INVESTIGATION OF POLYMER RHEOLOGICAL CHARACTERISTICS ON BUBBLE COALESCENCE IN FOAMING PROCESS USING FINITE ELEMENT METHOD

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Abstract

In order to gain some predictive capability on the final foam morphology, a computer program has been developed. A finite element method based on Galerkin formula is used to solve the governing equations of the bubble growth in 2D using Freefem++ software. These equations include momentum, continuity, convection-diffusion and ideal gas law equations. In addition, Oldroyd-B model is used to account for the viscoelastic behavior of the polypropylene. A moving mesh of unstructured triangular elements is used to track the deformation of the bubble surface. An implicit time marching technique is also used to increase the stability of the solutions. In order to model bubble coalescence, the bubble-bubble interaction has been considered and Considéré criterion is used to predict bubble coalescence base on thermodynamic instability. The effects of rheological characteristics such as relaxation time, zero-shear viscosity and viscoelasticity ratio on the cell coalescence are studied. Results show by increasing the relaxation time and zero shear viscosity of the polymer the stability of the bubble growth increase to a large extent. In addition as the viscoelasticity of the polymer increases, the stability of the bubble increase.

1. Introduction

The properties of sandwich structures depend on the properties of their cores. In the case of using foam as their core, the morphology of the bubbles mainly determines mechanical characteristics of the whole composite. Therefore, controlling bubble morphology of the foams is of great importance. Thermoplastic foams such as polypropylene ones are produced through the extrusion process. There are mainly 5 major steps in this process. (1) Dissolution of the physical foaming agent into the polymer at high pressure. (2) Depressurization to create phase instability and bubble nucleation. (3) Bubble growth (4) bubble impingement (when bubbles feel the presence of the other bubbles) and (5) bubble coalescence [1].

When two adjacent cells grow, the thin polymer layer between them undergoes a elongational and biaxial stretching. In the extreme condition, overstretching causes rupture in the cell wall. Therefore, neighboring cells can merge together and non-uniform cellular structure will be formed. This phenomenon is called “cell coalescence”.

Depending on the applications, any of these steps are needed to be controlled to yield the desirable properties. For many years, a vast number of researchers has tried to model the above-mentioned steps, in order to get a better understanding of each step and to optimize the conditions in the foaming process. In the nucleation stage, Classical Nucleation Theory (CNT) is a well know theory to explain nucleation mechanism, first developed by Gibbs and consider the cases such as homogeneous nucleation and heterogeneous nucleation [2]. This theory has been refined during years for better compatibility with various processes. More recent approaches proposed by Harvey et al. [3] and Dean [80] which are explaining the cell nucleation based on the preexisting voids as the principal mechanism in many bubble nucleation processes especially plastic foaming. This theory is called "Pseudo-Classical Nucleation" [2]. The bubble growth mechanism in the extrusion process is driven by the pressure and concentration differences between the bubble and surrounding polymer-gas solution and is modeled by mass and momentum equations. These models can be divided into single bubble model which consider a single bubble surrounded by an infinite sea of fluid with an infinite amount of gas available for growth which is not realistic but gave better understanding of bubble growth phenomenon [2], and Cell model which was first proposed by Amon and Denson [5], and later was modified for foaming of viscoelastic polymers such as Arefmanesh and Advani models [6] and Ramesh, Lee, Malwitz Model [7] . In recent years, thanks to the development of computational tools, more complex and accurate models can be implemented for explaining the viscoelastic behavior of polymers [8,9]. These models focused on the growth of a single bubble separated by a layer of polymer-gas solution from the other bubbles and grows independently in a limited amount of gas. In these cases, due to the symmetry, bubbles always remained spherical and only their final diameter was important. They did not consider the interaction of the bubbles during growth.

In the majority of applications at foam industries, bubbles nucleate close each other and except first few moments of their growth, they feel the effect of the surrounding bubbles and therefore bubble-bubble interactions become important.

Recent papers used Finite Element Analysis (FEA) to the describe the bubble growth in two dimensions. They picked a few growing bubbles and used FEA to capture the evolution of the bubble wall deformation. Pengtao Yue et al. [10] used An arbitrary Lagrangian-Eulerian method for simulating the growth of a group of bubbles of the same size. S.L. Everitt, et al [11,12] Analyzed the growth of same-sized and different sized bubble in a viscoelastic polymer. These works give us a more accurate prediction on the final foam morphology. If bubbles continue to grow after touching each other, impingement occurs and in extreme cases, the thin layer between them may be overstressed and bubble wall rupture happens.

