Please cite as: Inż. Ap. Chem. 2016, 55, 1, 40-41

Katarzyna TARABASZ, Marek HENCZKA

e-mail: k.tarabasz@ichip.pw.edu.pl

Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warsaw

Experimental investigations into foaming of biodegradable polymers using $scCO_2$

Introduction

A post-traumatic treatment is difficult because of more often lack of organs and tissue. To overcome this problem, in recent years bone tissue engineering has become a well-developed field of research [*Duarte et al., 2009*].

Tissue engineering covers new techniques from materials and life sciences to prepare biodegradable three-dimensional scaffolds for regeneration of damaged tissue [*Gloria et al., 2012*]. There are many methods to produce useful porous structures such as solvent casting-particle leaching, thermally induced phase separation, injection molding, extrusion, foaming, electrospinning [*Duarte et al., 2009*]. Polymer foaming technique is an essential process for bone scaffold fabrication because it doesn't require the use of harmful organic solvent and further purification and drying step the final product.

Foaming of polymers with gases or supercritical fluids is widely applied to preparation functionalized porous structures useful for biomedical application. Supercritical carbon dioxide ($scCO_2$) as physical foaming agent is a promising medium that can replace organic solvent [*Jenkins et al., 2006*]. Moreover $scCO_2$ is characterized by many favorable properties such as high diffusivity and good solubility in polymers [*Karimi et al., 2012*], wide availability, non-flammability. It can be removed from polymer by simple depressurization and potentially remaining residues are harmless.

Polymer $scCO_2$ – based foaming process involves two steps: saturating the polymeric material with $scCO_2$ and rapid depressurization stage [*Karimi et al., 2012*].

In the literature there are many papers that report on $scCO_2$ foaming a variety of polymeric materials. Moreover, such the materials must have mechanical and physical properties similar to replaced tissue. Poly(ε-caprolactone) (PCL) is an aliphatic semi-crystalline polyester of a low melting temperature of about 332÷337 K. PCL is a hydrophobic, biodegradable and biocompatible polymer so it is an essential material for bone scaffold preparation [*Salerno et al., 2011*].

In this paper an experimental system for production of porous three-dimensional solid-gas structure and preliminary results of investigations of polymer foaming are presented.

Experimental system

The experimental system for production of porous three-dimensional structure is depicted on Fig. 1. In order to investigate the course of the foaming process, a lab-scale high pressure experimental system consisting of carbon dioxide cylinder, $scCO_2$ pump, valves, high pressure cell, pressure and temperature gauge and back pressure regulator was built.

Carbon dioxide was fed to the high pressure cell from a CO_2 cylinder (– *1* by a *SFT* CO_2 pump (*Supercritical Fluids Technologies, Inc*., USA) – *3*. In order to precisely monitoring both temperature and pressure during the foaming process experimental system were equipped with a temperature and pressure controller – *5*. In order to maintain a constant value of pressure in a high pressure vessel and to control a depressurization rate a back pressure regulator (*Tescom*, USA) – *6* was applied. Stainless steel elements and valves enable an easy modification of the experimental setup, which allows to perform batch foaming processes using $scCO_2$ as blowing agent under wide range of experimental conditions. Using this system the foaming

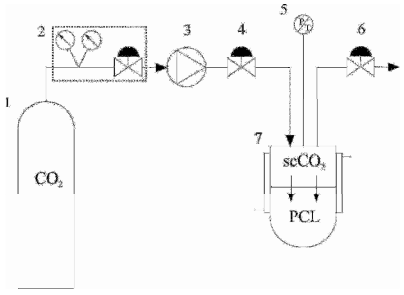

Fig. 1. Scheme of the experimental system: 1 – carbon dioxide cylinder, 2 – reducer, 3 – $scCO_2$ pump, 4 – valve, 5 – pressure and temperature gauge, 6 – back pressure regulator, 7 – high pressure cell.

experiments can be carried out in the following range of process parameters:

- temperature: 298÷473 K,
- pressure: 1÷20 MPa, $scCO_2$,
- flow rate: 0,01÷24 cm^3/min.

Moreover, the design of the experimental system allow to perform the foaming experiments in different modes. The experimental setup enables the modification of the method of contacting the $scCO_2$ with the polymer and its intensification, for example, by changing the contact area of the solid phase with the blowing agent.

