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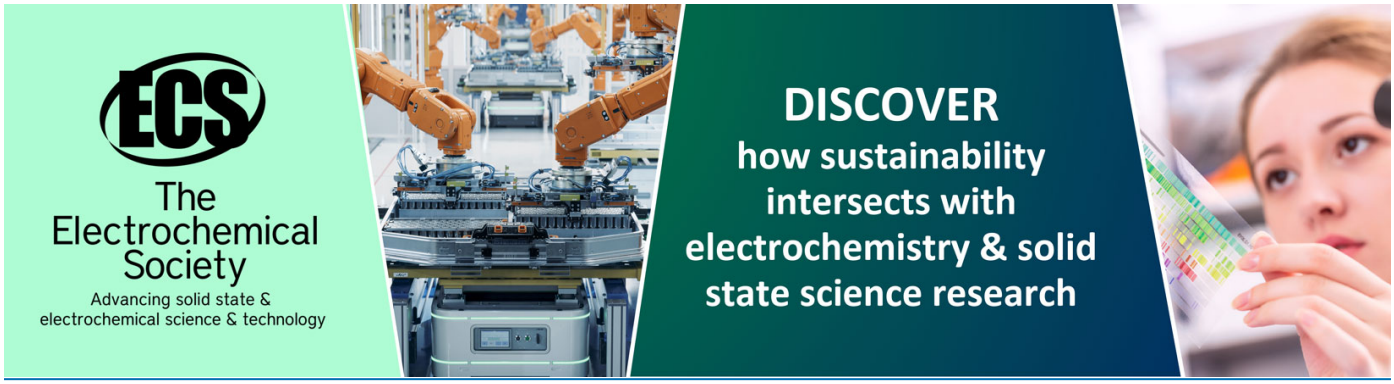

Preparation and characterization of PMMA graded microporous foams via one-step supercritical carbon dioxide foaming

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Abstract. Supercritical carbon dioxide ($ScCO_2$) foaming which is inexpensive and environmental friendly has been widely used to prepare polymer-based microporous materials. In this paper, PMMA graded microporous materials were foamed by PMMA matrix after an unstable saturation process which was done under supercritical condition of 28MPa and 50℃. The scanning electron microscopy (SEM) was utilized to observe the morphology of the graded foam. A gas adsorption model was proposed to predict the graded gas concentration in the different region of the polymer matrix. The SEM results showed that the solid and foam region of the graded foam can be connected without laminated layers. With the increasing thickness position of the graded microporous foam, the cell size increased from 3.4 to 27.5 μm, while the cell density decreased from 1.04×10^9 to 1.96×10^7 cells/cm^3. It also found that the gradient microporous structure of the foam came from graded gas concentration which was obtained in the initial saturation process.

1. Introduction

Supercritical fluids have received much more attention in science and technology in recent years for its distinctive properties. They can be used as foaming agent due to their many advantageous, such as high diffusion coefficient, strong solvent power and the plasticization of glassy polymers[1,2]. Among so many supercritical fluids, supercritical carbon dioxide ($ScCO_2$) has widely used because their properties of environmental friendly and low critical condition(31.1℃ and 7.38MPa)[3,4]. Microporous polymer which is foamed from polymer using $ScCO_2$ as blowing agent has smaller cell size and higher cell density compared to traditional foams. These qualities made them a high compressive strength or tensile strength[5]. In addition, the foam products prepared by supercritical CO_2 foaming technique can be well controlled and calibrated.

Functionally graded materials (FGMs) which have non-homogeneous composition and graded microstructure can apply to the fields of aerospace, biomedical and automotive industries[6,7]. There are so many methods to fabricate FMGs，such as chemical vapor deposition(CVD)[8], which is common used to prepare thin film FGMs. Powder metallurgy is another method to produce both thin film and bulk FGMs. But this method often needs many steps including the mixing, compaction, sintering and subsequent welding[9]. The research on polymer-based FGMs is quite limited compared to ceramic- and metal-based ones. Changchun Zhou's team had presented a two-step foaming method to prepare functionally graded microporous foams using $ScCO_2$ as blowing agent[10]. They first put the polymer sample in a pressure

vessel to absorb $ScCO_2$, then the sample was taken out from the vessel and foamed using a modified hot press device. The foaming process was mainly controlled by the saturation time, foaming temperature, and foaming time.