Current paper analyzes the steps 3 and 4 and 5 of the foaming process, meaning single bubble growth, bubble impingement, and bubble coalescence. Analysis of SBG results in the evolution of the gas pressure inside bubble and bubble radius which then, be used as an input for the next step which considers the interactions and impingement of the bubbles. Finally, based on the stress fields that is resulted from the analysis of step 4 and using Considéré criterion [1,13] the possibility of cell rupture is studied. The effect of Rheological characteristics such as polymer relaxation time, zero shear viscosity and elastic modulus on the bubble rupture is studied.

2. Theoretical background and modeling

2.1 Basic Formulas

The polymer behavior is described by Navier-stokes equation in two dimensions (conservation of momentum equation) as follows:

$$\rho\left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u}.\nabla\mathbf{u}\right) = -\nabla p + \nabla.\boldsymbol{\sigma} + \rho\mathbf{g}, \tag{1}$$

And the continuity equation:

$$\nabla.\mathbf{u} = 0, \tag{2}$$

Where $\rho, \mathbf{u}, t, p, \tau$ and $\mathbf{g}$ are melt density, velocity, time, pressure, stress and body force, respectively.

We assume isothermal conditions, incompressibility of the viscoelastic fluid and negligible inertia. Therefore equation (1) will be simplified as equation (3):

$$\nabla.\pi = 0, \tag{3}$$

which $\pi = -pI + \sigma$ is called Cauchy stress tensor and σ is called extra stress tensor.
The viscoelastic rheology is described by the Oldroyd-B model, which, more often, is used for dilute polymer solutions, same as the polymer of our interest. This model is easy to implement numerically and does capture the essential rheological features of interest. The extra stress tensor (σ) in this model is the sum of the Newtonian part σ_s (solvent stress) and viscoelastic part σ_p (polymer stress):

$$\sigma = \sigma_s + \sigma_p \tag{4}$$

The σ_s is the Newtonian stress tensor and is given by:

$$\sigma_s = 2\eta_s \mathbf{E} \tag{5}$$

Where $\mathbf{E}$ is the rate of deformation tensor and is given by:

$$\mathbf{E} = \frac{1}{2}(\nabla\mathbf{u} + \nabla\mathbf{u}^{\mathbf{T}}), \tag{6}$$

And polymer stress tensor, σ_p, is given by:

$$\sigma_p + \tau\left(\frac{\partial\sigma_p}{\partial t} + \overset{\nabla}{\sigma}_p\right) = 2\eta_p \mathbf{E} \tag{7}$$

Where $\mu_p = G\tau$ is the polymer viscosity, τ is the polymer relaxation time and $\overset{\nabla}{\sigma}_p$ is the upper convected derivative of polymer stress and can be calculated by the following equation:

$$\overset{\nabla}{\sigma}_p = \mathbf{u}.\nabla\sigma_p - \left(\nabla\mathbf{u}\sigma_p + \sigma_p\nabla\mathbf{u}^T\right) \tag{8}$$

After inserting the above equation (8) to the equation (7), equation (9) is obtained:

$$\sigma_p + \tau\left(\frac{\partial\sigma_p}{\partial t} + \mathbf{u}.\nabla\sigma_p\right) = 2\eta_p \mathbf{E} + \tau\left(\nabla\mathbf{u}\sigma_p + \sigma_p\nabla\mathbf{u}^T\right) \tag{9}$$

The total viscosity of the polymer melt is given by:

$$\eta = \eta_s + \eta_p = \mu + G\tau \tag{10}$$

Gas diffusion in the polymer melt is described by a convection-diffusion equation:

$$\frac{\partial c}{\partial t} + \mathbf{u}.\nabla c = \nabla.(D\nabla c) \tag{11}$$

