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Phenomenology of bubble nucleation in the solid-state nitrogen–polystyrene microcellular foams

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Abstract

Experimental results on bubble nucleation in the solid-state polystyrene–nitrogen system are presented. It was found that the bubble nucleation occurs over a period of approximately 30 s, and is not instantaneous as previously suggested. Over the range of nitrogen pressures explored, 4–14 MPa, the cell nucleation density increased exponentially. However this increase was many orders of magnitude less than predicted by the homogeneous nucleation model, indicating that the classical theory may not be applicable to nucleation in thermoplastic polymers near the glass transition.

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1. Introduction

Microcellular foams refer to thermoplastic foams with a very large number, typically exceeding 10^8 cells/cm^3, of very small bubbles, of order 10 μm diameter. The idea to introduce such small bubbles in thermoplastics was originally motivated by the possibility to reduce the amount of polymer used in a number of applications that use solid polymers, but do not need the full mechanical properties of the solid polymers.

Since the first patent on a process to make microcellular foams was issued [9], a number of efforts have been made to enable large-scale production of these novel materials. The strongest emphasis has been on development of extrusion processes (see, for example [10,15,16]).

Other approaches include a thermoforming process [6], and a sintering process where gas-saturated powder is first compacted and then heated to create a net-shaped part [14]. A semi-continuous process to convert a roll of film to a roll of solid-state microcellular foam has been described by Kumar and Schirmer [8], which presents an alternative to extrusion for production of foam sheets.

As the interest in this technology grows and we get closer to commercial realization, an understanding of the development of microstructure in these processes becomes important both from the viewpoint of process control as well as for optimization of the properties of the final product. For the extrusion-based processes, where the bubbles are formed in a polymer melt, a number of studies have been made that address the issues related to the growth of bubbles (see, for example [1,5,12,13]). This subject has been recently reviewed by Ramesh [11] where one can find the related bibliography.

In this paper we present experimental results on bubble nucleation in solid-state foaming of polystyrene using nitrogen as a blowing agent. The basic batch process used has been described previously (e.g. [7]). The term 'solid-state' is meant to convey an essential difference from the extrusion processes, namely that in this process the bubbles are formed in the rubbery state, near the glass transition temperature, and the polymer is never melted. Thus while surface tension effects play an important role in the bubble growth dynamics of extrusion foams, these effects are not important in the

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solid-state process. Instead, the viscoelastic properties of the gas–polymer system become important.

2. Experimental

Dow XP 6065 polystyrene with average molecular weight of 200,000 was injection molded to make circular discs of 50 mm diameter and 1.55 mm thickness. These discs were saturated with nitrogen at 2000 psi (13.79 MPa) pressure in a pressure vessel maintained at room temperature. The gas-saturated discs were heated in a glycerine bath at 115 °C. A Haake circulator/controller Model E3 was used to heat and circulate the glycerine. The bath temperature was controlled to ±0.2 °C.

To study the dynamics of cell nucleation and growth, the specimens were heated for different lengths of time ranging from 4 s to 4 min, and then quenched in room temperature water. The specimens were fractured after dipping in liquid nitrogen, and the exposed structure was studied using a scanning electron microscope (SEM). The micrographs were analyzed and the cell size and cell density were determined according to procedure previously described [7]. The cell density data reported is the number of cells per cubic centimeter of the solid polymer.

To explore the effect of nitrogen saturation pressure on cell nucleation, polystyrene samples were saturated at pressures of (a) 600 psi (4.14 MPa), (b) 1000 psi (6.89 MPa), (c) 1500 psi (10.34 MPa), and (d) 2000 psi (13.79 MPa), respectively, and foamed at 115 °C. The cell nucleation densities were determined as described above.