In this paper, we present a one-step foaming method to fabricate graded microporous foams using $ScCO_2$ as blowing agent. Microstructure gradient was created by controlling the gas adsorption process. The carbon dioxide will form concentration gradient inside the polymer during the adsorption process if the saturation time is appropriate. This gas concentration gradient will induce cell density gradient after foaming. This paper presents the fabrication and structural characterization of the polymer-based functional graded microporous foams.

2. Experimental

2.1. Materials

Polymethyl methacrylate (PMMA) was used as polymer matrix, acquired from Nantong Rayon Chemical Co., Ltd., China. The density of the material was 1.19 g/cm^3 and the glass transition temperature (Tg) was 106℃.PMMA solid matrix was cut into 2mm×15mm×15mm rectangular samples. The foaming agent CO_2 (>99.95%) was kindly supplied by Wuhan Yousheng Gas Limited Liability Company.

2.2. Foaming process

The PMMA sample was firstly absorb CO_2 under a supercritical condition at 28MPa and 50℃ for an hour. Then the pressure was rapidly released in 2s to introduce a thermodynamically unstable state. The CO_2 in polymer nucleates and foams. After foaming for 60s, the sample was shaped by cooling in ice and water.

2.3. Sample characterization

Scanning electron microscope (SEM) was used to characterize the morphology of the foam sample. The foam samples were freeze-fractured in liquid nitrogen and the fracture surface ware sputter coated with gold. The cell size and cell density were calculated according to the SEM images. Cell density and cell size analysis was conducted using ImageJ (National Institute of Health) and more than 100 cells were tested. The cell density was calculated using the following equation (1):

$$N = \left(\frac{nM^2}{A} \right)^{3/2} \quad (1)$$

Where N is the cell density (cells/cm^3), A is the area of the SEM image and M is the magnification factor, n is the number of cells counted from the SEM image[5].

3. Results and discussion

3.1 The morphology of uniform microporous foams

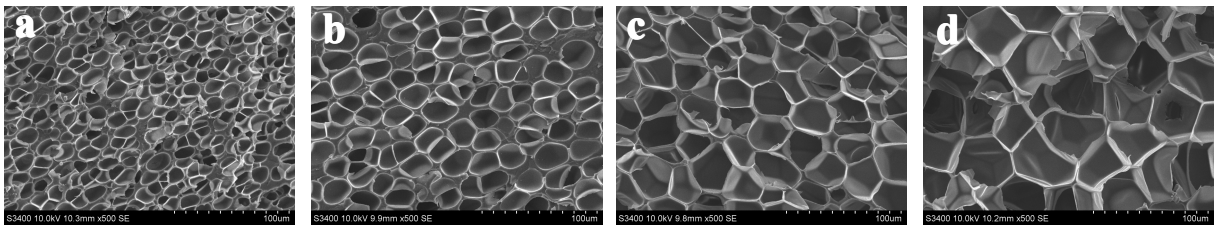

Figure 1. Morphology of microporpos uniform foams after saturating at 20MPa (a)65℃(b)80 ℃(c)110 ℃(d)140 ℃ for 6h

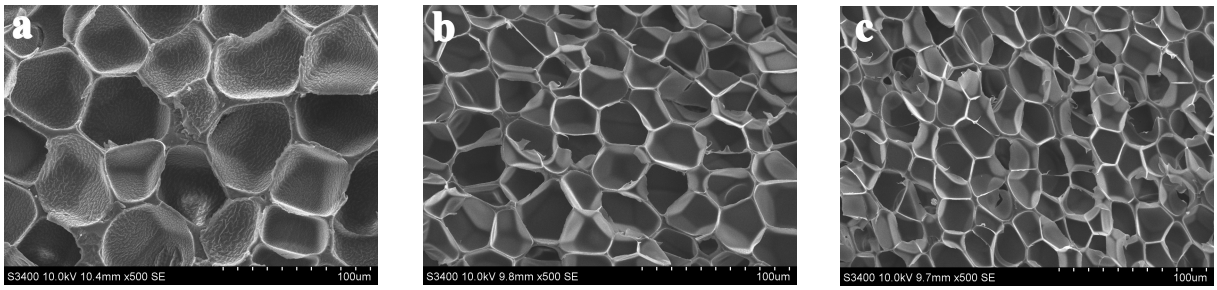

Figure 2. Morphology of microporpos uniform foams after saturating at 110℃ (a)12MPa；(b)20MPa；(c)24MPa for 6h.

