Micro- and Nanocellular Polymer Foams – Insulation Material of the Future

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Micro- and nanocellular polymer foams – insulation material of the future

Mikro- a nanocelulární polymerní pěny – izolační materiál budoucnosti

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Abstract

In the polymer foam industry, emphasis is placed on improving foam properties and making the production process more sustainable and ecological. By reducing the cell size of polymer foams below tens of micrometres we can improve their heat insulation properties and save material. Such polymer foams are called micro- or nanocellular foams depending on the range of their cell size.

Micro- and nanocellular foams can be prepared by pressure induced foaming with high pressure CO_2. We studied the influence of the foaming conditions (impregnation temperature and pressure, and depressurisation time) on the final foam structure with the aim of achieving the cell sizes as small as possible, having a narrow cell size distribution and reaching the bulk porosity above 90 %. The foam morphology was analysed by Scanning Electron Microscopy and Atomic Force Microscopy. Some morphology visualisations were also made by X-ray micro-tomography, but these visualisations are not demonstrated in this contribution.

We observed that higher impregnation temperature broadened the cell size distribution, but it also increased the porosity while keeping the average cell size below 10 µm. Furthermore, higher impregnation pressure narrowed the cell size distribution, induced formation of smaller cells and enabled to obtain foams with higher porosities.

1. Heat insulation properties of polymer foams: The influence of foam morphology

Polymer foams are two-phase systems of dispersed gas in polymer. This configuration provides the polymeric foam some excellent physical properties when compared to properties of a pure polymer. Polymer foams are used for their cushioning effect, as heat or acoustic insulators, as membranes and as absorbers of various mechanical deformations.

Heat insulation properties of polymer foams can be improved, for instance, by: (i) decreasing the cell size, (ii) reducing of gas pressure or (iii) absorbing thermal radiation by incorporating infrared adsorbing materials such as soot. By reducing the cell size into the range of micro- or nanometres we can prepare the so-called micro- or nanocellular foams, respectively. According to mathematical modelling, the heat insulation properties of micro- and nanocellular foams are improved by: (i) Knudsen effects (for cell sizes smaller than several micrometres; Baetens et al., 2010) and (ii) reduced heat radiation (for cell sizes smaller than approx. 100 µm; Kammerlen et al., 2010) while keeping the porosity around 95 % (Ferkl et al., 2013). Heat insulation properties of the polymer foams are also determined by the cell size distribution, cell shape and orientation, thickness of walls between the cells and porosity (discussed in detail by Ferkl et al., 2013 and his continuing research).

In this work, we foamed polystyrene (PS) films with sub- and supercritical CO_2. PS foams are mainly used as heat insulators (Weber et al., 2000). We evaluated the cell size distribution and bulk porosity (i.e., the volume percentage of cells in the bulk foam) of foams prepared at various

foaming conditions. The cell size distribution and the bulk porosity strongly affect heat insulation properties (Ferkl et al., 2013).

2. Foaming of polymers and characterization of foam morphology

We foamed PS films with high pressure CO_2 by inducing a pressure drop; this method is called a pressure induced foaming or pressure quench. The procedure of the pressure induced foaming was the following. First, we prepared thin PS films by high temperature pressing of PS powder. Foaming of PS in the form of a film enables us to have a well-defined system suitable for studying cell growth, coalescence and nucleation phenomena, which are still not fully understood (Jacobs et al., 2008). Then, the film was placed in a pre-heated pressure vessel and pressurized with CO_2. After reaching the sorption equilibrium, the vessel was quickly depressurized (in 5 or 45 s) to atmospheric pressure. The rapid pressure drop leads to an oversaturation of the system polystyrene-CO_2. Then, the phase separation and nucleation occur followed by the cell growth and coalescence of cells until the polymer vitrifies (i.e., until the system crosses its glass transition temperature T_g) and stabilises its structure.

The impregnation temperature at the impregnation CO_2 pressure has to be set above the T_g of the polystyrene-CO_2 mixture otherwise the sample will not foam. The T_g of the system polystyrene-CO_2 should be well below the room temperature at CO_2 pressures above 200 bar (Arora et al., 1998).

The absorption time needed for establishing the sorption equilibria was estimated as
$$t = l^2 / D,$$
where l is the half-thickness of the film and D is the diffusion coefficient, which was experimentally determined for the system polystyrene-CO_2 at 80 °C and 243 bar to be $D = 2.4 \times 10^{-10} \ m^2/s$ (Arora et al., 1998). To be on the safe side, we chose a lower diffusivity of $1 \times 10^{-11} \ m^2/s$ and we enabled the sample to absorb CO_2 for at least $5t$.

