



Polymer Communication

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

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ABSTRACT

In this work, ultrasonic irradiation (UI) was used as the external energy source to assist polystyrene foaming process by using supercritical CO₂ 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.

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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 10⁹ cells/cm³, 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 CO₂ and N₂, 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., micro-jetting, turbulence, acoustic streaming [13]. They form ideal micro-reactors 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.

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In the present communication, we report the solid state foaming of polystyrene (PS) under UI by using temperature rising process and supercritical CO₂ (scCO₂) 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 CO₂ 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 CO₂ 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):

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

where n is the number of cells on the SEM micrograph, M the magnification factor, A the area of the micrograph (cm²), and VE the expansion ratio of the foamed sample, which can be estimated as:

$$VE = \frac{\rho}{\rho_f} \quad (2)$$

3. Results and discussion

Samples were saturated in the scCO₂, 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/cm³ 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

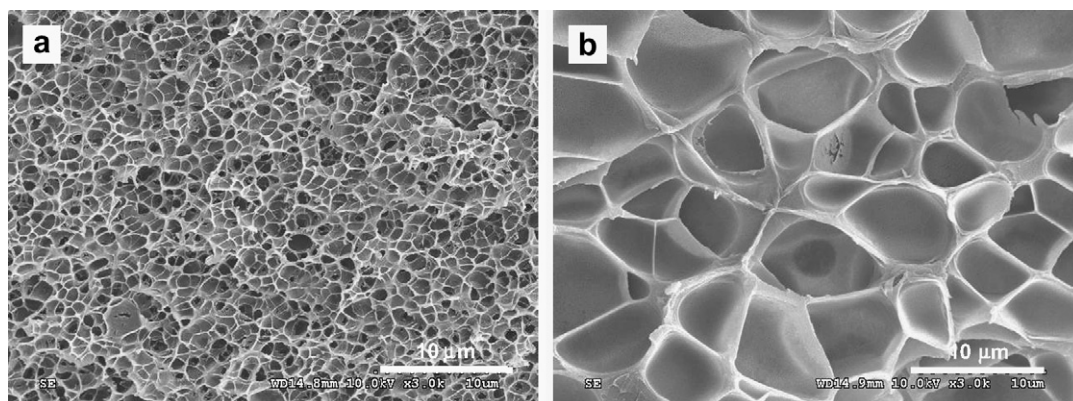


Fig. 1. SEM micrographs of foamed PS samples obtained by foaming with UI (a) and without UI (b). Saturation conditions: 20 MPa, 35 °C; foaming conditions: 70 °C, 30 s.

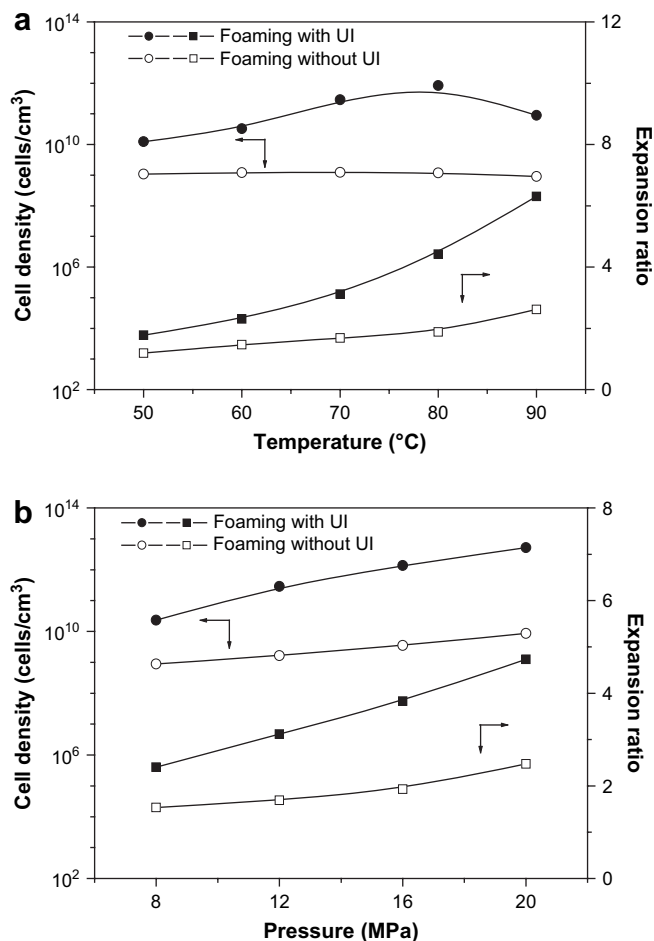


Fig. 2. The cell density and expansion ratio of PS foams obtained by saturating at 12 MPa and foaming at various temperatures (a), and saturating at various pressures and foaming at 70 °C (b), with and without UI.

enhanced the cell nucleation and reached high cell density and expansion ratio simultaneously. The UI has much significant effect in increasing the cell density and expansion ratio than the saturation pressure does.