3. Results

3.1. Dynamics of bubble nucleation

One objective in performing this set of experiments was to see if there is significant additional nucleation after the initial ‘spontaneous’ nucleation. From micrographs of foam samples, the cell density was determined at different foaming times. The size of each bubble in the micrographs was determined to get an idea of cell size distribution at different foaming times. Fig. 1 shows the number of cells in different size ranges at foaming times of 10, 15, 20, and 30 s, respectively. Note that up to a foaming time of 10 s, all cells are 6 μm or less. However, at a later time, say 20 s, 18 bubbles out of 57 in the micrograph, or about 30%, are 6 μm or less, suggesting that these smaller bubbles were nucleated later. At 30 s, only two bubbles out of a total of 47 in the micrograph are less than 5 μm suggesting that the rate of nucleation has slowed down considerably by this time due to depletion of the driving force.

Cell density as function of foaming time is shown in Fig. 2. We see that the cell density rises till about 30 s foaming time and then starts to decrease reaching a limiting cell density of

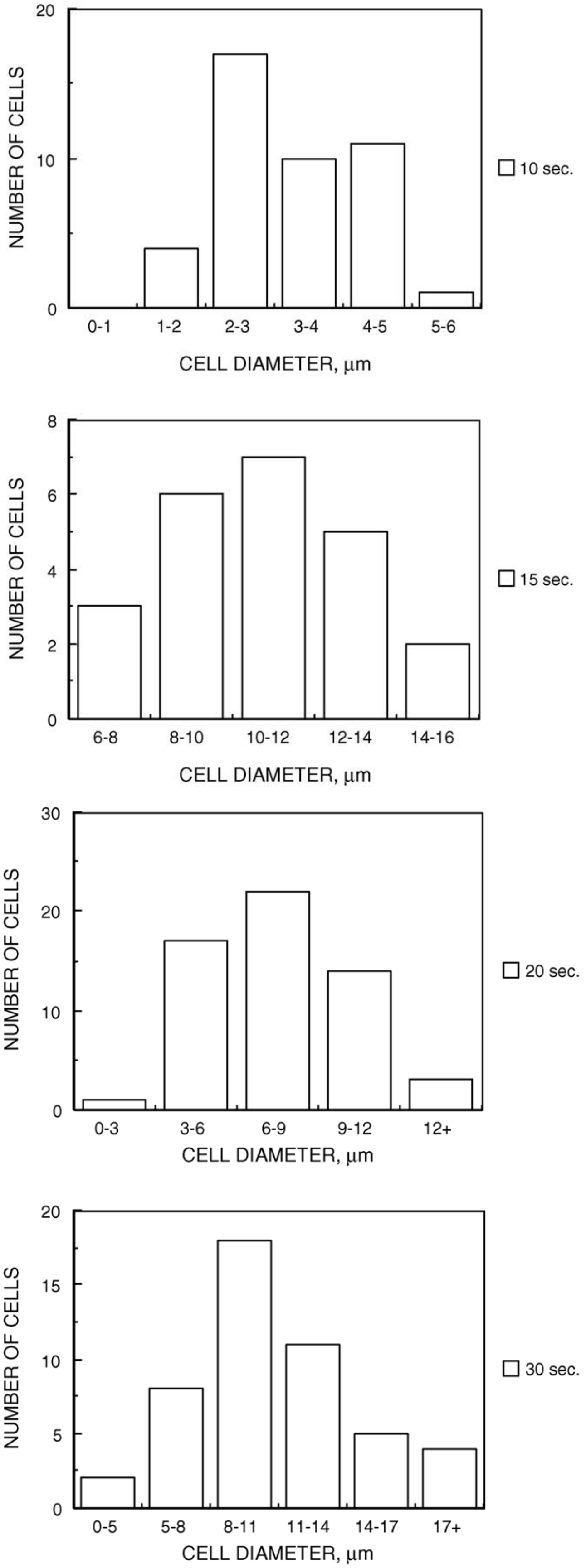

Fig. 1. Histogram of cell size distribution in the early stages of foaming.