In order to investigate the saturation temperature on the morphology of the microporous foams, we do many experiments at different saturation temperature and the results were showed in figure 1. The cell size was increasing from 12.4 to 43.5 μm with the temperature. The cells began to deform at high temperature. Then we prepare uniform foams at different pressure. The results were showed in figure 2. It was clear that the cell size was decreasing from 48.5 to 22.4μm with the saturation pressure. In conclusion, the foams with smaller cell size and good shape can be prepared at low temperature and high pressure. So we choose to prepare the graded microporous foams at 28MPa and 50℃.

3.2. The morphology of graded microporous foams

Figure 3 shows the morphology of graded microporous foams after saturating at 28MPa and 50℃ for one hour. It can be seen that gradient structure can be successfully gotten at a high pressure and low temperature condition. The diffusion depth of CO_2 in PMMA matrix is about 1386μm. In the region near the cortex of the foam sample, more CO_2 gas nucleates and foams that induce a high cell density and a thin pore wall. However, the cell size gradually increased toward the region inside the foam sample. Less CO_2 nucleates and foams in that region, so it has a low cell density and a thick pore wall. Unlike other functional graded materials which are made by lamination method[11,12], there is no need to use a bonding agent to prepare a graded microstructure in this study. The solid and foam region can be bonded gradually without laminated layers.

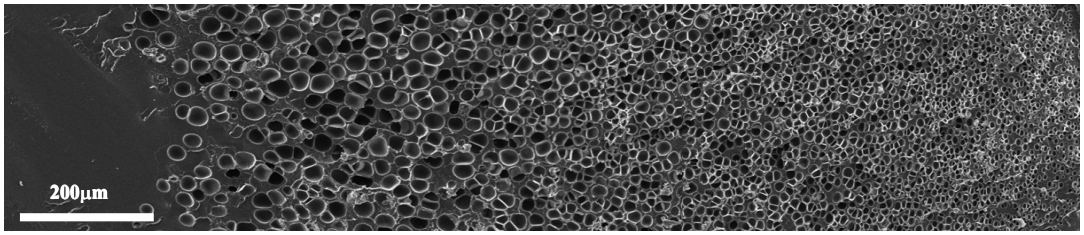

Figure 3. Morphology of graded microporpos foams after saturating at 28MPa and 50℃ for 1 hour

3.3. Cell density and cell size analysis

The cell size and cell density were calculated from the SEM image of graded microporous foams. The image was cut into different regions according to the thickness position. The foamed region represents the low thickness position while the solid region represents the high thickness position. The average cell density and cell size were measured in each region.

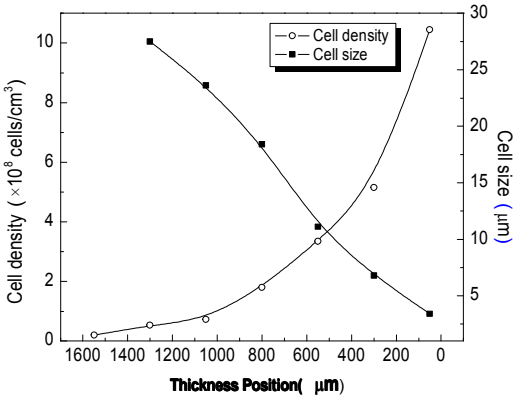

Figure 4. The relationship between the location of the bubbles and the cell size or cell density after saturated at 28MPa and 50℃ for one hour

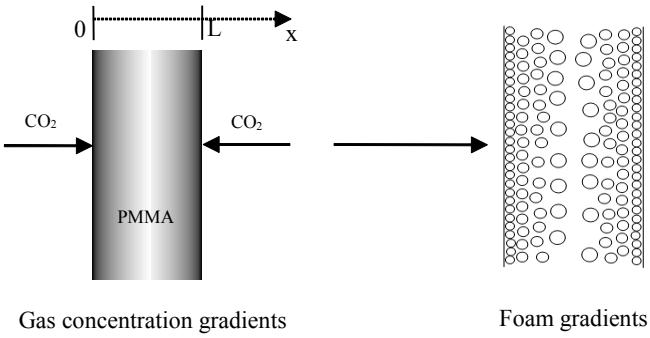

Figure 5. The formation of gas concentration gradients and foam gradients

Figure 4 shows the relationship between the location of the cells and the cell size or cell density. The cell size was changed along with the position of the graded foam. When the cell was near the surface of the foam, the size was small and the smallest size was about 3.4μm. While the size of the biggest cell which located in the deep position of sample was about 27.5 μm, almost 8 times bigger than the smallest one.

