Chinese Chemical Letters Vol. 12, No. 2, pp. 183–184, 2001

Preparation of PMMA Foam by Supercritical CO_2 with Ethanol

Zhi Min LIU, GuanYing YANG, Dan LI, Bu Xing HAN*

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

Abstract: Supercritical CO_2 with ethanol as blowing agent foamed poly(methylmethacrylate) (PMMA) fiber at 308.15K and in the pressure range from 12-15MPa. The foam structure was detected using scanning electron microscope. It was found that the concentration of ethanol in the fluid is a major parameter to affect the foam structure.

Keywords: PMMA, Foam, CO_2.

Supercritical (SC) CO_2 can plasticize many amorphous polymers, which reduce the glass transition temperature of the polymers significantly. Recently, it was used as blowing agent to foam amorphous materials such as poly(methyl methacrylate) (PMMA)[1,2], polystyrene (PS)[3], polycarbonate (PC)[4] and poly(ethylene terephthalate) (PET)[4]. In this foaming process, a polymer is saturated with SC CO_2, and followed by rapid depressurization to atmospheric pressure. The microcellular foams can be obtained for some polymer materials. We tried to foam PMMA fiber using supercritical CO_2, and found that pure SC CO_2 and pure liquid ethanol could not foam the polymer at 308.15K in the pressure range from 9 to 15 MPa. However, SC CO_2 with ethanol cosolvent of very low concentration could foam it. In this paper, we report some of the results.

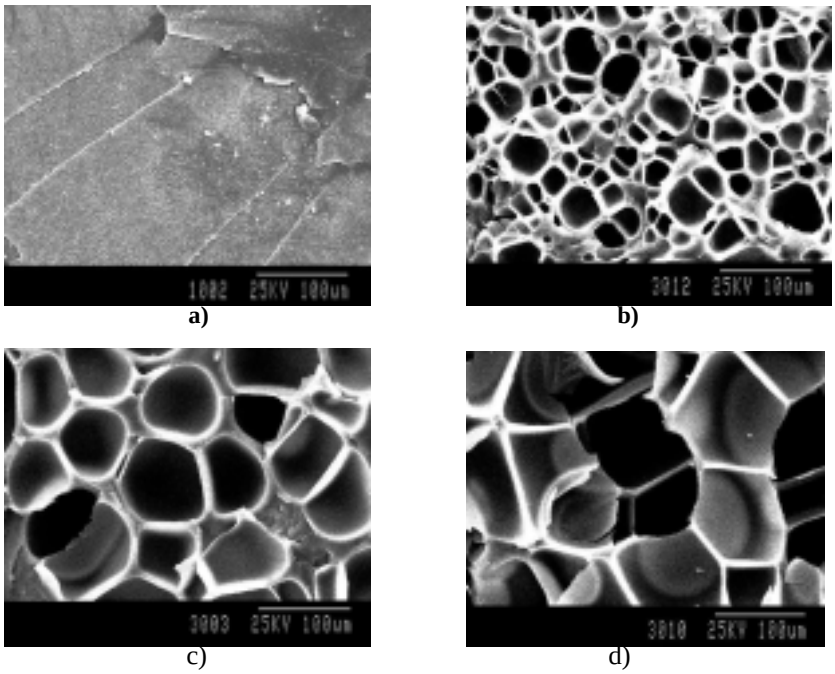
CO_2 with a purity of 99.995% was supplied by Huanxin Gas Company. Ethanol with a purity of 99.9% was purchased from Beijing Chemical Reagent Plant. PMMA fiber of 1mm in diameter was prepared in Institute of Chemistry, Chinese Academy of Sciences.

Experiments were carried out in a stainless steel high-pressure view vessel. PMMA fiber was placed in the vessel. The air in the vessel was removed by vacuum, and suitable amount of ethanol was charged. After thermal equilibrium, CO_2 was charged into the vessel using a high-pressure pump to the desired pressure. The pressure was maintained for 24h to ensure equilibrium absorption of CO_2 by the polymer. The pressure was then rapidly released (in about 4 seconds) to atmosphere pressure. It was observed that the polymer was foamed. After the system was evacuated for 1h, the foamed polymer fiber was taken out.

The foamed polymer fiber was fractured at liquid nitrogen temperature and its cross section was examined using scanning electron microscope (SEM). Some of the results are shown in **Figure 1**. Pure SC CO_2 can not foam the PMMA fiber under the

experimental conditions as shown in **Figure 1a**. Experiment showed that pure CO_2 could not foam the PMMA fiber either at 308.15K. However, SC CO_2 with small amount of ethanol can foam the PMMA fiber, as seen clearly from **Figure 1b** to **Figure 1d**. The mechanism of foaming may be that SC CO_2 swells PMMA fiber and significant amount of the CO_2 and ethanol are absorbed and the polymer is plasticized. Thus foams are formed during the depressurization process. **Figure 1b to Figure 1d** indicate that the size of the cells can be controlled by pressure and ethanol concentration.

Figure 1 SEM images of foamed PMMA by SC CO_2 with different ethanol concentrations and pressures at 308.15 K.
a) 0.00mol/L, 12MPa, b) 0.19mol/L, 15MPa, c) 0.19mol/L, 12MPa, d) 0.47mol/L, 12MPa



a) **b)**

c) d)

Acknowledgment:

The authors are grateful to the National Natural Science Foundation of China for financial support (29725308, 29633020).

References:

1. S. K. Goel, E. J. Beckman, *Polym. Eng. Sci.* **1994**, *34*, 1137.
2. S. K. Gael, E. J. Beckman, *Polym. Eng. Sci.* **1994**, *34*, 1148.
3. K. A. Arora, A J. Lesser, T. J. McCarthy, *Polym. Eng. Sci.* **1998**, *38*, 2055.
4. M. T. Liang, C. M. Wang, in CD Proceeding of the 5th International Symposium on Supercritical Fluids,2000, Atlanda, USA.

Received 3 July, 2000