, and especially those prepared at the lowest pressure (130 bar), did not present so pronounced and uniform porous structure (see for example Fig. 1a).

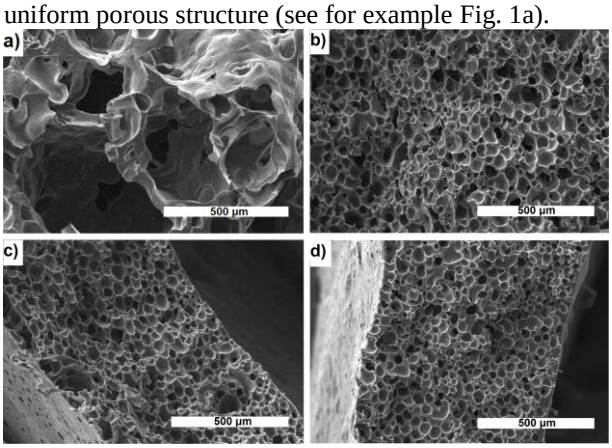

Fig 1: Porous samples obtained from polymer solutions with initial polymer concentration a)10%, b)15%, c)22%, d)30% w/v, at 45 ^oC and 180 bar.

The effect of pressure and temperature (in some selected initial polymer polymer concentration) temperature on the morphology of the final porous structure (pore size, porosity and cell density) will be presented and discussed.

Using the pressure induced phase separation (pressure quench) technique, foams with uniform structures can be produced from dense semicrystalline polymer samples in a foaming temperature window, below the neat polymer melting point Therefore, such foaming window was determined for PLLA-*co*-TMC at two different pressures 150 bar and 210 bar.

At the pressure of 150 bar, the temperature range of 110-160 ºC was investigated. The sample processed at 110 ºC was compact with no signs of foaming. The sample that was prepared at 160 ºC completely melted at equilibrium sorption conditions, and no signs of foaming were also observed, probably due to the collapse of the porous structure after the depressurization of the system. The foaming of the dense samples at the temperature range 120 – 150 ºC yielded uniform porous structures, which are shown in Fig. 2.

At the pressure of 210 bar, the temperature range of 50-140 ºC was examined. All samples processed at temperatures below 95 ºC were rather compact with no remarkable signs of foaming, while the sample processed at 95 ºC revealed localized and non-uniform pore formation. The samples processed at temperatures above 130 ºC were melted, and no clearly-shaped porous structures were formed. Rather uniform porous structures were obtained by dense sample foaming at 210 bar at the temperature range 110-130 ºC.

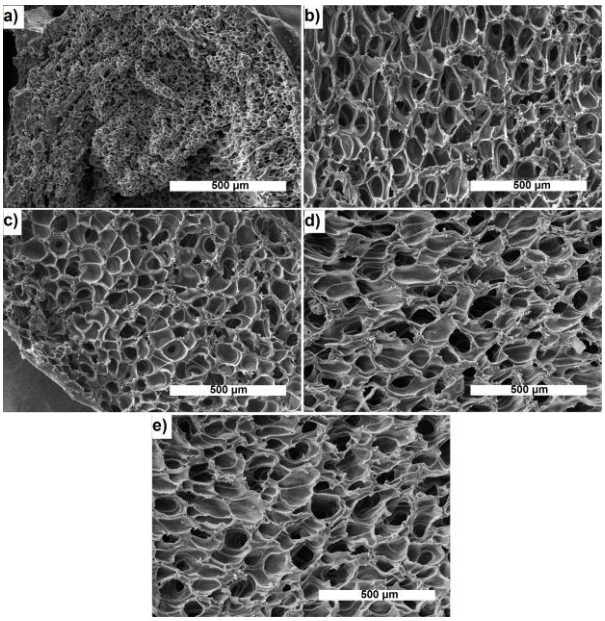

Fig 2: Porous samples produced with pressure induced phase separation method at 150 bar a) 120 ºC, b)130 ºC, c)140 ºC, d)145 ºC, d)145 ºC, e)150 ºC.

The effect of pressure and temperature (in some selected initial polymer polymer concentration) temperature on the morphology of the final porous structure (pore size, porosity and cell density) will be presented and discussed.

CONCLUSIONS:

Porous PLLA-*co*-TMC structures were successfully fabricated using two different supercritical CO_2 techniques. The foaming of PLLA-*co*-TMC using the pressure quench method is not applicable at temperatures far below the melting point (165.6 ºC) of the neat polymer. By using CO_2 as antisolvent, rather uniform porous structures (with pore size ranging from 24 to 190 μm) were produced in the temperature range of 35 to 65 ºC, within a relatively wide range of pressures and initial polymer concentrations. The effective fabrication of porous PLLA-*co*-TMC structures using such technique constitutes a promising alternative to encapsulate pharmaceutical substances into porous structures that can be used as scaffolds for tissue engineering applications.

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