It is well established that three important stages, i.e., nucleation, growth and coalescence, determine the cell morphology of polymer foams. In the present study, it is important to know the working mechanism of UI in the foaming process. Two series of tests were designed to answer two questions: when should the UI be started and how long should it be lasted? Consequently, the UI was introduced at different starting time and lasted for different length of time at the foaming temperature of 70 °C and the total foaming time of 30 s. Fig. 3 shows the cell density and expansion ratio vs. starting time of UI and length of UI time. As shown in Fig. 3(a), the cell density of PS foams was 2.9×10^{11} cells/cm³ by introducing the UI at the very start of foaming, while it decreased to 3.2×10^9 by introducing UI 3 s later, and to 2.3×10^9 cells/cm³ 5 s later, and then leveled off. As shown in Fig. 3(b), the cell density was only 1.2×10^9 cells/cm³ by foaming without UI; it increased to 2.3×10^{10} cells/cm³ for UI length of 2 s, and to 1.4×10^{11} cells/cm³ for 3 s and to 2.3×10^{11} cells/cm³ for 5 s, and then leveled off. These results indicate that the earlier the UI was used, the more significant increase in cell density. The UI length of 5 s, which was just the period of cell nucleation [5,21], was enough to affect the ultimate cell density. Therefore, the function of UI was critically and mostly on the cell nucleation.

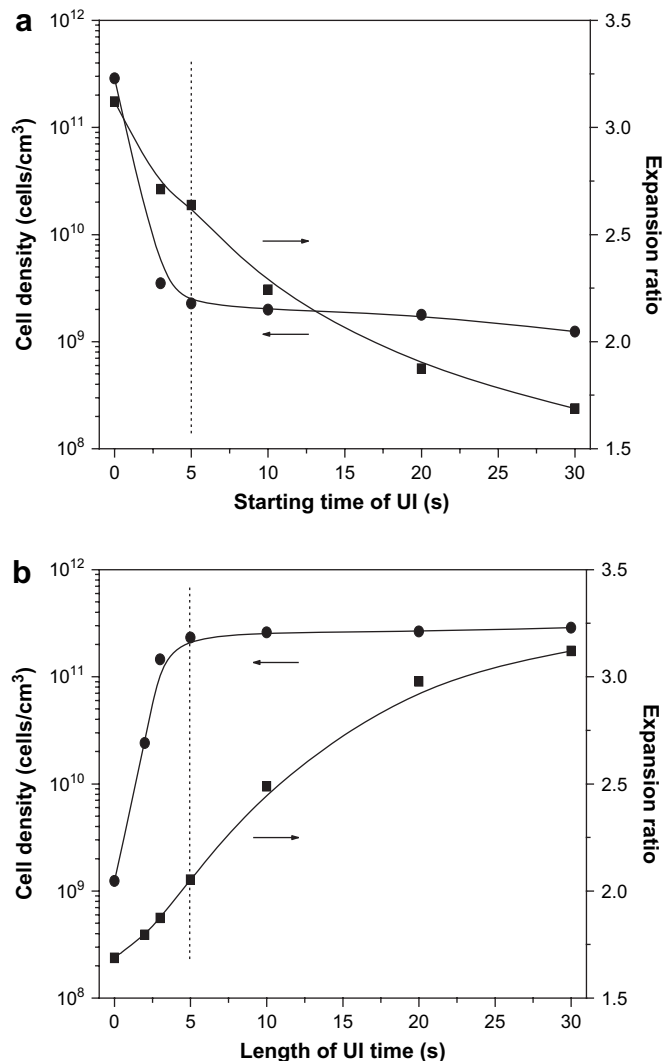


Fig. 3. The cell density and expansion ratio of PS foams (a) as a function of the starting time of UI, where the UI was introduced at this time after the start of foaming and lasted to the end of foaming, and (b) as a function of the length of UI time, where the UI was introduced at the start of foaming and lasted for this length of time. The total foaming time was 30 s. Saturation conditions: 12 MPa, 35 °C; foaming conditions: 70 °C.

