

Effect of organic co-blowing agents on the morphology of CO₂ blown microcellular polystyrene foams



Andra Nistor^a, Martin Topiar^b, Helena Sovova^b, Juraj Kosek^{a,c,*}

^a University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic

^b Institute of Chemical Process Fundamentals of the CAS, v.v.i., Rozvojova 2/135, 165 02 Prague 6, Czech Republic

^c New Technologies – Research Centre, University of West Bohemia, Teslova 9, 306 14 Pilsen, Czech Republic

ARTICLE INFO

Keywords:

Polystyrene
Closed-cell microcellular foam
Co-blowing agent
CO₂

ABSTRACT

Microcellular polystyrene (PS) foams blown with supercritical CO₂ in batch processes have usually porosities lower than desired for good heat insulators. Porosities can be increased by co-blowing agents. We studied effects of *n*-pentane (nC5) and cyclopentane (cC5) on foaming in a batch. Neat PS films were impregnated first with nC5 or cC5, then with high-pressure or supercritical CO₂, and finally foamed. Cell diameters and bulk porosities were determined from SEM images. The co-blowing agents reduced the solid skin, they acted mainly as plasticizers, both porosity and cell diameters increased with their concentration. After crossing a particular concentration, the cell size remained almost constant. Impregnation of neat PS with high-pressure liquid CO₂ near room temperature enabled to prepare foams with cell diameters below 10 μm and porosities about 80 %, which has not been reported before. Hence, organic co-blowing agents could be used to increase the porosity of CO₂ blown foams.

1. Introduction

The use of CO₂ for the preparation of closed-cell micro- and nano-cellular polymer foams received a great interest during last decades. CO₂ is regarded as a green, non-flammable and inexpensive blowing agent and offers good heat insulation properties to foams (as long as CO₂ is kept inside cells). Furthermore, micro- and nanocellular foams have improved mechanical and thermal insulation properties [1–4]. By decreasing the cell size, we will improve the material properties and consequently less material will be needed to maintain the same heat insulation properties; thus, material and production, transportation and other costs will be saved in the end. Up to now, most of the studies have focused on the cell downsizing regardless of the foam porosity (in literature, expressed also as expansion ratio, number cell or foam density) as was pointed out, for example, in the work of Okolieocha et al. [5] and Costeux [1]. Generally, the porosity of CO₂ blown foams can be increased by: a) adding nucleation agents, b) using co-blowing agents, c) preparation of polymers with highly CO₂-philic phases, and of course by d) setting optimized foaming conditions.

In this work, we focus on the use of co-blowing agents as they enable a simple process control and, especially, there is no need to modify the polymer. Co-blowing agents have been used in the extrusion foaming of thermoplastic polymers for a long time. Since high-

pressure/supercritical CO₂ (scCO₂) is in some polymers less soluble and has a high diffusivity, finding a suitable co-blowing agent could help to overcome the disadvantages causing the formation of higher-density polymer foams.

Co-blowing agents in the CO₂ foaming of polymers have been used in the following studies. Salerno et al. [6] used scCO₂-ethyl lactate (EL) mixtures to foam polyesters, namely polycaprolactone (PCL) and polylactic acid (PLA). The addition of a small amount (≥0.2% molar fraction) of EL to the scCO₂ decreased the glass transition temperature (*T*_g) of the polymer-solvent system below the operating temperature and as a result improved the morphology uniformity of PLA foams. ScCO₂-ethanol mixtures as a blowing agent for foaming of PCL were used in the work of Tsivintzelis et al. [7] The prepared foams exhibited more uniform morphologies compared to foams prepared only with scCO₂. With increasing ethanol's weight fraction in scCO₂ larger bubbles were formed; thus, the foams had lower foam densities.