Then, the foam samples were cryo-cut and investigated by Scanning Electron Microscopy (SEM) and in some cases also with Atomic Force Microscopy (AFM). Further, the images were analysed in the software LUCIA from Laboratory Imaging Company.

3. Results and discussion

The pressure induced foaming can be controlled by the following parameters: initial impregnation temperature T and pressure p, and depressurisation period τ. For the foaming experiments we used PS sample without nucleation agents, with $T_g = 100°C$ and molecular weight $M_W = 280\ 000$ g/mol.

3.1 The influence of depressurisation period

The oversaturation dynamics of the system can be controlled by the depressurisation period τ. The temporal degree of the oversaturation is higher when we depressurise the system faster. Thus, the faster depressurisation leads to the higher nucleation density and to smaller cells (Figure 1). In addition, the slower we depressurise the vessel the more time have the cells to grow and coalesce until the system vitrifies and as a result we observe larger cells (Figure 1).

In both foams displayed in Figure 1 was the porosity almost the same (about 6 %). The CO_2 solubility in PS in both experiments was the same since the PS samples were impregnated at the same pressure and temperature. Faster depressurisation caused the formation of more nuclei; but on the other hand, the cells had less time to grow before vitrification. In the slowly depressurised sample the cells had more time to grow and coalesce and as a result we have a lower number cell density (4.5×10^5 cm^{-2}) than in the case of the faster depressurised sample (43.0×10^5 cm^{-2}). Since we are interested in having the cell size as small as possible and the cell distribution as narrow as possible, all the following foaming experiments were depressurised in 5 s.
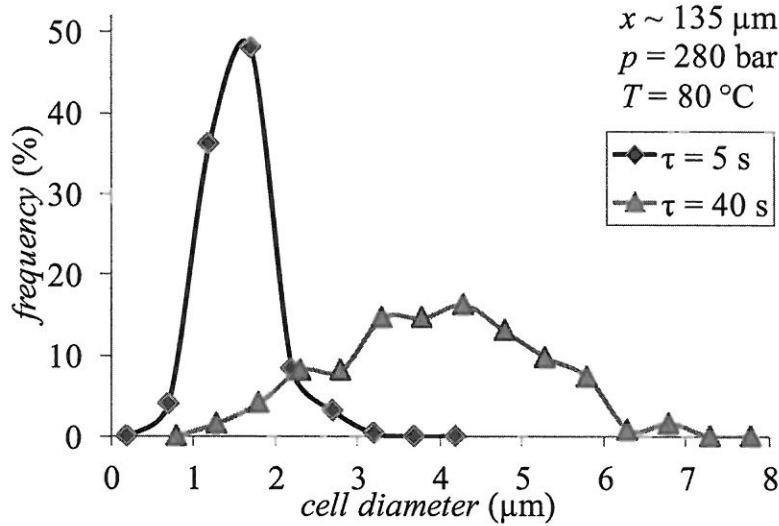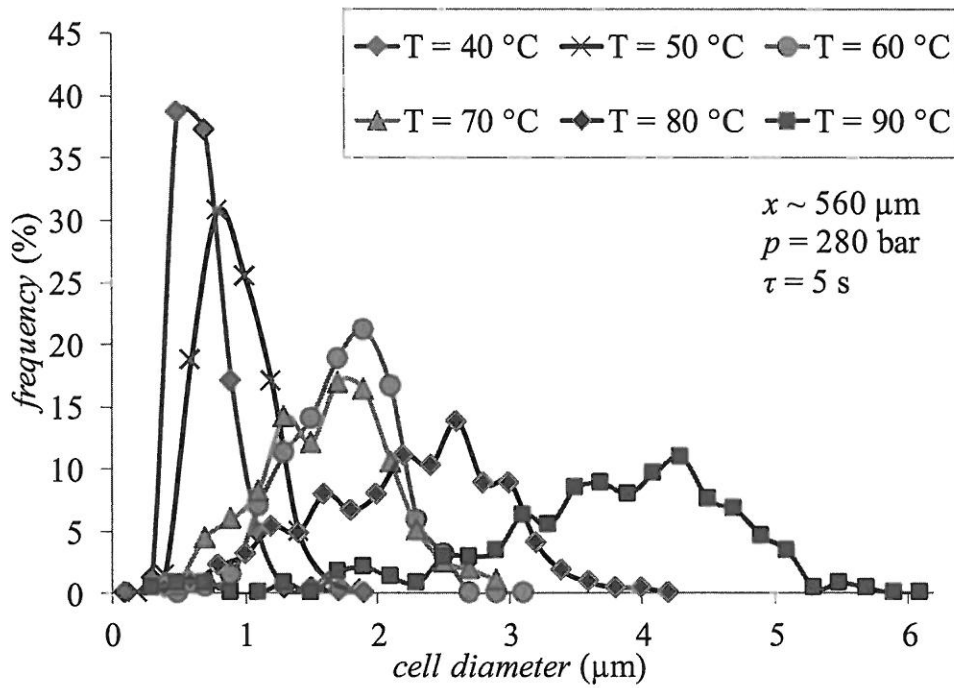