It is known that an enhancement in cell nucleation often increases the cell density and decreases the cell size, these two effects inversely affect the expansion ratio of the final foam, which was the main reason for the low expansion ratio of most microcellular foams. However, as shown in Fig. 3(b), the expansion ratio of obtained PS foams obviously increased from 1.7 to 3.2 and the cell density from 1.2×10^9 to 1.4×10^{11} cells/cm³ with increasing the length of UI time. According to the results shown in Supplementary data, the introduction of UI promoted the cell growth, and did not induce obvious cell coalescence. Therefore, both the enhanced cell nucleation and cell growth by UI account for high expansion ratio of final foams and high growth rate of expansion ratio with foaming time (shown in Supplementary data).

To further investigate the influence of UI on the cell nucleation, PS samples were saturated at 2 MPa and 35 °C, and then foamed at 70 °C for 300 s with and without UI. It is shown in Fig. 4(a) that saturated PS sample did not foam without UI, because the foaming temperature was lower than the T_g of the saturated PS [11,21], which is about 87 °C under 2 MPa of CO₂ [22]. Although the UI itself does not generate cell structure in bulk PS samples either, the

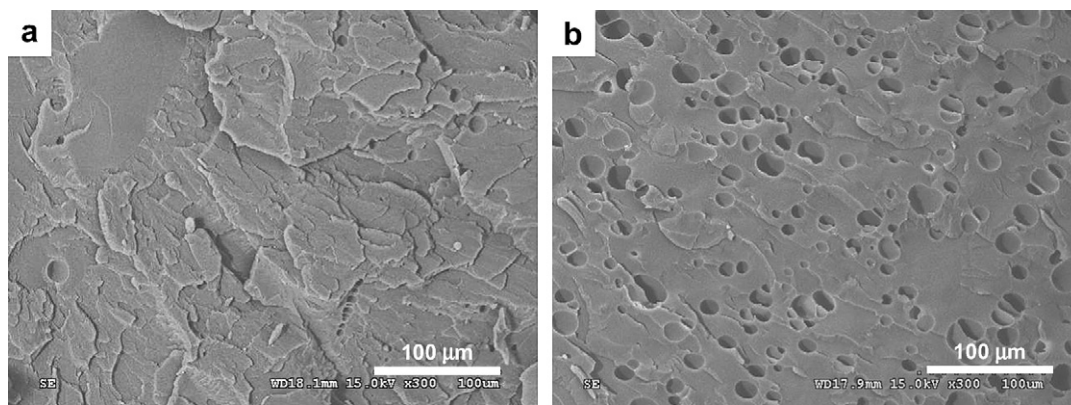


Fig. 4. SEM micrographs of foamed PS samples obtained by foaming without UI (a) and with UI (b). Saturation conditions: 2 MPa, 35 °C; foaming conditions: 70 °C, 300 s.

saturated PS samples could be foamed under UI, which is shown by the obvious cell structure in Fig. 4(b). It is known that polymers cannot be foamed at glassy state mostly due to the restriction of cell nucleation and/or cell growth [21]. The high intensity of ultrasound wave excited the motion of CO₂ molecules and decreased the energy barrier for cell nucleation. This seems to explain the formation of well-defined cells in final foams, although PS was in its glass state during the foaming process. This supplies more evidence that the introduction of UI enhanced the cell nucleation.

The above analysis was further proved by two series of experiments, where the PS sorption of CO₂ was conducted at 12 MPa and 35 °C with and without UI. In the study, the uptake experiments were repeated three times for one condition to show the experimental errors of CO₂ solubility measurements. As shown in Fig. 5, the difference between the two CO₂ uptake curves was obvious, especially at longer saturation time. PS samples exhibited a higher CO₂ solubility and quick CO₂ diffusion rate in the presence of UI. It is well established that the absorbed CO₂ molecules exist in pre-existing holes, including the free volume and the excess free volume in polymer matrix [23]. So, the increase in CO₂ solubility means much more new free volume holes and/or larger hole size were induced in the presence of UI in the saturated PS [24]. This influence of UI on free volume was also expected to affect PS foaming process. As suggested by Martini et al. [25], free volume holes which had similar size to critical nuclei would act as the

potential nuclei sites, and high content of free volume hole and/or larger hole size would facilitate the formation of stable nuclei in PS foaming process. Moreover, the high motion ability of CO₂ molecules increased the diffusion rate of CO₂ in PS matrix [26], which facilitated the cell growth and foam expansion in PS foaming process to some extent.

4. Conclusion

The results presented in this communication demonstrate that the introduction of UI decreased the energy barrier for cell nucleation and significantly increased the cell density in PS foams. Furthermore, it is found that the simultaneous increase in the cell density and expansion ratio was realized in the presence of UI. This unique phenomenon is supposed to be an effective method to fabricate microcellular foams having high expansion ratios under less severe processing conditions, and to provide new insight into the mechanism of cell nucleation.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at [10.1016/j.polymer.2008.04.002](http://dx.doi.org/10.1016/j.polymer.2008.04.002).

