IN-SITU VISUALIZATION AND CELL GROWTH MODELING IN A POLYMERIC FOAMING PROCESS

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Abstract

In this paper, we consider a two-dimensional model of the foam nucleation process of CO$_2$ in polystyrene (PS) matrix by random initiation of growing bubbles in time and space. The model was extended to account for the simultaneous cell nucleation, growth, and collapse processes of the foaming bubbles at two different viscosities of PS resins. By means of connection among neighboring bubbles, secondary nucleation behaviors emerged from a multi-bubble system were attempted in simulations. The resulting cell size distribution (CSD) of bubbles shows power law behaviors for both simulations and experiments. The cell size distribution and morphologies obtained from the numerical simulation agreed with the snapshot pictures of the experiments qualitatively and quantitatively. Finally, different nucleation and growing rates were investigated to understand the relationship between the bubble nucleation/growth and final morphology of the foam structure. Potential applications lie in the analysis of the resulting micro-/nano-cellular structures due to secondary nucleation and the foam stabilization.

Introduction

Nucleation is a well-studied problem from boiling to crystal growth. In the foaming process, the cell nucleation is a very critical step, as it directly influences the cell size distribution and thus the mechanical and thermal properties of the polymer foam matrix. The heterogenous nucleation can start with the formation of micro-bubbles trapped on the inside of small crevices or cavities [1]. These cavities are randomly distributed across the polymer matrix and act as nucleation sites when temperature and pressure become favorable. Once the micro-bubbles are nucleated, some of them can continue to grow due to the induced energy given to the system. Experimentally, this energy can be provided by lowering the solubility of gas in the polymer/gas solution and by inducing a rapid pressure drop [2]. The pressure difference between the bubble and the ambient pressure provides the driven force for the gas diffusion through the bubble surface and the bubble growth.

If the dissolved gas concentration within the influence region of the bubble is below the nucleation threshold, new micro-bubbles form around the primary bubble as shown in Fig. 1. These bubbles keep on growing by consuming the dissolve gas in their own influence region or cell until reaching a plateau behavior. The simultaneous nucleation and growth of secondary bubbles are attributed to the tensile stresses generated in the surrounding melted plastic of the primary bubble [3]. Beyond this point, the experimental foaming process showed a significant bubble-to-bubble interaction that may change the overall growing rate for the bubble expansion.

Simple computational models have addressed some of these issues in regard to the simultaneous nucleation, cell growth, and collapse, and their effects on the cell size distribution of the final foam structure. In particular, the diffusion-induced bubble growth with simultaneous nucleation and growth has been described by several integral models of coupling of mass transfer and momentum equations [9-10]. A simple model of continuous nucleation and detachment of time that scales with the diffusion time was presented in [1]. Here a cell model is developed to simulate the effects of neighboring bubbles, where the term ‘cell’ makes reference to the union of a single bubble and the surrounding influence volume. The limitation of this work was determined by multibubble systems, where the nucleation rate breaks away from the single cell picture.

Similarly, M. Emami et al. [4] analyzed in the bubble diameter and the cell size distribution of an evolved cellular structure during different stages of the foaming process. From their visual experiments, it was observed how the bubble density decreases towards the end of the foaming process due to coalescence effects and the gas redissolution between bubbles. However, these effects were not reflected in the proposed numerical model.

Finally, to account the remaining stages of the foaming process, bubble growth models have been extended in a large number of papers [11-14]. As the number of bubbles increases, the gas concentration profile around the bubble decreases and the intercellular distance
between cells becomes narrower. This leads to the termination of the bubble nucleation and the coalescence between cells. The coalescence stage and the morphological change of a group of nano-cells in a PS-CO$_2$ system was tracked by W. Zhu et al. in [5]. Experimental results exhibit the shrinkage and eventual collapse of the smaller cells after the bubble-bubble interaction, which makes it difficult for fresh cells to survive in practical foaming processes. Therefore, the cell size distribution concluded to depend on both the nucleation rate, and the bubble growth dynamics [6].

In the present study, a novel computational model approach is proposed to further clarify the effect of the interaction between neighboring bubbles during the foaming process. Secondary nucleation effects are considered as a result of the interconnected multibubble system. The model proposed was verified based on analyzing the experimental data available in the literature. Since most of the common nucleation models include a good basis on nucleation and cell growth, simultaneous nucleation, cell growth, and collapse were considered in this study.

