J. of Supercritical Fluids 88 (2014) 66–73

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Polycarbonate foams with tailor-made cellular structures by controlling the dissolution temperature in a two-step supercritical carbon dioxide foaming process

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ARTICLE INFO

Article history:
Received 5 November 2013
Received in revised form 21 January 2014
Accepted 22 January 2014
Available online 7 February 2014

Keywords:
Polycarbonate foams
Supercritical carbon dioxide
Two-step foaming
Tailor-made cellular structure
Physical aging

ABSTRACT

Closed-cell polycarbonate foams were prepared using a two-step foaming process, which consisted of the initial dissolution of supercritical CO_2 ($scCO_2$) into PC foaming precursors and their later expansion by heating using a double contact restriction method. The effects of the parameters of both CO_2 dissolution and heating stages on the cellular structure characteristics as well as on the physical aging of PC in the obtained foams were investigated. A higher amount of CO_2 was dissolved in PC with increasing the dissolution temperature from 80 to 100 °C, with similar CO_2 desorption trends and diffusion coefficients being found for both conditions. PC foams displayed an isotropic-like microcellular structure at a dissolution temperature of 80 °C. It was shown that it is possible to reduce their density while keeping their microcellular structure with increasing the heating time. On contrary, when dissolving CO_2 at 100 °C and later expanding, PC foams presented a cellular morphology with bigger cells and with an increasingly higher cell elongation in the vertical growth direction with increasing the heating time. Comparatively, PC foams obtained by dissolving CO_2 at 100 °C presented a more marked physical aging after CO_2 dissolution and foaming, although this effect could be reduced and ultimately suppressed with increasing the heating time.

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1. Introduction

The use of supercritical carbon dioxide ($scCO_2$) has become one of the most common strategies to prepare thermoplastic-based polymer foams. The processing conditions used in both gas dissolution and expansion stages play an essential role in the characteristics of the resulting foams, as for instance it is known that carbon dioxide acts as polymer plasticizer, decreasing its glass transition temperature [1]. As a result, the expansion is facilitated due to decreased polymer viscosity, easily leading to cell coalescence and as a consequence to an increase in cell size and a decrease in cell density [2].

The dissolution of $scCO_2$ into polymers and later expansion is commonly done in one [3] or two stages [4], in this last case the first stage corresponding to CO_2 dissolution into the polymer and the second one to its expansion. Particularly, polycarbonate (PC) foams have been prepared inside high pressure vessels using $scCO_2$ and one-step or two-step expansion [5,6]. In the case of two-step foaming, the expansion stage is done either inside the same vessel used to initially dissolve the carbon dioxide or in oil baths in order to foam the gas-saturated samples obtained at the end of the dissolution stage [7–9]. Two-step foaming has been shown to present the advantage of effectively separating cell nucleation from cell growth, ultimately leading to the formation of foams with a wide range of foam densities and a microcellular core structure with cell nucleation densities in the order of 10^9 cells/cm^3. Likewise, CO_2 dissolution during the first step enables to reduce the temperature required to nucleate and grow the cells, as CO_2 has a plasticizing effect on the polymer, significantly reducing its glass transition temperature, thus enabling for a better control of the developed cellular morphology (smaller and more isotropic-like cells) and, as a result, of the physical properties of the foamed materials [9].

In amorphous polymers such as PC cooled below their glass transition temperature, as happens during CO_2 dissolution in a foaming process, the molecules can be frozen-in at a non-equilibrium state, with later annealing resulting in an enthalpy relaxation towards an equilibrium state, resulting in changes in the structure and as a consequence in the physical properties of the polymer [10]. This enthalpy relaxation, known as physical aging [10], can be detected by the appearance of an endothermic peak in the glass transition of the polymer using experimental techniques such as

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http://dx.doi.org/10.1016/j.supflu.2014.01.013

differential scanning calorimetry (DSC) [11,12]. It has been shown that mechanical properties of PC such as the elastic modulus and hardness increase with aging while others such as the impact strength decrease [13], which has been related to an increasingly higher free volume relaxation of the polymer, although no simple correlation has been established between these mechanical properties and changes in the endothermic glass transition peak resulting from aging.

In this work we present the preparation using a two-step foaming process of closed-cell PC foams with tailored cellular structures that varied from isotropic-like microcellular to highly oriented and with bigger cells by controlling the dissolution temperature of $scCO_2$, as well as the effects of foaming on the physical aging of PC, as the cellular structure morphological aspects and relaxation state of PC are of extreme importance in terms of regulating the final properties of the resulting foams.