References

- [1] Suh NP. *Macromol Symp* 2003;201:187–201.
- [2] Lee LJ, Zeng C, Cao X, Han X, Shen J, Xu G. *Compos Sci Technol* 2005;65:2344–63.
- [3] Zeng C, Han X, Lee LJ, Koelling KW, Tomasko DL. *Adv Mater* 2003;15:1743–7.
- [4] Cao X, Lee LJ, Widya T, Macosko C. *Polymer* 2005;46:775–83.
- [5] Zhai WT, Yu J, Wu LC, Ma WM, He JS. *Polymer* 2006;47:7580–9.
- [6] Okamoto M, Nam PH, Maiti P, Kotaka T, Hasegawa N, Usuki A. *Nano Lett* 2001;1:295–8.
- [7] Siripurapu S, DeSimone JM, Khan SA, Spontak RJ. *Adv Mater* 2004;16:989–94.
- [8] Ema Y, Ikeya M, Okamoto M. *Polymer* 2006;47:5350–9.
- [9] Yuan MJ, Turg LS. *Polymer* 2005;46:7273–92.
- [10] Werner P, Verdejo R, Wöllecke F, Altstädt V, Sandler J. *Adv Mater* 2005;17:2864–9.
- [11] Arora KA, Lesser AJ, McCarthy TJ. *Macromolecules* 1998;31:4614–20.
- [12] Siripurapu S, DeSimone JM, Khan SA, Spontak RJ. *Macromolecules* 2005;38:2271–80.
- [13] Young FR. *Cavitation*. London: Imperial College Press; 1999.
- [14] Palchik O, Kataby G, Mastai Y, Gedanken A. *Adv Mater* 1999;11:1289–92.
- [15] Kim H, Lee JW. *Polymer* 2002;43:2585–9.
- [16] Wang J, Severtson SJ, Stein A. *Adv Mater* 2006;18:1585–8.
- [17] Swain SK, Isayev AI. *Polymer* 2007;48:281–9.

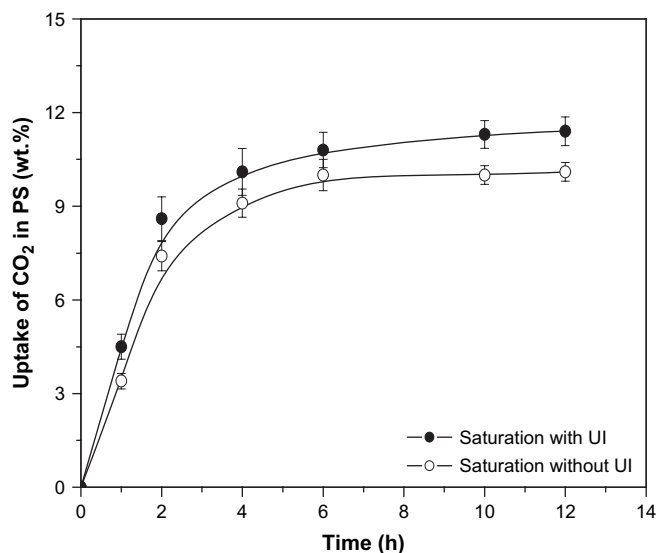


Fig. 5. Uptake of CO₂ in PS samples for different saturation time, assisted with and without UI. Saturation conditions: 12 MPa, 35 °C.

- [18] Byon SK, Youn JR. *Polym Eng Sci* 1990;30:147–52.
- [19] Youn JR, Park H. *Polym Eng Sci* 1999;39:457–68.
- [20] Isayev AI, Mandelbaum S. *Polym Eng Sci* 1991;31:1051–6.
- [21] Krause B, Mettinkhof R, van der Vegt NFA, Wessling M. *Macromolecules* 2001;34:874–84.
- [22] Zhang Z, Handa YP. *J Polym Sci Part B Polym Phys* 1998;36:977–82.
- [23] Bonavoglia B, Storti G, Morbidelli M, Rajendran A, Mazzotti M. *J Polym Sci Part B Polym Phys* 2006;44:1531–46.
- [24] Hong X, Jean YC, Yang H, Jordan SS, Koros WJ. *Macromolecules* 1996;29:7859–64.
- [25] Martini JE. MS thesis. Mechanical Engineering Department, MIT; 1981.
- [26] Kuipers MWA, van Eck D, Kemmere MF, Keurentjes JTF. *Science* 2002;298:1969–71.