Figure 1: The cell size distribution of foams prepared at the same impregnation conditions ($p = 280$ bar, $T = 80°C$) with the film thickness x about 135 μm but depressurised at different depressurisation periods (5 and 40 s).
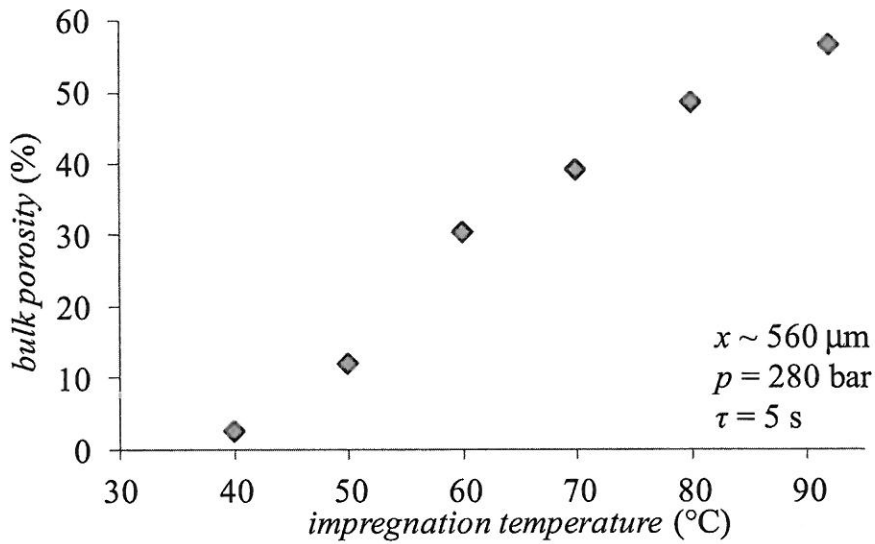
3.2 The influence of impregnation temperature

The CO_2 solubility in PS and the viscosity of this system are inversely proportional to the impregnation temperature T. Thus, at higher impregnation T the CO_2 solubility in PS will be lower and this will lead to the formation of fewer nuclei (Arora et al., 1998; Tsivintzelis et al., 2007). The diffusivity of CO_2 in PS and the time necessary for vitrification of PS is proportional to the impregnation T.

Assuming all the above mentioned factors, higher impregnation T leads to cell growth and thus increases the average cell size, but it also broadens the cell size distribution (Figure 2). On the other hand, the presence of larger cells (i.e., foaming at higher impregnation T) increases the foam porosity (Figure 3). Since our aim is having higher porosities (above 90 %) and smaller cells (below 10 μm) with narrow distribution, one possibility how to increase the porosity could be using nucleating agents. Nucleating agents form nuclei and are commonly used in the foaming process to increase the porosity.

Figure 2: The cell size distribution of foams prepared at the same impregnation conditions (p = 280 bar, τ = 5 s) with the film thickness x about 560 μm but impregnated at different temperatures.
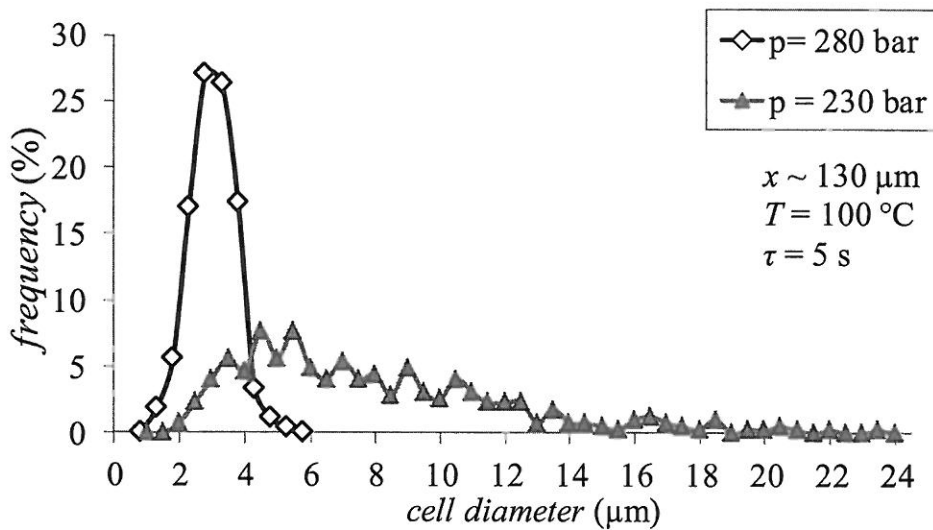