Where c and D are the gas concentration and diffusivity in the polymer melt.
Each bubble gains mass at a rate equal to the mass flux of dissolved gas (blowing agent) diffusing into the bubble. the conservation of the mass for the bubble yields the following equation

$$\frac{dm_b}{dt} = -\oint_{bubble\ surface} D\nabla c.\mathbf{n}ds \tag{12}$$

Where m_b is the gas mass inside the bubble, $\mathbf{n}$ is the normal direction to the bubble surface pointing into the bubble and D is the diffusion coefficient. The gas in the bubble remains at thermodynamic and mechanical equilibrium, and obeys the ideal gas law:

$$\mathrm{p}_b \mathrm{V}_b = \mathrm{m}_b\ \mathrm{R}_g \mathrm{T} \tag{13}$$

Where P_b is the gas pressure,V_b is the bubble volume, and R_g and T are the specific gas constant and absolute temperature. according to our assumption, we only consider the isothermal case where T is a constant.

According to [13], The Considéré criterion, which is a thermodynamic relation of stress and strain was employed to evaluate the condition of interface rupturing. The Considéré criterion is expressed as:

$$H_c \equiv \frac{d\tau_{22}}{d\epsilon_{22}} - \tau_{11} \geq 0 \tag{14}$$

Where τ_{22} and ε_{22} are stress and strain in the y-direction. When the value of H_c becomes less than zero, it indicates that the material breaks up due to the thermodynamic instability. This criterion is used in this work to define if coalescence happened in each case or not.

2.1 Boundary Conditions

On the bubble surface, there is no shear stress and the normal stress obeys the Young-Laplace equation:

$$(-p+\sigma).\mathbf{n} = (-p_g + S\nabla.\mathbf{n}).\mathbf{n} \tag{15}$$

Where $\kappa = \nabla.\mathbf{n}$ is the surface curvature and S is the surface tension.

Gas concentration is given by Henry's law:

$$\mathrm{c=H\ p_g} \tag{16}$$

Where H is Henry's law constant.

In the case of single bubble growth, we will consider zero flux condition on the outer boundary and zero velocity field in the polymer at the initial time.

Table 1. Material and Process Parameters for the Single Bubble Growth (SBG) Condition

Initial Bubble Radius	$R_0=1$ µm
Diffusion Coeficient	$D=4.26 \times 10^{-9}$ m^2 /s
Soulubility Coeficient	$K_{H=}$ 3.61 × 10^{-5} mol N m
Surface Tension	$\sigma = 11.5 \times 10^{-3}$ N/m
Initial Pressure	$P_g = 1.11 \times 10^7$ Pa
Ambient Pressure	$P_f = 1.01 \times 10^5$ Pa
Temperature	T =423.8 K
Zero-Shear Viscosity	$\eta_0 = 4.90 \times 10^4$ N s m^{-2}
Gas Constant	R_g= 8.3144 J K^{-1} mol^{-1}

3. Results and Discussion

3.1. Single Bubble Growth

Analysis has been conducted on the growth of a single bubble without considering the other bubbles interaction. In order to check the validity of our model, we have adopted the same processing parameters that were used by Xingming Xu. Et. al [9]. Those parameters are listed in table (1). The evolution of the bubble pressure and bubble radius is illustrated in Figure (1) and compared with Xu results. When the polymer exiting the die of the extruder, the pressure of the melt drops from high pressure (11.1×10^5 Pa) to the ambient pressure. Therefore small bubbles which are nucleated before, face a large pressure gradient at their interface with the melt. This huge pressure difference is the driving force for the bubble expansion and the reason for rapid pressure drop at the first 0.1s. This rapid expansion at the initial stage provides enough momentum for the bubble to continue its growth even after losing its pressure difference. On the other hand, the growth of the bubble causes concentration difference inside the melt and leads to the gas diffusion to the bubble and further facilitate bubble expansion. This concentration obeys Henry's law at the bubble surface and is affected by the velocity field that is generated around the bubble. Therefore, we can conclude that at the initial stages of the growth, pressure difference dominates the bubble growth but at the later stages when there is no pressure difference, the diffusion of the gas to the bubble becomes the dominant driving force for the further expansion of the bubble. As you can see, there are some small differences between our results and Xu. These differences are due to different rheological model that has been adopted in this paper.

