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Solid-state foaming of biodegradable polyesters by means of supercritical CO_2/ethyl lactate mixtures: Towards designing advanced materials by means of sustainable processes

Aurelio Salerno *, Ugo Clerici, Concepción Domingo

Institute of Materials Science of Barcelona (ICMAB-CSIC), Campus de la UAB, Bellaterra 08193, Spain

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ABSTRACT

In this work, a clean and sustainable approach for the design and manufacture of biodegradable foams with controlled pore structures is reported. Porous polycaprolactone (PCL), polylactic acid (PLA) and poly(L-lactide/caprolactone) (PLC) homo- and co-polymers have been prepared by a supercritical solid-state foaming technique. The process has been carried out at low temperature, in the range of 35–40 °C, and at the pressure of 20 MPa. Supercritical CO_2 ($scCO_2$), pure or with a 0.2% molar fraction of ethyl lactate (EL), has been selected as the blowing agent. Foaming has been induced by a pressure quench approach and by using either a low (0.5 min) or a high (6 min) depressurization time. Results showed that blowing agent uptake and foaming was strongly affected by the thermal properties and crystalline structure of the polymers. Furthermore, adding a small amount of EL to $scCO_2$ decreased the plasticization temperature of the polymeric materials, finally improving foams uniformity and polymer foaming. Hence, homogeneous foams could be manufactured avoiding the use of toxic chemicals and at a temperature as low as 35 °C for PLA and PLC, and as low as 40 °C for the more crystalline PCL.

1. Introduction

The solid-state foaming of biodegradable polymers is a very powerful and sustainable approach to produce porous materials by means of environmentally friendly processes [1]. The physical and chemical structure of biodegradable polymeric foams can be fine tuned by the appropriate materials selection and by the optimization of the operating parameters. As a direct consequence, polymeric foams can be able to fulfill the desired performance for specific applications, such as energy or mass absorption and tissue engineering [2,3].

The solid-state foaming is a two steps process [1,4]. In the first step, the polymer is saturated with the blowing agent, which is typically supercritical CO_2 ($scCO_2$), at high pressure and at a temperature lower than the melting temperature of semi-crystalline polymers. Once saturation is completed, a controlled pressure quench provokes the formation of a supersaturated $scCO_2$/polymer solution and the nucleation and growth of pores inside the polymeric matrix.

Foaming of polymers with $scCO_2$ is advantageous in terms of both environmental concerns and foams design and manufacturing. Indeed, $scCO_2$ is non-toxic, non-flammable, chemically inert and inexpensive [5]. The sorption of even small amounts of CO_2 by polymers results in substantial changes in their physical properties, which dictate their processing and foaming characteristics. The important physical properties include viscosity, permeability, interfacial tension, and glass transition temperature [6]. Consequently, the optimization of the $scCO_2$ foaming process may open a wide range of opportunities for designing novel multi-functional materials and products for both industry and research fields.

* Corresponding author.
E-mail address: asalerno@icmab.es (A. Salerno).

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Biodegradable polyesters, such as polycaprolactone, polylactide and its co-polymer, are excellent candidate materials for foams fabrication. Indeed, these polymeric materials are synthesized starting from renewable resources and their biodegradation and mechanical properties can be easily controlled via polymer modification and blending [7]. Furthermore, foaming of polyesters can be carried out in order to design and fabricate biodegradable foams with a wide range of pore structures.