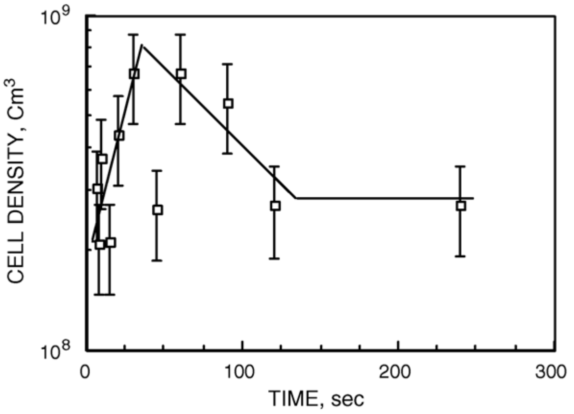

Fig. 2. Plot of cell density as a function of foaming time.

about 2×10^8 cells/cm^3 after 90 s of foaming. The early cell density rise has been plotted in Fig. 3 where we see that up to about 30 s of foaming, the cell density can be considered to increase exponentially with time. Beyond this time, the rate of nucleation decreases, as the driving force for nucleation gets depleted.

Our data shows that most of the nucleation of cells in the nitrogen–polystyrene system takes place over a finite time which is at least on the order of 30 s and is not ‘instantaneous’ as assumed by previous investigators [3]. The cell density starts to decrease after the cells get large enough to hit each other. This happens at a cell size of approximately 12 μm in this experiment. As the cells grow further they coalesce, reducing the cell density. This phenomenon is evident in Fig. 4, where cell density has been plotted as a function of cell size. Although additional nucleation is possible after cells begin to coalesce, it is expected to be minimal, given that the number of ‘young’ cells, under 5 μm in size, at 30 s is approximately 5% of total cells (Fig. 1).

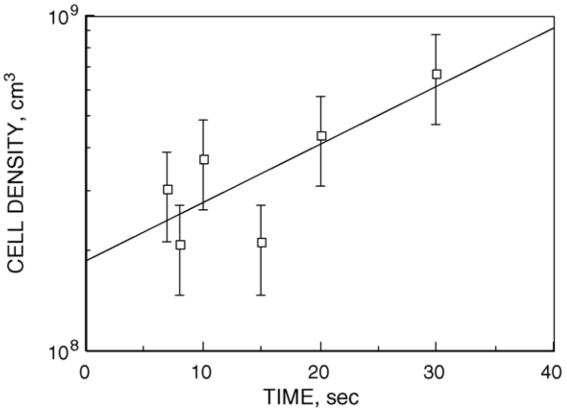

Fig. 3. Cell density as a function of foaming time in the early stages of foaming.

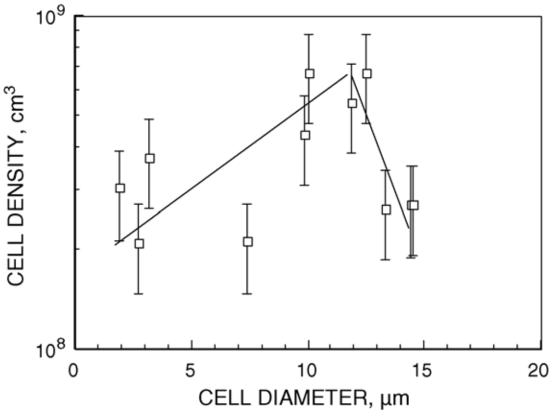

Fig. 4. Cell nucleation density as a function of cell size.

3.2. *Effect of nitrogen pressure on cell nucleation*

Fig. 5 shows micrographs of samples foamed at different gas saturation pressures. The foaming time was kept low in order to prevent cell growth to a point where coalescence can occur, affecting the cell density measurements. An increase in the number of cells with higher saturation pressure can be seen from these micrographs. Cell density data has been plotted in Fig. 6 as a function of nitrogen saturation pressure. Note that the cell density has been plotted on a log scale. We see that the number of cells nucleated increases exponentially with saturation pressure, at least for the range of saturation pressures in our experiments.The observed relationship between the cell nucleation density and the saturation pressure can be described by

$$N_0 = A\, e^{\alpha P_s} \qquad (1)$$

where N_0 = number of cells/cm^3, and, P_s = saturation pressure in atm.