Figure 3: The dependence of the bulk porosity on the impregnation temperature T for foams prepared at the same impregnation conditions (p = 280 bar, τ = 5 s) with the film thickness x about 560 μm.
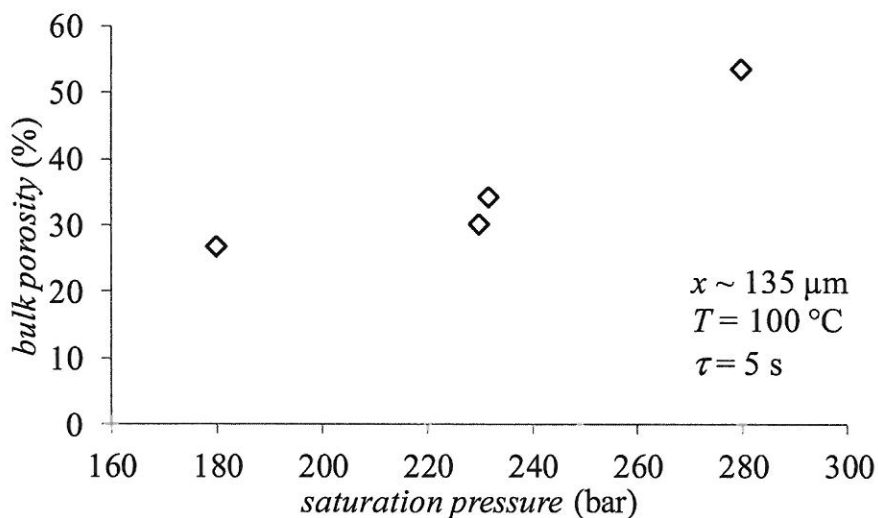
3.3 The influence of impregnation pressure

The impregnation pressure p mainly affects the CO_2 solubility in PS. Higher CO_2 solubility in PS (obtained at higher impregnation pressure) leads to the formation of more nuclei and thus to cells of smaller size (Arora et al., 1998; Tsivintzelis et al., 2007; Jacobs et al., 2008). In addition, higher impregnation pressure causes a larger oversaturation of the system polystyrene-CO_2 during the depressurisation and as result we observe a narrow distribution of cell sizes (Figure 4). Furthermore, the increase in impregnation pressure leads to the increase of resulting foam porosity (Figure 5).

The solubility of CO_2 in PS and thus the foam morphology can be controlled, for instance, by adding a co-solvent. However, the presence of co-solvents increased the average cell size (Stafford et al., 1997; Nistor et al.).

Figure 4: The cell size distribution of foams prepared at the same impregnation conditions ($T = 100°C$, $\tau = 5$ s) with the film thickness x about 130 µm but impregnated at different pressures.

Figure 5: The dependence of the foam bulk porosity on impregnation pressure p of foams prepared at the same impregnation conditions ($T = 100$ °C, $\tau = 5$ s) with the film thickness x about 130 µm.

4. Conclusion

We studied the influence of foaming conditions on the final structure of micro- and nano-cellular PS foams prepared by the method of pressure induced foaming with sub- and supercritical CO_2. The foamed PS films were analysed by SEM and the cell size distribution and bulk porosity were determined.

We observed that faster depressurisation to atmospheric pressure caused the formation of smaller cells with a narrower cell size distribution. Therefore the following foaming experiments were conducted at fast depressurisation (in 5 s). Higher impregnation temperatures increased the average cell size and broadened the cell size distribution. On the other hand, higher impregnation temperatures increased the bulk porosity while preserving the cell size below 10 μm. Higher impregnation pressures caused the formation of smaller cells with a narrow distribution and increased the porosity.

It seems that microcellular foams with porosity above 90% could be prepared by incorporating nucleating agents. The nanocellular foams could be prepared by increasing the impregnation pressure and decreasing the impregnation temperature. However, the best foaming conditions have not been determined yet.

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