Regarding thermoplastic polymers, poly(vinyl alcohol)/micro-fibrillated cellulose composites were extrusion foamed with CO₂-H₂O in the work of Zhao et al. [8]. H₂O as co-blowing agent affected mainly the plasticization and decreased the melting point. Uniform cell morphology and high cell densities were reached. Extruded polystyrene (PS) containing carbon particles was blown with CO₂-H₂O [9]; water acted as co-blowing agent. A small amount of H₂O (< 1.1 wt.%) was

* Corresponding author at: University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic.
E-mail address: juraj.kosek@vscht.cz (J. Kosek).

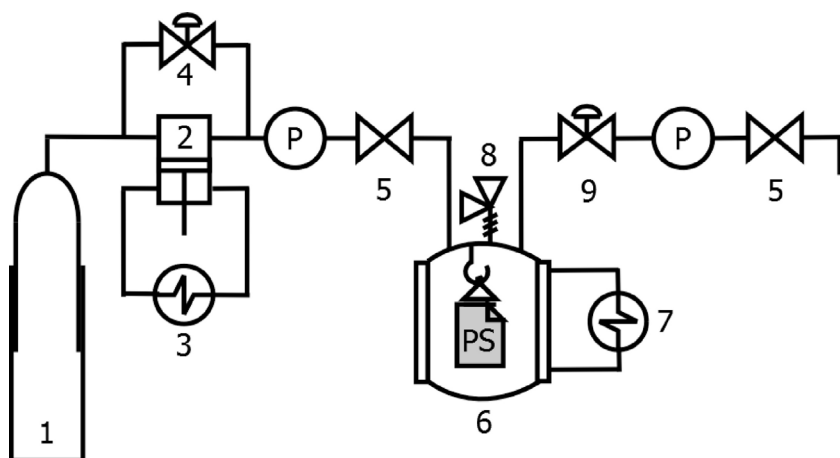


Fig. 1. Scheme of the foaming apparatus set-up with a polystyrene (PS) film placed inside: 1: CO₂ cylinder, 2: high pressure pump, 3: chiller, 4: back pressure regulator, 5: high-pressure valve, 6: vessel with PS film, 7: heating bath, 8: quick release valve, 9: micrometric valve.

added first to the activated carbon. The presence of water lowered the temperature in the centre of the foam and had a little effect on the thermal conductivity of the resulting foam. The mixture of N₂ and CO₂, both in their supercritical state, was used to study the nucleation process in PS within a batch foaming set-up [10]. Foams with the highest number cell densities (2.44×10^8 cells/cm³) were prepared when using a mixture of 75 % CO₂ and 25% N₂ at the impregnation conditions of 100 °C and 100 bar, and with a depressurization speed of 150 bar/s. Under these conditions N₂ exhibits the highest nucleation power and CO₂ the highest expanding ability of bubbles. According to this study, CO₂ has a higher plasticization and solubility effect, and N₂ has a better bubble nucleation power.

The blending of CO₂ with an alcohol or a ketone was also proposed for extruded PS sheets of high compressive strength [11]. In the same patent, the authors suggest using as co-blowing agent C3- to C5-hydrocarbons and/or hydrogen-containing chlorofluorocarbon or fluorinated hydrocarbon. In order to scientifically understand the role of each blowing agent, Gendron et al. [12] studied extruded PS blown with CO₂-ethanol. The achieved foam densities were in the range of 25–30 kg/m³ (that is a porosity of about 97.6 and 97.1 %, respectively) with an adequate cell morphology and the cell diameter in the range of tens micrometres. Furthermore, they observed that the CO₂ plasticization effect on PS is limited at about 4 wt.% of CO₂ and that it diminished with the addition of ethanol. Similarly in a different work [13], extruded PS foams were prepared by using CO₂ and 2-ethyl hexanol, which acted as an efficient additional plasticizer. As a result, PS foams of about 30 kg/m³ density (and porosity approx. 97.1%) were prepared. The determining factor for the cell size was the CO₂ concentration. At 3.5 wt.% CO₂ concentration, all resulting samples had the cell diameter below 100 μm. Additionally, a foam with a bimodal cell size distribution was observed.

