

# Microcellular Polystyrene Foams: Improved Heat Insulators

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## ABSTRACT

According to heat transfer simulations, microcellular polystyrene (PS) foams could have improved heat insulation properties. We studied the influence of various foaming conditions on the structure of microcellular PS foams. PS samples were foamed via pressure induced foaming using supercritical CO<sub>2</sub>. Then, the foams were analysed and the cell size distribution and porosity were estimated. We prepared foams with the cell size below 1 µm. However, the highest porosity of the prepared foams was about 60 %, but porosities above 95 % are required for heat insulators. The foaming process is significantly affected by heat transport and mass transport of CO<sub>2</sub> in polymer. We propose to increase the foam porosity by the use of co-solvent.

## INTRODUCTION

Polystyrene (PS) foams with closed cells find use mainly as heat insulators in the construction industries. In the last decade, the industry emphasises more ecological and sustainable processes. Thus, the aims are, for example, to improve the properties of already existing materials, to lower the consumptions of the raw materials and to use environmentally friendly solvents. Micro- and nanocellular PS foams satisfy all the above mentioned aims. By decreasing the cell size to the range of micro- or even nanometres while maintaining a high porosity (above 90 %) we can not only save raw material [1] but also improve the heat insulation properties of the foams [2]. Micro- and nanocellular PS foam can be prepared by supercritical CO<sub>2</sub> (scCO<sub>2</sub>), which is assumed to be a so-called green solvent, i.e., environmentally friendly. However, in order to be able to produce foams with desired morphology/properties (i.e., with the best possible heat insulation and mechanical properties) we have to better understand the foaming process. This contribution tries to extend the present knowledge about the foaming process.

## PRESSURE INDUCED FOAMING USING SUPERCRITICAL CO<sub>2</sub>

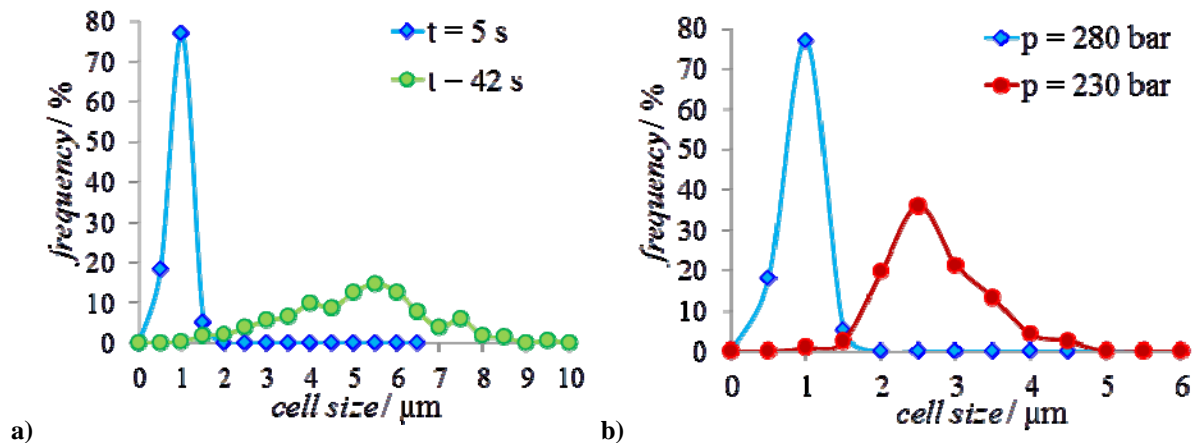
We prepared microcellular PS foams from PS films and particles using scCO<sub>2</sub>. The sample was placed in a high pressure vessel and heated up to a given temperature (the so-called impregnation temperature). Then, the vessel was pressurized with scCO<sub>2</sub> at a given (impregnation) pressure. After reaching the sorption equilibrium the vessel was fast depressurized. The oversaturation of the system induced nucleation followed by cell growth and coalescence until the foam has stabilised during the vitrification.

The foam morphology was analysed by various methods such as X-ray microtomography, Scanning Electron Microscopy, Atomic Force Microscopy and helium pycnometry. We estimated the cell size distribution and the foam porosity, which strongly influence the heat insulation properties.