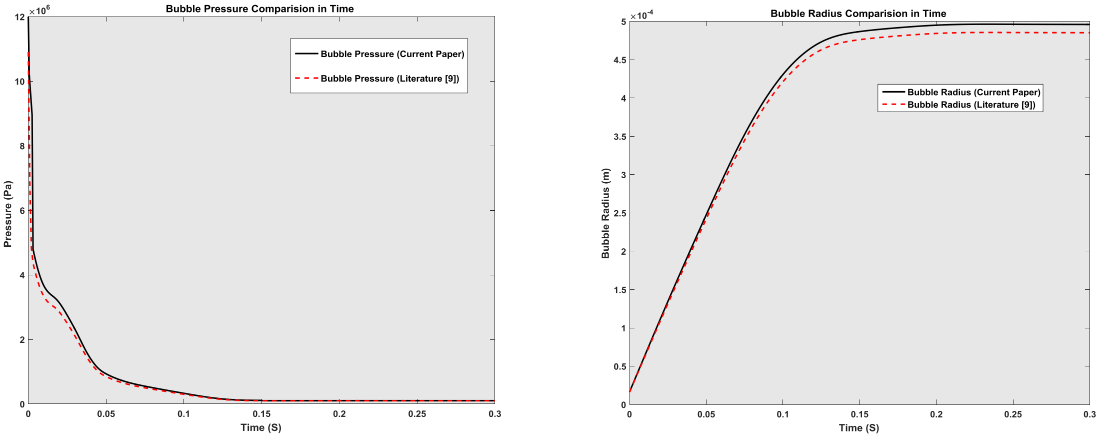

Figure 1. Validatity of the bubble pressure and bubble radius with time.

3.2. Multi Bubble Growth

Depending on the nucleation density of the foam, which can be predicted by CNT, two or more bubble may interact with each other and affect the growth of their neighboring bubbles. This can be clearly observed by nonspherical bubble margins which is the result of growth in the stress field created by other bubbles. Before impingement (IM), bubbles grow under SBG conditions. Therefore SBG stage is the preliminary step for the impingement stage and the result of the SBG simulation should be used as the input for IM stage. It is assumed that two bubbles with the same initial conditions, nucleate far enough from each other that at R=50 µm, their centers are d=50 µm apart from each other. This condition will be used as a base in our simulation. The effect of rheological properties on the growth stability based on Considéré criterion has been examined. The instability time from the assumed base state was measured in each case. Simulations and literature [1] admit that the most suceptible point for instability is the point that is exactly in the middle of two equal bubbles due to its high stresses, therefore, Considéré criterion has been applied to that point.

3.2.1 Zero Shear Viscosity

The effect of zero shear viscosity was examined and simulation results are shown in figure (2). The viscosity range from 0.27×10^5 Pa to 1.08×10^5 Pa. As can be seen in figure (2), polymer with higher viscosity better resisted against the bubble growth rate and retarded the instability state which resulted in a longer stability time.

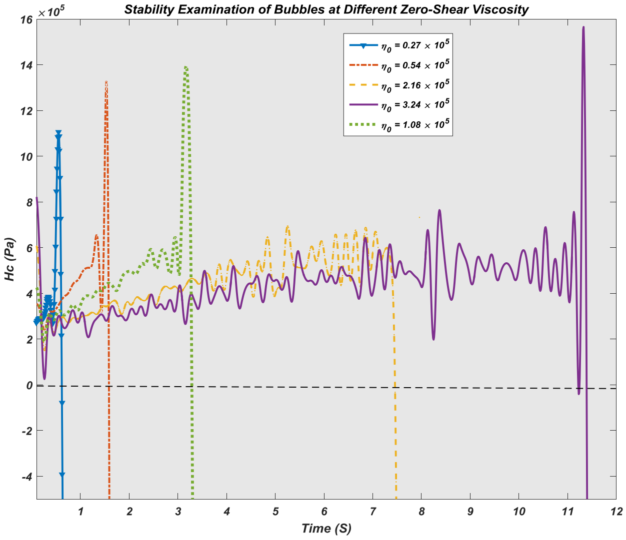

Figure 2. Effect of zero-shear viscosity on the stability of the bubble growth.

3.2.2 Polymer relaxation time

Relaxation time is the time required by a polymer to accumulate stresses in response to a disturbance either a sudden initiation or cession of flow [6]. Polymers with shorter relaxation time can faster accumulate stresses in the polymer around the bubble, therefore, lower bubble growth and lower stability will result due to the high-stress region around the bubble [8].