In Eq. (1) A and α are empirical constants. The solid line in Fig. 6 is described by

$$N_0 = (1.46 \times 10^6)\, e^{0.0454 P_s} \qquad (2)$$

4. Discussion

The first goal of our experiments was to establish the time over which most of the cell nucleation takes place. These experiments were done with pure polystyrene (with no additives). As there is no second phase of another material present, homogeneous nucleation is believed to be the mechanism responsible for cell nucleation. Colton and Suh [3] has calculated homogeneous and heterogeneous nucleation rates in polystyrene at different nitrogen saturation pressures as a function of the concentration of a nucleating agent such as zinc stearate. In the second part of this paper [4], Colton compares the predicted nucleation rates to the experimentally obtained cell nucleation density. In order to make this direct comparison Colton made an implicit assumption that

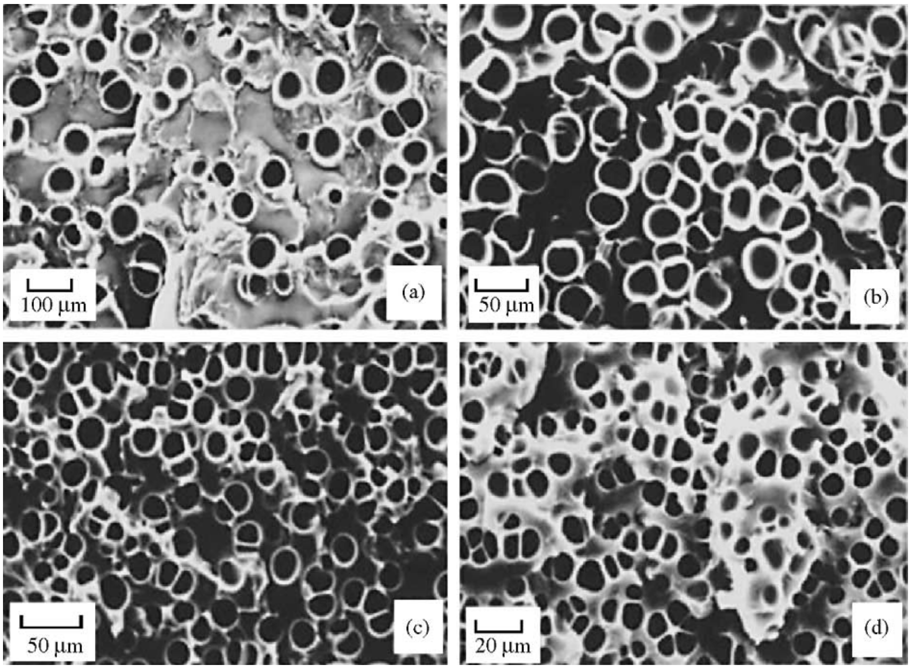

Fig. 5. Scanning electron micrographs of microcellular polystyrene samples nucleated at different nitrogen saturation pressures: (a) 600 psi (4.14 MPa); (b) 1000 psi (6.89 MPa); (c) 1500 psi (10.34 MPa); and (d) 2000 psi (13.79 MPa). The nucleation density increases exponentially with nitrogen saturation pressure.

all nucleation occurs within one second. In other words, if we assume that cell nucleation is ‘spontaneous’ and that all nucleation occurs in the first second, then the nucleation rate also gives the total number of cells per cubic centimeter. Colton has implicitly made this assumption in comparing his calculated nucleation rates to the experimental cell nucleation densities. In this work, Colton [2,4] experimentally investigated the effect of various concentrations of zinc stearate that provided heterogeneous nucleation sites on cell nucleation density. As a baseline he also got data on pure polystyrene with no nucleating agent. Thus this baseline data with no additives is directly comparable to the experiments in this study where all experiments were performed on pure polystyrene without any additives.

The data on cell size distribution in Fig. 1 shows the presence of young or recently nucleated cells up a time of 30 s. Note that at 10 s all bubbles are young, that is, have a diameter of 5–6 μm or less. The fraction of young bubbles decreases with time as expected. At a time of 30 s, the young bubbles comprise less than 5% of the total cells, indicating that the driving force for cell nucleation has largely depleted by this time. Thus cell nucleation in this system occurs over a time of approximately 30 s.