**Experimental**

**Materials and Sample Preparation**

PS MB3150 used in this study was supplied by AmSty North America LLC. It has a MFI 3g/10 min at 200 °C /5 kg and a glass transition temperature of 95 °C. The physical blowing agent is CO$_2$ (99% purity). After melt blending, PS samples were compression-molded with a Carver Press into disks of 4 mm diameter and 0.4 mm thickness.

**Experimental Procedure**

This study was conducted using a modified version of the batch foaming visualization system developed by A. Wong et al. [3] that allows the in-situ observation of the PS foaming process. The visualization system consists of a batch foaming chamber (see Fig. 2), a syringe pump (ISCO 500D), and two cartridge heaters with Proportional-Integral-Derivative (PID) feedback control.

To conduct the experiment, a PS sample is loaded into the foaming chamber, which was pre-heated at temperature of 160 °C during 10 minutes. This temperature was maintained throughout the experiment. Then the CO$_2$ was injected into the foaming chamber and the content was adjusted by controlling pressures through the syringe pump. The high injection pressure promotes the CO$_2$ to diffuse into the polymer sample. In this study, the residential time for the saturation of the samples was about 60 minutes. Finally, a sudden pressure drop was induced by opening the gas exit valve.

**Sample Characterization**

Cell count characterization of the microscopy images presented in Figure 3 is conducted using basic computer techniques of image process analysis in Matlab. The presented method uses basic morphological operations and Watershed transforms to segment the cells as a red-green-blue (RGB) image (see Fig. 3.d). Morphological operations include preliminary local contrast adjustments and adaptive filtering that eliminate the noise before the extraction of the dimmer cells. This follows by binarization techniques preformed to extract the perimeter of cells and/or cell groups. The cell borders and the image background are clearly differentiated by a scale range of intensities from positive to negative. The local minima in the image approximately corresponds to the cell nuclei, while the highest intensity is identified with the cell borders. Finally, the resulting RGB image determines the approximate value of the number of cells.
Simulation Model Description

The notion of free volume is used to explain some aspects of the polymeric behavior and our own model definition of the foaming process. The proposed model has the advantage of having very clearly quantifiable output, as it is measured against a cross-section of a two-dimensional hard core lattice. It quantifies the particular amount of free space that would be occupied by the lattice (either polymer or gas) in a solid-like manner.

The increase of free space is associated with the increase in the amount of bubbles or with the increase in the bubble size. In simulation domains, the expansion associated with the increase in the free space, occurs when the number of nearest lattice neighbors increases or the distance to nearest neighbors decreases. Therefore, the model prediction reflects the maximum amount of the potentially (thus ‘free’) space available in the system due to the interaction between bubbles.

Based on this general conception of free volume, a simple pattern formation has been used to recreate the interaction between bubbles, simulating the different phases of the foaming process. Initially, a lattice of $10^6$ sites (1000 x 1000 sites) is randomly populated with several small seeds that nucleate at a constant rate (homogeneous nucleation). The initial probability of these sites to nucleate and to become bubbles is $p$. Bubbles can also nucleate as a result of defects of the polymer matrix in the case of heterogeneous nucleation. From the simulation point of view, these defects are considered as nucleated bubbles in the cell that nucleate as a result of the initial seeds. Once formed the bubbles are in a metastable phase and grow at a constant rate as there is enough available free volume for expansion.
At each time step, all bubbles and nearest neighboring sites are investigated once as to the possibility $p$ of growing in size. The investigation sequence is randomly ordered. Each bubble is allowed to peripherally grow by one cell (increase the size to one cell in any direction) assuming that there is no overlapping with other bubbles. As soon as two or more bubbles touch each other, the growth of all of the adjoined bubbles stop. The touching bubbles can be considered as belonging to the same stable cell, a cell that no longer grows over time unless other evolving cells happen to touch it.

The system continues to evolve until no other cell can grow in time, so that all of them have at least one adjoining cell. The snapshots of typical evolutions of the system can be found in Figs. 5 and 6 (Lower raw).

**Results**

Figure 4 shows a series of micrographs obtained by visual observation experiments of PS foaming. The black dots are bubbles. After CO$_2$ pressure was released, numerous bubbles were nucleated and grown in the PS sample. These pictures suggest that the nucleation and bubble growth occurred simultaneously. The nucleation rate, however, seemingly slows down in speed, while the bubble growth continues until coalescence starts. As it was expected, the effect of coalescence and interaction between bubbles are visible at a very early stage of the foaming process.