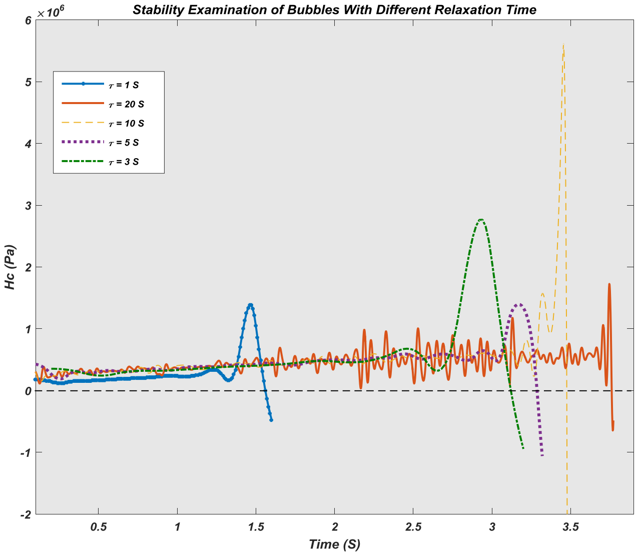

Figure 3. Effect of relaxation time on the stability of the bubble growth

3.2.3 Polymer / Solvent Viscosity Ratio

By changing the ratio of (polymer viscosity η_p /solvent viscosity η_s), better stability resulted. As can be seen in the Figure (4), by increasing the ratio of the polymer viscosity and consequently increasing the viscoelasticity of the polymer, better stability obtained meaning interface rupture occurred at the later stage.

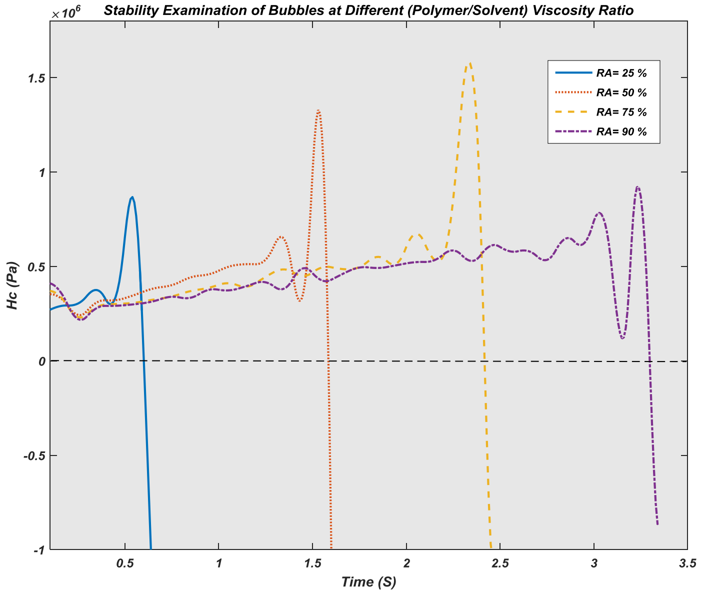

Figure 4. Effect of viscoelasticity on the stability of the bubble growth.

4. Conclusions

Finite element simulation of bubble growth in two dimensions is presented in this paper. For solving momentum and mass equations, FreeFem++ software has been used. The numerical results can be used to predict the bubble situation such as bubble radius, pressure, and gas concentration through the polymer at any time after nucleation. Results show that bubble growth in a real situation is a two-stage process. the first one is when a bubble grows freely in a limited amount of gas solved in the polymer melt. The second stage is when these bubbles interacting with each other either by competing to consume the limited amount of gas or by influencing each other with the stress field resulted from their growth. Rheological properties such as zero shear viscosity and relaxation time have a great impact on the behavior of bubbles. The simulation showed that higher zero-shear viscosity and longer relaxation time result in more stable growth and retard bubble rupture and bubble coalescence. In addition, it is showed that at a constant zero-shear viscosity, if one could increase the (polymer/solvent) viscosity ratio, (eg. crosslinking) it would result in a more stable bubble growth. At last, Numerical analysis proved to be a useful tool for predicting the bubble behavior, not even in the independent growth step, but also in the later bubble-bubble interaction situation and finally bubble rupture.

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