Performing of foaming process

In performed experiments poly(ε-caprolactone) (Mn = 80,000) in pellet form (~3 mm) manufactured by *Sigma-Aldrich*, Italy was used. Carbon dioxide (CO_2) of purity grade 4,5 was purchased from *Linde Gaz Sp. z o.o., Poland* and used as a blowing agent in foaming experiments.

In general the foaming experiments were conducted in a three-step batch process. First the polymer pellets was placed in a stainless steel high pressure cell – 7 (inner diameter: 45 mm, height: 80 mm), where they were melted and saturated with a $scCO_2$. Thereafter cooling and decompression the experimental system were carried out.

In order to explore the utility of the experimental system, a number of tests were performed. The system allowed to prepare porous sponges by supercritical foaming of poly(ε-caprolactone) (PCL) under adequate operating conditions. In Tab. 1 the range of process parameters for performed experiments is summarized.

In the first step of the batch foaming experiment PCL pellets were melted and saturated with a gas at appropriate conditions. Carbon dioxide penetrates phase of the melted polymer by diffusion. Then a rapid cooling the system to the foaming temperature was conducted and a gas nuclei inside the polymer matrix were created.

Tab. 1. Foaming process parameters

Stage		Process parameter
I	Melting and saturation of the polymer with $scCO_2$	Temperature: 323÷373 K Pressure: 8÷18 MPa Time: 1÷4 h
II	Mixture cooling	Temperature: 298 K Pressure: 8÷18 MPa Time: 0,08÷0,5 h
III	Mixture decompression	Depressurization rate: 0,007÷4 MPa/s

Please cite as: Inż. Ap. Chem. 2016, 55, 1, 40-41

The vessel was kept at desired pressure and temperature for minimum of 300 s to a maximum of 1800 s. In the third stage the experimental setup was depressurized with both fast or slow rate. When foaming pressure was reduced to ambient one the growth of foam bubbles were noticed. Finally porous sponges was taken out from high pressure cell and maintained at ambient condition for 24 hours. Residues of CO_2 were removed from porous structures by evaporation. Finally the effect of process parameters on final porous structure were investigated and various important parameters of the foam were identified.

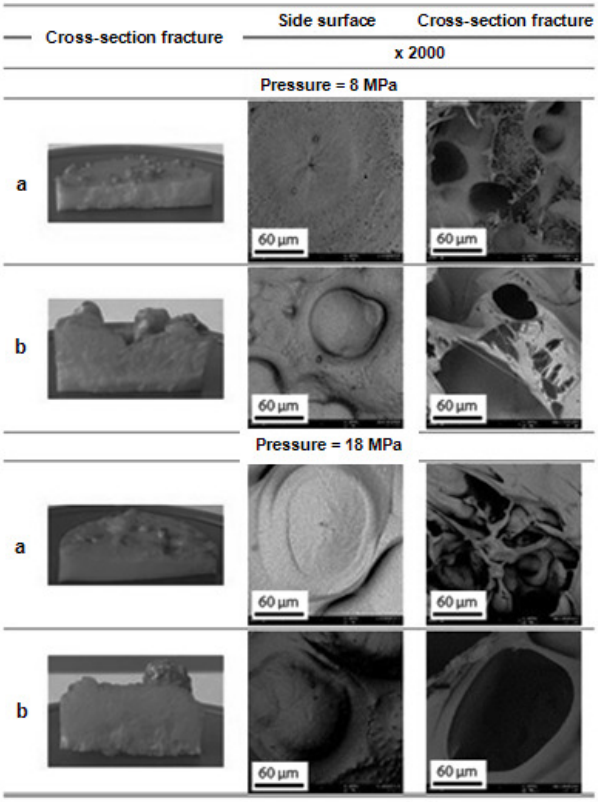

Fig. 2. Effect of foaming parameters on morphology of porous structures for depressurization rates: a) 0.007 MPa/s and b) 4 MPa/s