## INFLUENCE OF FOAMING CONDITIONS ON THE FOAM MORPHOLOGY

The foam morphology can be controlled by the impregnation temperature ( $T$ ) and pressure ( $p$ ), and by depressurisation period ( $t$ ). Nevertheless, the morphology is also affected by characteristic sample size ( $x$ ), additives, and co-solvents [3]. In order to prepare foams with a high porosity (above 90 %), we have to induce high nucleation density in the sample. The nucleation density is affected by the depressurisation period and the impregnation pressure

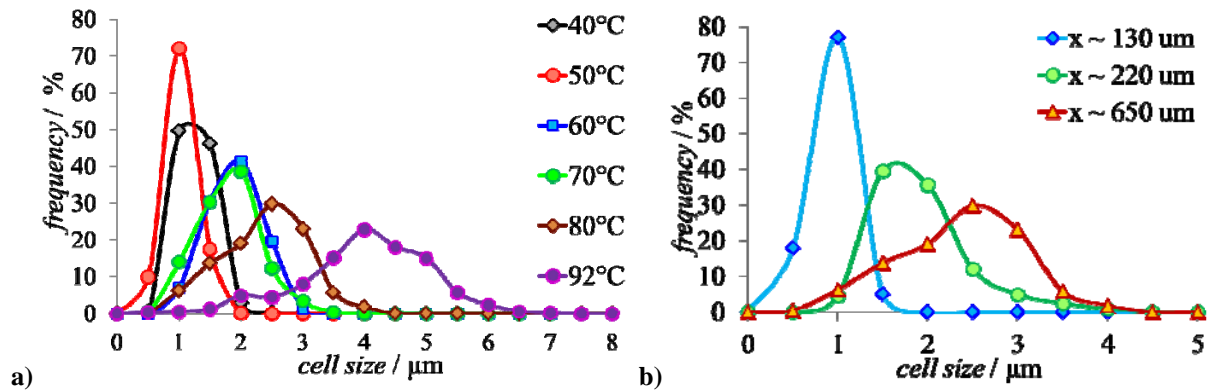
The faster we depressurise the system the higher is the oversaturation. As a result we obtain a higher nucleation density, i.e., a lot of smaller cells (Fig.1a). Similar effect is achieved by the elevated impregnation pressure. At higher impregnation pressures the solubility of scCO<sub>2</sub> in PS increases. Again we obtain the foam structure with a narrow cell size distribution and smaller cells (Fig. 1b).



**Figure 1:** Cell size distribution dependence on a) the depressurisation period  $t$  at  $T = 80^\circ\text{C}$  and  $p = 280$  bar, b) the impregnation pressure  $p$  at  $T = 80^\circ\text{C}$  and  $t = 5$  s. The unfoamed film thickness was  $x \sim 125$  μm.

The scCO<sub>2</sub> solubility in PS is also influenced by the impregnation temperature. When we increase the impregnation temperature the scCO<sub>2</sub> solubility in PS will decrease. Thus, at higher impregnation temperatures the nucleation density will be lower. However, the temperature affects the period over which the sample remains in its rubber state, i.e., above the glass transition temperature  $T_g$ . The coalescence and Ostwald ripening of cells is taking place above  $T_g$ . During the vitrification (crossing the  $T_g$  toward the glassy state) the cells stop growing and the foam stabilises. Thus, the impregnation temperature affects the time of cell growth. Therefore, at higher temperature we observed larger cells and a broader cell size distribution (Fig. 2a).

