Polymer 49 (2008) 2430–2434

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polymer Communication

Ultrasonic irradiation enhanced cell nucleation: An effective approach to microcellular foams of both high cell density and expansion ratio

Wentao Zhai [a,b], Jian Yu [a,*], Jiasong He [a,*]

[a] Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[b] Graduate School, Chinese Academy of Sciences, Beijing 100039, China

ARTICLE INFO

Article history:
Received 10 December 2007
Received in revised form 25 March 2008
Accepted 2 April 2008
Available online 4 April 2008

Keywords:
Cell nucleation
Microcellular foam
Ultrasonic irradiation

ABSTRACT

In this work, ultrasonic irradiation (UI) was used as the external energy source to assist polystyrene foaming process by using supercritical CO_2 as the physical blowing agent. It is shown that by introducing the UI at the very start of foaming, the resultant polymer foam exhibited significant and concurrent increase in cell density, i.e., three orders of magnitude, and expansion ratio, i.e., 1–3 times, compared to those without UI. Further experiments indicate that the enhanced cell nucleation induced by UI was the main reason for this unique phenomenon. This method also provided new insight into the mechanism of cell nucleation.

1. Introduction

Over the past decades considerable efforts have been put forth to fabricate polymer microcellular foams. Having a cell size smaller than 10 μm and a cell density greater than 10^9 cells/cm^3, microcellular foams offer reduced material cost while superior mechanical performances, e.g., impact strength, toughness, and fatigue life compared to unfoamed polymers [1]. This makes them highly competitive in many applications such as automotive, construction, sporting equipments, and so on. Moreover, the unique processing characteristics of microcellular foams significantly reduced the energy consumption. However, microcellular foams have inherent lower expansion ratio than conventional foams, because the higher cell density of the former usually restricts cell growth and consequent foam expansion. Therefore, novel approaches are needed for achieving high expansion ratio of microcellular foams along with high cell density.

The microcellular foaming process typically requires much higher nucleation rates than the conventional one. Adding a small amount of nano-size inorganic fillers into polymers as a heterogeneous nucleation agent has been verified as an effective method to enhance the cell nucleation due to the reduction in the energy barrier for the nucleation [2–10]. Generally, there is an increase in cell density about 1–2 orders of magnitude [2–5,8]. However, the cell growth and foam expansion are always limited by the increased stiffness of such formed polymer nanocomposites. Increasing the concentration of foaming agents is also expected to enhance the cell nucleation according to the classical homogeneous nucleation theory [11]. However, the solubility of physical foaming agent, such as CO_2 and N_2, in polymer matrix is very low, and hence the enhancement of the cell nucleation and growth by increasing pressure would confront very high cost from a processing standpoint, including more energy consumption, more investment for the equipment safety at high working pressure. Moreover, the corresponding decrease of cell size often offsets the effectiveness in increasing the expansion ratio. Recently, Siripurapu et al. [7,12] found that the cell density significantly increased by physically constraining a film between external hard surfaces during the foaming process. They attributed it to the reduction in individual cell coalescence. Obviously, it is very difficult to obtain microcellular foams with high expansion ratios.

It is known that the ultrasound wave generates a number of bubbles in a liquid, whose collapse causes local extreme conditions, e.g., high temperature, high pressure and other effects, e.g., microjetting, turbulence, acoustic streaming [13]. They form ideal microreactors for liquid phase chemical reactions [14]. In polymer melts, the ultrasonic irradiation (UI) was evidenced as a powerful tool to degrade polymers [15], disperse nanoparticles [16,17] and so on. The UI was also utilized to assist melt extrusion foaming of polymers because the "negative" pressure generated during the rarefaction phase of ultrasound wave improved the cell nucleation [18–20]. Only a slight effect observed in increasing the cell density of polymer foams might be resulted from the significant cell coalescence at elevated foaming temperature.

* Corresponding authors. Tel./fax: +86 10 62613251.
E-mail addresses: yuj@iccas.ac.cn (J. Yu), hejs@iccas.ac.cn (J. He).

0032-3861/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.04.002

In the present communication, we report the solid state foaming of polystyrene (PS) under UI by using temperature rising process and supercritical CO_2 ($scCO_2$) as the physical foaming agent. PS was selected because of its broadly reported foaming behavior, and the UI was used as the external energy source. The cell density was increased about three orders of magnitude and expansion ratio about 1–3 times, compared with those without UI. This significant and concurrent increase in cell density and expansion ratio has not been reported previously for microcellular polymer foaming.

2. Experimental part

2.1. Materials and sample preparation

The polystyrene used was PS 666D ($M_w = 243{,}000$, $M_n = 36{,}000$), Yanshan Petrochemical Corporation, China. The CO_2 with a purity of 99.9% was purchased from Beijing Analytical Gas Factory. The PS granules were dried at 80 °C under vacuum for 24 h, and sheets with 1 mm thickness were obtained by melt compression at 200 °C. The sheets were cut into specimens with dimensions of 5×25 mm for batch foaming.