In Fig. 7 we have plotted the predicted cell density for homogeneous nucleation and the experimental cell nucleation data at different nitrogen saturation pressures. Colton’s baseline data with no additives is seen to be in good agreement with our measurements. Note that our foaming temperature

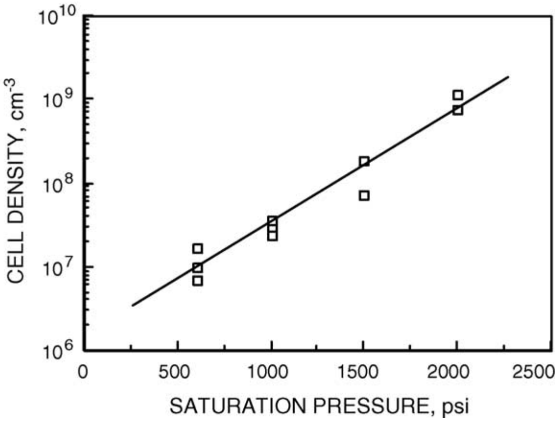

Fig. 6. Plot of cell nucleation density as a function of nitrogen saturation pressure (1000 psi = 6.895 MN/m^2).

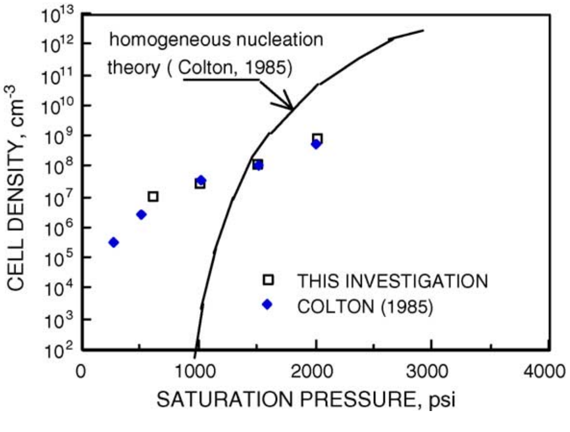

Fig. 7. Comparison of homogeneous nucleation theory and experimental results (1000 psi = 6.895 MN/m^2).

was 115 °C while Colton's calculations and experiments were conducted at 110 °C. It is clear from Fig. 7 that there is a gross disagreement between the experimental data and the cell density predicted by the homogeneous nucleation theory. For an increase in saturation pressure from 1000 psi (6.89 MPa) to 2000 psi (13.79 MPa), the homogeneous nucleation theory predicts the cell density to increase from 10^2 to 10^{10} cells/cm^3—an increase of eight orders of magnitude. The measured cell density increases from 5×10^7 at 1000 psi (6.89 MPa) to 9×10^8 at 2000 psi (13.79 MPa)—a significant, 20-fold increase, but some six orders of magnitude less that predicted. The cell nucleation phenomenon is much less sensitive to saturation pressure than is suggested by the homogeneous nucleation theory. In terms of predictions at a given saturation pressure, the theory is not consistent. For example, at 1000 psi (6.89 MPa) saturation pressure, the measured cell density is about five orders of magnitude higher than the predicted value of 10^2 cells/cm^3. At 2000 psi (13.79 MPa) saturation pressure, the measured cell density is about two orders of magnitude lower than the theoretical prediction. Clearly, the cell nucleation phenomenon in polystyrene is not well described by the classical homogeneous nucleation theory.

There is another phenomenon that likely has bearing on the discrepancy between the homogeneous nucleation theory and experimentally observed cell density. Initially, when cells nucleate, there is a large surface area of bubble surfaces created and the system is not in thermodynamic equilibrium. The total system energy can be decreased by an increase in the size of the cells, thus reducing the total interfacial area. Thus there is a preference for the diffusional mass transfer process to assist in cell growth, at the expense of continued cell nucleation. This interfacial area reduction process is termed Ostwald ripening (see, for example [17,18]). Thus Ostwald ripening, which comes into play immediately after initial nucleation, tends to reduce the cell density, thereby promoting the observed discrepancy between experiment and homogeneous nucleation model.