However, the majority of studies with co-blowing agents deal with the extrusion process. In our previous work [14], we showed that the PS foam porosity could be increased by pre-impregnating PS with toluene before the CO₂ batch foaming at the expense of larger cell sizes. Toluene was suggested to affect the final foam morphology not only by enhancing the CO₂ solubility in PS, but also by lowering the T_g of the system. In this work, we use separately *n*-pentane (nC5) and cyclopentane (cC5) as co-blowing agents for the CO₂ batch foaming of PS. Closed-cell microcellular PS foams were prepared via the pressure induced foaming method, a one-step process. The effect of nC5 and cC5 on the cell size distribution (CSD) and bulk foam porosity was studied to optimize the CO₂ foaming conditions so that higher porosities could be achieved. The results show that with nC5 or cC5 we can reach foam porosities up to 80 % without using any nucleation agents and even at impregnation temperatures at which foaming of neat PS with pure CO₂ has not been possible yet.

2. Experimental procedure

In the following paragraphs, we briefly describe the foaming apparatus and procedure, as well as the foaming conditions. First, PS films of an average thickness 400 μm were prepared by hot pressing of commercial PS pellets (without any nucleation agents) from the Sigma Aldrich company with the molecular weight $M_w = 280$ kDa, PS density $\rho_{PS} = 1040$ kg/m³ and glass transition temperature $T_g = 100$ °C. PS films were first pre-impregnated with nC5 or cC5, subsequently with high-pressure/sc-CO₂, and then foamed. nC5 was purchased from Lach-Ner (without any impurities and the boiling point being 36 °C) and cC5 from Sigma Aldrich (reagent grade, 98%; with the boiling point 50 °C).

2.1. Foaming apparatus and procedure

The pre-impregnation of PS films was carried out in a closed glass jar filled with liquid nC5 or cC5. The PS film was placed on a holder so that the sample was pre-impregnated only by the vapor phase. To shorten the time of the pre-impregnation, the jar was placed into a laboratory oven, which was set to 40 °C. The mass-uptake of the co-blowing agent was determined gravimetrically by a common analytical balance. When the desired mass fraction was achieved, the sample was quickly placed into a high-pressure vessel to impregnate it with CO₂. The mass fraction of nC5 or cC5 in PS was in the range from 0–7 g nC5/100 g PS and 0–26 g cC5/100 g PS, respectively.

The batch foaming with high-pressure/sc-CO₂ was conducted out in a 27 mL high pressure vessel (I.D. 24 mm), which was immersed in a temperature-controlled silicone bath (Fig. 1). A high-pressure liquid pump (Ecom ALPHA 50-CO₂) with a pressure control unit (Tescom 26-1761-22) was used to pressurize and adjust the CO₂ pressure. The pre-impregnated PS film was hung up in the pressure vessel, which was then pressurized with CO₂. The experimental conditions in the vessel (CO₂ pressure and temperature) stabilized for a period of about 20 min, after which the vessel was disconnected from other parts of apparatus by closing the high-pressure valves. After a given time, the sorption equilibrium was reached. The sorption time was calculated from the characteristic diffusion time, which is proportional to the half-thickness of the polymer film with the power of two and inversely proportional the diffusivity of CO₂ in PS (in detail described in [14]). Finally, the vessel was during 5 s depressurized to atmospheric pressure and the PS sample foamed due to supersaturation. The CO₂ impregnation/foaming conditions presented in this work were the same for all experiments (with exception of the impregnation temperature) – the impregnation pressure was 280 ± 5 bar, the depressurization period to atmospheric pressure was 5 s and the impregnation temperature ranged from 30 to 80 °C (with exception of 50 °C).

Note, that the pre-impregnation with nC5 or cC5 is a non-equilibrated process. But in the subsequent step the impregnation with CO₂ is

Download English Version:

<https://daneshyari.com/en/article/6477662>

Download Persian Version:

<https://daneshyari.com/article/6477662>

[Daneshyari.com](https://daneshyari.com)