The specific interaction of $scCO_2$ with polymer molecules is an important parameter to determine the foaming behavior and, ultimately, foams pore structure features, such as porosity, mean pore size, pore shape and interconnectivity. For semi-crystalline polymers, including studied polyesters, the heterogeneous distribution of the polymeric chains in the polymer bulk, going from a random chain conformation in amorphous regions to highly ordered structures in crystalline domains, significantly affects $scCO_2$/polymer interaction. For example, it has been demonstrated that, depending on the operating conditions (e.g. temperature, pressure and time of saturation), the melting temperature of a semi-crystalline polymer can be depressed to a value down the operating saturation temperature [8]. This melting point depression has a positive effect in the solid-state foaming process, because allows for a more uniform sorption of $scCO_2$ inside the polymeric material. However, it is important to consider that CO_2 sorption enhances the free volume and mobility of the polymeric chains and, therefore, can induce the realignment of the chains in the amorphous region to a lower free energy crystalline structure [8–10]. Furthermore, polymer plasticization can be enhanced by the addition of proper plasticizer to $scCO_2$ to achieve a better control over foam fabrication [11].

In this work, a comparative investigation regarding the solid-state foaming of three different biodegradable polyesters, namely polycaprolactone (PCL), polylactic acid (PLA) and poly(L-lactide/caprolactone) (PLC), is reported. These polymers are of great interest in both industrial and research fields. The process has been carried out at low temperatures, in the range of 35–40 °C, at a saturation pressure of 20 MPa and using either $scCO_2$ or a binary mixture of $scCO_2$ and ethyl lactate (EL) as the blowing agent. EL, belonging to the lactate esters family, is an economically and environmentally friendly alternative to traditional organic toxic solvents [12,13]. The main aim of this work is to present a comparative study of the effects of adding EL to $scCO_2$ in the three studied polymers, related to an enhancement of foaming and an increase in the control of the pore structure features, as recently shown for binary mixtures of $scCO_2$/ethanol [14] and $scCO_2$/acetone [15,16]. The effect of blowing agent mixture composition, operating temperature and depressurization time on polymers foaming was assessed by means of scanning electron microscope (SEM) image analysis, density measurements and Image analysis, and the results were correlated to the thermal properties of the polymers and the extent of sorption of the blowing agent.

Table 1
Processing conditions used in the foaming tests.

Test number	EL molar fraction (%)	Temperature (°C)	Depressurization time (min)
1	0	35	0.5
2	0.2		
3	0	35	6
4	0.2		
5	0	40	0.5
6	0.2		
7	0	40	6
8	0.2		

2. Experimental

2.1. Materials

In this study, three different biodegradable polyesters, namely PCL (Sigma–Aldrich, Madrid, Spain), PLA and PLC with 70/30 L-lactide/caprolactone copolymer (Purac Biochem, Gorinchem, the Netherlands), in the granular form or as pellets, were used for foams preparation. Ethyl lactate (photoresist grade; purity ⩾ 99.0%) was provided by Sigma–Aldrich (Madrid, Spain) and used without further purification. CO_2 with a purity grade of 99.995 wt% was purchased from Carburos Metálicos S.A., Air Products Group (Barcelona, Spain).

2.2. Methods

2.2.1. Polymer pre-treatment

Samples for sorption measurements and foaming tests were first pre-treated by a compression molding process to prepare 1 mm-thick films. The process was performed using a heater (RCT basic, IKA, Staufen, Germany), settled at the temperature of 110 (PCL), 140 (PLC) or 210 °C (PLA), where the sample was placed and molded by applying a small pressure (0.1 MPa) for 5 min.

2.2.2. Thermal characterization of the polymers

Differential scanning calorimetric (DSC) analysis was performed to assess the thermal properties of the raw polymers. During measurements, the material was first

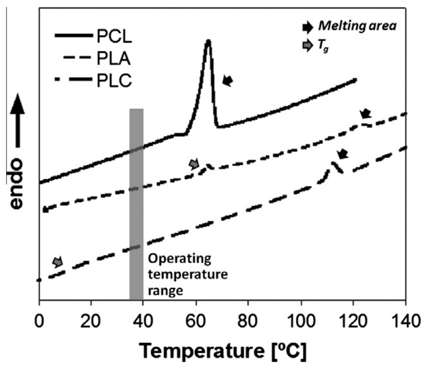

Fig. 1. DSC curves of the different studied polymers. The grey region indicates the temperature range used for the solid-state foaming of the polymers.