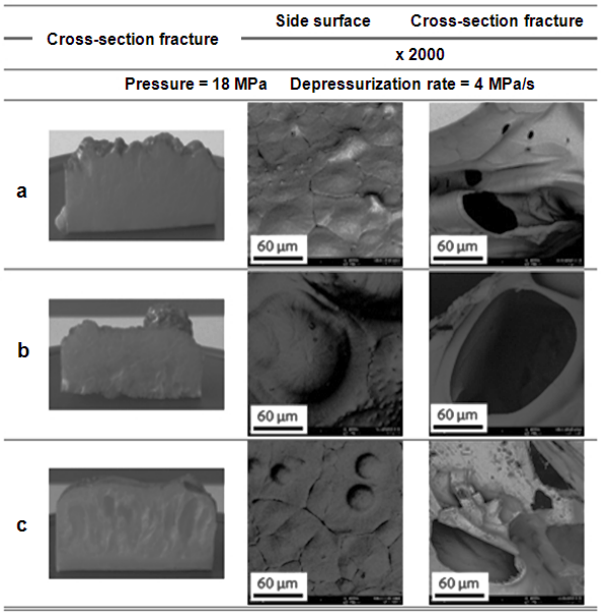

Fig. 3. Effect of foaming parameters on morphology of porous structures for temperature: a) 323 K, b) 343 K, and c) 373 K

As it was proved the experimental system is efficient to produce of three-dimensional porous solid-gas foams which structure strongly depends on the process parameters. In Fig. 2 and 3 the effect of experimental variables on morphology of solid-gas structure is presented.

The morphology of side surface and cross-section fracture of the porous structure was analyzed using *Phenom* scanning electron microscope (SEM). As shown in Fig. 2 the average pore size decreases and density of foam increases with increase of both pressure and depressurization rate.

The structure of porous foam is non-uniform and a variety of pores shape from oval to round are noticed. In addition foams are covered by a dense nonporous skin. Moreover a fast depressurization leads to formation of a more thin layer of skin, which is easy to damage. In Fig. 3 effect of temperature on structure of porous foam was presented. As it was shown in this case, the shape of the pores is more elongated than in the previous samples. Moreover the mean pore size increases and density of foam decreases with increasing temperature.

Conclusions

The design of experimental system for supercritical CO_2 foaming of biodegradable polymers was presented. The application of the $scCO_2$ in the polymer foaming process overcomes the drawbacks of classical methods for the preparation of three-dimensional solid-gas foams.

The applied experimental system allows to produce of porous three-dimensional solid-gas sponges for biomedical application by batch foaming technique. Preliminary experiments were performed to provide the proof of usability of the system for this purpose.

The system was adopted for production of porous structures by supercritical foaming of poly(ε-caprolactone) under different experimental conditions. On the basis of SEM microphotographs can be concluded that the use of an experimental system allows to produce of foam with appropriate morphological and mechanical properties and to study of impact of $scCO_2$ on foam structures.

The experimental system allows to carry out the foaming process in a wide range of operating conditions. Moreover tested range of variables enables the production of foams with an appropriate structure and mechanical properties. Effect of foaming pressure and depressurization rate on final three-dimensional porous structure was identified. It was identified that the mean pore size decreases and density of foam increases with increase of both foaming pressure, temperature and depressurization rate.

REFERENCES

Duarte A. R. C., Mano J. F., Reis R. L., (2009). Perspectives on: Supercritical fluid technology for 3D tissue engineering scaffold applications. *J. Bioactive Comp.Polym.*, 24, 385-400, DOI: 10.1177/0883911509105796

Gloria A., Causa F., Russo T., Battista E., Della Moglie R., Zeppetelli S., De Santis R., Netti P. A., Ambrosio L., (2012). Three-dimensional poly(ε-caprolactone) bioactive scaffolds with controlled structural and surface properties. *Biomacromolecules*, 13(11), 3510–3521. DOI: 10.1021/bm300818y

Jenkins M. J., Harrison K. L., Silva M. M. C. G., Whitaker M. J., Shakesheff K. M., Howdle S. M., (2006). Characterisation of microcellular foams produced from semi-crystalline PCL using supercritical carbon dioxide. *Eur. Polymer J.*, 42, 3145-3151. DOI:10.1016/j.eurpolymj.2006.07.022

Karimi M., Heuchel M., Weigel T., Schossig M., Hofmann D., Lendlein A., (2012). Formation and size distribution of pores in poly(ε-caprolactone) foams prepared by pressure quenching using supercritical CO_2. *J. Supercrit. Fluids*, 61, 175-190, DOI:10.1016/j.supflu.2011.09.022

Salerno A., Di Maio E., Iannace S., Netti P. A., (2011), Solid-state supercritical CO_2 foaming of PCL and PCL-HA nano-composite: Effect of composition, thermal history and foaming process on foam pore structure. *J. Supercrit. Fluids*, 58, 158-167. DOI:10.1016/j.supflu.2011.05.009