The cell density was also gradually changed along with the thickness position which demonstrated an opposite variation of the cell size. In low temperature, the deepest thickness position showed the lowest cell density, as low as 1.96×10^{7}cells/cm^3. The cell density reached 5.15×10^{7}cells/cm^3 at the position of 300 μm and got the highest value in 50 μm, about 1.04×10^{9}cells/cm3, almost 2 orders higher than that in the deeper position.

3.4. The CO_2 adsorption and the formation of concentration gradients

Figure 5 shows the gradient structure formation process. First, the $ScCO_2$ saturated in PMMA solid matrix in which will form a concentration gradient. The final diffusion depth was L/2. Then, after a quick pressure relief, the gas in the saturated sample became unstable and tended to foam. So the concentration gradient will induce a foam gradient. The gas concentration in the surfaces of the sample was quiet high so that there were a large amount of cells in the surfaces and the cell size was small. However, the gas concentration in the centre of the saturated sample was lower, so the cells became bigger and the number of cells was limited.

In addition, the CO_2 can reduce the polymer's glass transition temperature (T_g)[14], the higher the gas concentration, the lower the glass transition temperature. If the temperature is higher than T_g, the polymer tend to foam. In this study, the gas concentration in different position of the sample was different. In the surfaces of the solid matrix, it was easy for the gas immersion. The gas concentration was high there, so it induced a lower T_g and it was easy for that region to foam. However, in the centre of the solid matrix, it took a long time to make the sample fully saturated. The gas concentration low, so the T_g was higher there. It is hard for the sample to foam in that region.

4. Conclusion

（1）The polymer-based functionally graded materials were prepared through a one-step supercritical foaming method which using CO_2 as blowing agent.

（2）The gradient structure can be successfully gotten at a high pressure and low temperature condition. The cell size and cell density were changed gradually along with the thickness position.

（3）The graded microporous structure of the foam came from graded gas concentration which was obtained in the initial saturation process.

Acknowledgements

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References

[1] A.I. Cooper 2000 *J. Mat. Chem.* **10** 207-234
[2] I. Tsivintzelis, A.G. Angelopoulou and C. Panayiotou 2007 *Polymer* **48** 5928-5939
[3] C. Jiang, J. Pi and Q. Pan 2009 *Poly. Mat. Sci. and Eng.* **25** 162-165
[4] P.G. Jessop and W. Leitner1999, *Chemical Synthesis using Supercritical Fluids*(Wiley,VCH, Weinheim)
[5] L. Chen, L. S. Schadler and R. Ozisik 2011 *Polymer* **52** 2899-2909
[6] Bandyo padhyay A, Krishna B, Xue W and Bose S. 2008 *Sci. Mater. Med.* doi: 10.1007/s10856-008-3478-2.
[7] Wang B.L and Mai Y.W 2007 *J. Therm. Stresses.* **30(6)**:523–58.
[8] Groves J and Wadley H 1997 *Compos. B* **28(1-2)** 57-70
[9] Kawasaki A. and Watanabe R. 1997 *Ceram. Int.* **23(1)**73–83
[10] C.C. Zhou, P.Wang and W.Li 2011 *Compos. B* **42** 318-325
[11] Gupta N. 2007 *Mater. Lett.* **61(4–5)** 979–82
[12] Chen Z, Yan Q, Huang Z, Shen Q and Zhang L 2009 *Adv. Mater. Res.* **66** 284–7
[13] Wang H and Li W 2008 *J. Manuf. Sci. Eng. Trans. ASME* **130(2)** 41–49
[14] J.A.R.Ruiz，Jean M.T., M. Pedros and M.Dumon *J. of Supercritical Fluids.***57** *87-94*