Direct measurements of the simulated number of bubbles found in the literature [7] further confirmed the dynamic changes in the foam structure observed by the experimental results. The profile of the bubble surface density presented in Fig. 7 consists of four characteristic stages. Initially, a slow introduction period is required to establish steady-state nucleation conditions in stage I. According to K. C. Russell [8], the probability of bubble nucleation in this stage is proportional to $\exp(-W^*/kT)$, where $W^*$ is the minimum work required to make the system unstable with respect to transformation, and $kT$ is the product of Boltzmann’s constant and the absolute temperature. This is followed by a steady state nucleation (stage II), where the number of bubbles increases linearly with respect to time. During stage III the bubble nucleation decreases significantly due to supersaturation and secondary nucleation effects. Immediately after the secondary nucleation, early stages of coalescence and gas redissolution promote a rapid decline in the number of bubbles (stage IV). As a result, the number of nucleated bubbles that are generated and survive through stages II and III decreases in stage IV at a progressively slower rate.

The trend of the decline in bubble density after nucleation is notably similar for both resins; however, resins with higher melt viscosity of the polymer matrix effectively restricted the mechanism of bubble coalescence. This behavior indicates that higher melt viscosity/elasticity resulted in a lower rate of bubble density reduction.

Simulated results by the bubble nucleation, growth, and collapse model were compared with the experimental data observed in the literature [7]. Figures 5 and 6 show good agreement between the experimental and simulation series of micrographs obtained at different stages of the foam development. In addition, a Gaussian distribution was applied as a fitting curve with 95% confidence bounds to the experimental results of the number of bubbles at the two different viscosities (Fig. 7).
Generally, the polystyrene samples with high viscosity resulted in lower average bubble diameters during all stages of the foaming process (see Fig. 8). This can be explained by the remaining gas around each bubble in the polymer matrix. Higher viscosity yields to a higher bubble density at the early stage of growth. With the larger number of formed bubbles, the amount of gas consumed for creating the bubbles becomes larger and hence, the concentration of remaining gas in the polymer matrix decreases. Consequently, the rate of mass transfer for dissolved gas from the matrix polymer to bubbles decreases, which leads to the lower bubble diameter and lower rate of bubble growth.

Figure 8. Temporal change in diameter of selected foaming bubble.

Figure 9 shows the ranked cell size distribution (CSD) at the final stage of the foam development. Small cells are more frequent than large cells. The logarithm of frequency declines linearly with the logarithm of size. We observe that to a first approximation, the CSD plotted in a log-log scale is consistent with a simple power law form. This relation was observed after cell stabilization with the final foam structure of both simulation and experimental results. From the simulation point of view, and as many other processes in nature, recursive repetition of simple multiplicative transformations result from initial random conditions. In this case, average diameters of the multiplicative transformation determines the slopes of the power law lines. In the case of the experiments, we must also account for the fact that bubbles cannot grow indefinitely. The upper bound on growth causes the cell size distribution in Fig. 9.b to reduce into a narrower frequency distribution and the slope to drop below the power law line obtained for the simulation case.

Figure 9. Comparison between the experimental and numerical simulation results of cell size distribution of bubbles in log-log scale. The group sizes in the plots are rank according to decreasing size (hence Zipf-like). A power law distribution was observed for both experiments and simulation of the resulting HV and LV polystyrene final foam structure.

**Conclusion**

A high-pressure chamber with glass windows made the visual observation of foaming possible. Using the chamber, batch foaming experiments were conducted by pressure release, and the simultaneous nucleation, bubble growth rate, and collapse were observed at very early stages of the foaming process. Series of micrographs of PS samples with different viscosities were analyzed using process image analysis techniques. The simulation model and experimental results showed good agreement. This provided a mean to directly analyze the foaming process via the number of bubbles, the bubble diameter, and the cell size distribution. In the first stage, an introduction period establishes the required time for the steady state
nucleation conditions. Then the number of bubbles increases linearly with time, due to the spontaneous appearance of more bubbles. Immediately after the secondary nucleation, coalescence effects result in fewer but larger bubbles. An underlying result of power law distributions was found in the cell size distribution of the final foam structures of experimental and simulation data.

References