5. Summary

In this study bubble nucleation in the solid-state polystyrene–nitrogen system was investigated. It was found that the bubble nucleation occurs over a period of approximately 30 s, and is not instantaneous as previously suggested. Over the range of nitrogen pressures explored, 4–14 MPa, the cell nucleation density increased exponentially. However this increase was many orders of magnitude less than predicted by the homogeneous nucleation model, indicating that the classical theory may not be applicable to nucleation in thermoplastic polymers near the glass transition.

References

[1] A. Arefmanesh, S.G. Advani, Non-isothermal foam growth in polymeric foams, in: V. Kumar, S.G. Advani (Eds.), Cellular Polymers, MD-vol. 38, ASME, 1992, pp. 25–40.

[2] J.S. Colton, The nucleation of microcellular thermoplastic foam, PhD Thesis, Mechanical Engineering, MIT, 1985.

[3] J. Colton, N.P. Suh, Nucleation of microcellular thermoplastic foam with additives. Part I. Theoretical considerations, Polym. Eng. Sci. 27 (7) (1987) 485.

[4] J. Colton, N.P. Suh, Nucleation of microcellular thermoplastic foam with additives. Part II. Experimental results and discussion, Polym. Eng. Sci. 27 (7) (1987) 493.

[5] A.N. Gent, D.A. Tompkins, Nucleation and growth of gas bubbles in elastomers, J. Appl. Phys. 40 (6) (1969) 2520–2525.

[6] V. Kumar, N.P. Suh, A process for making microcellular thermoplastic parts, Polym. Eng. Sci. 30 (20) (1990) 1323–1329.

[7] V. Kumar, J.E. Weller, Production of microcellular polycarbonate using carbon dioxide for bubble nucleation, ASME J. Eng. Ind. 116 (1994) 413–420.

[8] V. Kumar, H. Schirmer, A semi-continuous process to make microcellular foams, US Patent No. 5,684,055 (November 1997).

[9] J.E. Martini-Vvedensky, N.P. Suh, F.A. Waldman, U.S. Patent No. 4,473,665 (1984).

[10] C.B. Park, A.H. Behravesh, R.D. Venter, A strategy for the suppression of cell coalescence in the extrusion of microcellular high-impact polystyrene foams, in: K.C. Khemani (Ed.), Polymer Foams Science and Technology, ACS Symposium Series 669, 1997, pp. 115–129.

[11] N.S. Ramesh, Bubble growth in thermoplastic foam extrusion, in: V. Kumar (Ed.), Porous, Cellular and Microcellular Materials, MD-vol. 82, ASME, 1998, pp. 71–74.

[12] N.S. Ramesh, N. Malwitz, Bubble growth dynamics in olefinic foams, in: K.C. Khemani (Ed.), Polymer Foams Science and Technology, ACS Symposium Series 669, 1997, pp. 115–129.

[13] J.H. Saunders, R. Hansen, The mechanism of foam formation, in: K.C. Fritsch, J.H. Saunders (Eds.), Plastic Foams, Marcel Dekker, 1972, p. 39.

[14] K.A. Seeler, V. Kumar, Net-shape sintered microcellular foam parts, SPE Technical Papers, vol. XLIII, 1997, pp. 2032–2036.

[15] B. Seibig, Q. Huang, D. Paul, Design of a novel extrusion system for manufacturing microcellular polymer, SPE ANTEC Technical Papers, vol. XLV, 1999, pp. 2090–2094.

[16] M. Shimbo, K. Nishida, S. Nishikawa, T. Sueda, M. Eriguti, Foam extrusion technology for microcellular foams, in: V. Kumar (Ed.), Porous, Cellular and Microcellular Materials, MD-vol. 82, ASME, 1998, pp. 93–98.

[17] P.W. Voorhees, The theory of Ostwald ripening, J. Stat. Phys. 38 (1985) 231–252.

[18] P.W. Voorhees, Ostwald ripening of two-phase mixtures, Annu. Rev. Mater. Sci. 22 (1992) 197–215.