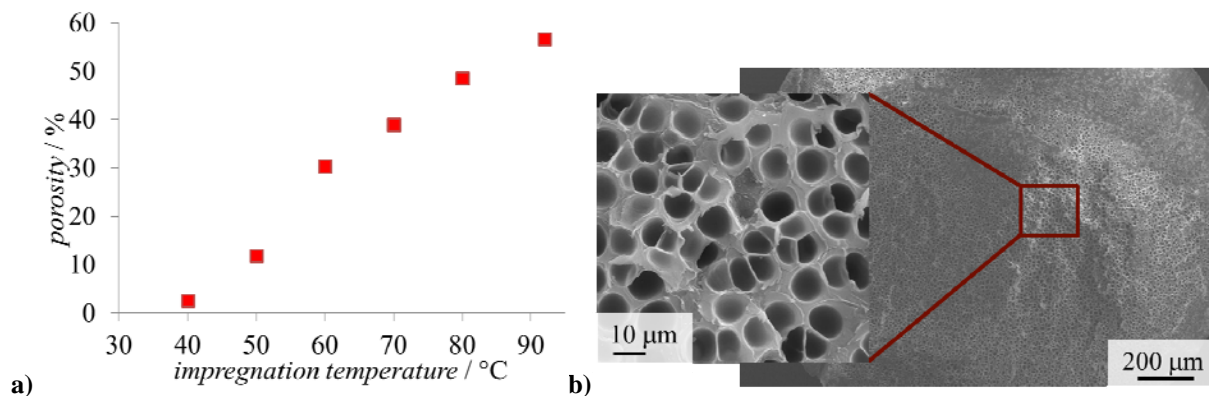
The heat and mass transport effects are also observable as the influence of the film thickness on the foam morphology. In thicker films we observed a broader cell size distribution and larger cells (Fig. 2b). In the film centre the cells were larger than at the film surface, which corresponds to expected spatial profiles of temperature and CO<sub>2</sub> concentration affected by transport processes.



**Figure 2:** Cell size distribution dependence on a) the impregnation temperature  $T$  at  $p = 280$  bar and  $t = 5$  s; the unfoamed film thickness was  $x \sim 550$  μm, b) the film thickness  $x$  at  $p = 280$  bar,  $T = 80$  °C and  $t = 5$  s.

Not only the cell size influences the heat insulation properties but also the porosity. Although the solubility of  $\text{scCO}_2$  in PS should be sufficient for extensive foaming (according to literature at 243 bar  $\text{CO}_2$  and temperature 80°C the solubility in PS is about 11.8 wt. % [4]), the porosity is still not as high as expected. We observed that at a higher impregnation temperature the porosity increased (Fig. 3a). The porosity increased due to the presence of larger cells. However, it seems that heat transport highly affects the morphology. During the fast depressurisation and thus expansion of  $\text{scCO}_2$  the system cools down. This cooling also influences the period for which PS- $\text{CO}_2$  mixture remains rubbery. Therefore, at lower impregnation temperature the system cools so fast that the nuclei do not have enough time to form or grow. A similar effect has the diffusion on the formation of a compact skin on the foamed film surface, which lowers the film porosity in some cases about 10 %.

In the foaming industry the porosity of the foams is increased by using nucleation agents. Therefore, we carried out foaming experiments with industrial PS particles containing nucleation agents and other additives such as flame retardants. Although we would expect an increase in the porosity, we observed mainly an increase in the cell size (Fig. 3b). It seems that the nucleation agent influences also the cell coalescence. We propose that another possibility how to increase the nucleation density is using a co-solvent to increase the  $\text{scCO}_2$  solubility in PS.



**Figure 3:** a) Influence of impregnation temperature  $T$  on bulk porosity. The unfoamed film thickness was  $x \sim 550$  μm, impregnated at  $p = 280$  bar and depressurized for  $t = 5$  s. The cell size distribution is presented in Fig. 2a). b) Scanning Electron Microscopy image of the foamed industrial PS particles with additives with the porosity 50 %.

## CONCLUSION

We studied the influence of various foaming process parameters on the final foam morphology. The study was focused on obtaining a foam morphology, which should have improved heat insulation properties, i.e., micro- and nanocellular structure with porosities above 90 %.

We prepared PS microcellular foams with cell size below 1  $\mu\text{m}$ . We observed that with increasing impregnation pressure, decreasing impregnation temperature and at faster depressurisation periods the cell size distribution narrows and the cells are smaller. However, the highest obtained porosity was about 60 %. The foaming process is highly influenced by the heat and mass transport. We propose that a possible solution how to increase the porosity is by using a co-solvent.

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