2.2. Gas solubility measurement

The PS sheet was enclosed in a high-pressure vessel. The vessel was flushed with low-pressure CO_2 for about 3 min and preheated to 35 °C with a water bath, followed by increasing the pressure to 12 MPa and maintained for different intervals of time with or without UI. Then, the samples were removed following a rapid venting of the vessel, and immediately transferred to a digital balance (sensitivity of 0.1 mg) to record the mass loss as a function of time. In the saturation process with UI, the high-pressure vessel was put into the ultrasonication water bath running at a frequency of 20 kHz. The temperature of the ultrasonication water bath was controlled by a circulating chiller.

2.3. Batch foaming

The basic process of polymer saturation was the same to that of gas solubility measurement without UI. After the saturation for 10 h, the samples were removed from the vessel after a rapid quench of pressure and transferred within 1 min to the ultrasonication water bath running at different procedures. After 30 s of foaming, the foamed samples were quenched in cold water.

2.4. Characterization

The mass densities of samples before (ρ) and after (ρ_f) foaming treatment were determined via water displacement method according to ISO 1183-1987. The uptake of water by the sample can be neglected during the measurement due to a smooth skin and closed cells of these foamed samples. The morphology of foamed samples was observed with a Hitachi S-530 scanning electron microscope (SEM). The samples were freeze-fractured in liquid nitrogen and sputter-coated with gold. The cell size and cell density were determined from SEM micrographs. The cell diameter was the average of sizes of at least 100 cells on the SEM micrographs. The cell density (N_0), the number of cells per cubic centimeter of solid polymer, was determined from Eq. (1):

$$N_0 = \left[\frac{nM^2}{A}\right]^{3/2} \times \mathrm{VE} \tag{1}$$

where n is the number of cells on the SEM micrograph, M the magnification factor, A the area of the micrograph (cm^2), and VE the expansion ratio of the foamed sample, which can be estimated as:

$$\mathrm{VE} = \frac{\rho}{\rho_f} \tag{2}$$

3. Results and discussion

Samples were saturated in the $scCO_2$, and then foamed in a water bath with UI and without UI for comparison. The foaming temperature was as low as 50–90 °C to prevent the possible cell coalescence during the foaming process. Fig. 1(a) shows a typical SEM micrograph of PS foam obtained by saturating at 20 MPa and 35 °C and foaming at 70 °C for 30 s with UI. The resultant PS foams exhibited uniform and well-defined closed cells with diameters of about 1 μm. Obviously, this cell size was much less than that of PS foam prepared without UI as shown in Fig. 1(b).

The influence of UI on the PS foaming was investigated in a range of saturation pressures (8–20 MPa) and foaming temperatures (50–90 °C). The results of the cell density and expansion ratio are shown in Fig. 2. In the case of PS foaming with UI, the cell density of PS foam was significantly increased about hundreds to thousands times and expansion ratio 2–4 times by comparison with those foamed without UI. Moreover, as shown in Fig. 2(b), a high cell density of 2.3×10^{10} cells/cm^3 and an expansion ratio of 2.4 were obtained at a saturation pressure as low as 8 MPa with the assistance of UI, while they were obtained only at 20 MPa without UI. These results indicate that the introduction of UI significantly

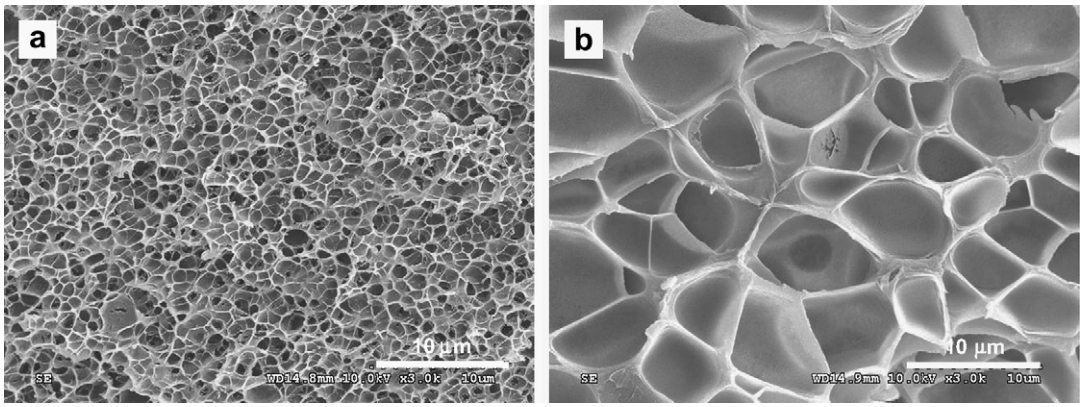

Fig. 1. SEM micrographs of foamed PS samples obtained by foaming with UI (a) and without UI (b). Saturation conditions: 20 MPa, 35 °C; foaming conditions: 70 °C, 30 s.