2. Materials and methods

2.1. Preparation of PC foam precursors

Polycarbonate (Lexan-123R-PC, supplied by Sabic in the form of pellets), with a density of 1.2 g/cm^3 and melt flow index (MFI) of 17.5 dg/min, measured at 300 °C and 1.2 kg, was compression-moulded at 220 °C and 45 bar in a hot-plate press (IQAP LAP PL-15) to circular-shaped plates with a thickness of 3.5 mm and diameter of 74 mm in three steps: (1) in the first step the PC pellets initially placed in the circular-cavity mould were softened at 220 °C during 10 min; (2) the second step consisted in removing possible air trapped between the PC pellets by initially pressurizing and releasing the pressure several times gradually increasing the pressure from 5 to 45 bar and keeping a constant pressure of 45 bar during 1 min at 220 °C; (3) in the third and last step the circular-cavity mould containing the PC was quickly transferred to the cooling station of the press, where it was cooled down for 5 min under a constant pressure of 45 bar. The circular-shaped PC plates obtained at the end of this step were used as foaming precursors. The samples used in the CO_2 desorption experiments were directly machined from these plates to a typical diameter value of 40 mm.

2.2. Foaming process: Stage I—Supercritical carbon dioxide dissolution

Once obtained by compression-moulding, the PC foam precursors were foamed by placing them inside a high pressure vessel and initially dissolving supercritical carbon dioxide ($scCO_2$). Two $scCO_2$ dissolution temperatures were used: 80 and 100 °C, in both cases applying a total dissolution time of 210 min. The $scCO_2$ was introduced in the vessel at room temperature at a pressure of 70 bar, reaching a final dissolution pressure of 140 and 170 bar, respectively, for a dissolution temperature of 80 and 100 °C. Once carbon dioxide was dissolved into the foam precursors, these were cooled down to room temperature by re-circulating water through the vessel's cooling jacket while keeping the vessel pressurized at 15 °C/h. After slow depressurization of the $scCO_2$ at room temperature, the PC foam precursors containing CO_2 were taken out from the vessel and left to stabilize at room temperature and atmospheric pressure for 120 min. Analysis of the internal morphology of the PC foam precursors containing CO_2 did not show any pre-foaming.

2.3. Foaming process: Stage II—Double contact restricted foaming

The PC foam precursors containing CO_2 obtained at the end of Stage I were once again placed in the circular-cavity mould and foamed in the hot-plate press by compression-moulding at a constant temperature of 165 °C and constant pressure of 60 bar. The circular-cavity mould and metal plates used in this stage were preheated at 165 °C prior to positioning of the precursors and foaming. The compression-moulding double contact used in this stage guaranteed the homogeneous heating of the precursors and ensured flatness of the surfaces for later characterization. After applying a heating time that varied between 40 and 120 s, the applied pressure was suddenly released, allowing the PC foam precursors containing CO_2 to expand in both vertical and width directions. After the expansion, the obtained foams were quickly removed from the plates and left to cool at room temperature by direct contact with air.

2.4. CO_2 desorption experiments

Desorption experiments were carried out in order to measure the CO_2 diffusion coefficient in PC for the two different dissolution temperatures. As previously mentioned, the samples used in these experiments were directly obtained from the PC foam precursors by reducing their diameter to 40 mm. After applying the conditions already indicated in Stage I of the foaming process, i.e., a $scCO_2$ dissolution temperature of 80 or 100 °C and pressure of 140 or 170 bar for a total dissolution time of 210 min, samples were cooled down to room temperature, removed from the vessel and quickly transferred to a balance in order to record the evolution of CO_2 mass loss with the desorption time.

The maximum concentration of CO_2 in the samples after decompression (M_0) was calculated by extrapolating to zero desorption time following the initial slope method [14]. Assuming one-dimensional diffusion in a plane sheet, the CO_2 diffusion coefficient (D_d) was determined by plotting M_t/M_0 as a function of t/l^2, where M_t is the CO_2 concentration at time t and l is the thickness of the sample, according to the following equation [15]:

$$\frac{M_t}{M_0} = 1 - \frac{8}{\pi^2}\exp\left(-\frac{D_\mathrm{d}t}{l^2}\right) \tag{1}$$

The CO_2 diffusion coefficient was determined from the slope of the M_t/M_0 vs. t/l^2 curve taking into account the last data range and the calculated value of M_0.

2.5. Cellular structure characterization

The density of the several PC foams was measured according to standard procedures (ISO 845), while the relative density was calculated by dividing this value by the density of the unfoamed precursor. Scanning electron microscopy (SEM) was used to analyze the cellular structure of the foams. Samples were prepared by cryogenically fracturing the foams in liquid nitrogen and sputter depositing a thin layer of gold at their surface using a BAL-TEC SCD005 Sputter Coater (argon atmosphere). Micrographs were obtained using a JEOL JSM-5610 scanning electron microscope applying a voltage of 10 kV and a working distance of 40 mm.

The average cell sizes in the vertical (ϕ_{VD}) and width (ϕ_{WD}) foaming directions were measured using the intercept counting method [16]. The cell aspect ratio (AR) was determined by dividing the value of the average cell size in the vertical direction by that measured in the horizontal one, i.e., $AR = \phi_{VD}/\phi_{WD}$. The cell nucleation density (N_f, in number of cells per volume of unfoamed material) was calculated using the following equation:

$$N_f = \left(\frac{n}{A}\right)^{3/2}\left(\frac{\rho_s}{\rho_f}\right) \tag{2}$$

where n is the number of cells per area A of micrograph (in cm^2) and ρ_s and ρ_f are, respectively, the solid and foam densities.

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