Experiment and Numerical Simulation of Non-Isothermal Bubble Growth in Polymer Foaming

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Abstract. A numerical simulation for non-isothermal bubble growth in polymer foaming were performed. The mathematical model based on the cell model was established to solve momentum equation, mass equation, diffusion equation and constitutive equation. We assumed the foaming polymer melt cooled at a set rate and took into account the effect of temperature on the rheological properties of the polymer-gas melt, Henry’s law constant, diffusion coefficient and surface tension. A PS/CO₂ system was used herein as a case example to investigate the change of bubble growth behavior under non-isothermal circumstances and the effect of cooling speed on bubble growth. A batch foaming experiment with different cooling patterns was conducted to verify the simulation results. The results demonstrate that the main reasons to hinder the bubble growth are the increase of Henry’s law constant and the decrease of diffusion coefficient during the cooling process. Increase the cooling rate is an effective way to produce foamed plastics with high bubble density and finer bubble size.

1. Introduction
A large number of bubbles can reduce the consumption of materials that improve the mechanical properties of products [1-3]. The foaming process of microcellular plastics mainly includes cell nucleation, growth and stability. The bubble growth processes is the key step to determine the final bubble structure and quality of foamed plastics. Thus, it is necessary to study bubble growth in the microcellular molding process, which can promote the development of microcellular foaming technology.

Various researchers have previously investigated the bubble growth phenomenon during the foaming process. The early researchers assumed that a single bubble grew in an infinite sea of polymer melt with an unlimited amount of dissolved gas [4, 5]. However, the amount of dissolved gas for bubble growth is finite and will eventually be depleted. Amon and Denson [6] introduced the well-known cell model to analyze a large amount of gas bubbles growth in close proximity to each other. The model can describe the actual foaming process more realistically because bubbles expand with finite dissolved gas in the model. Otsuki and Kanai [7] simulated the dynamic growth behavior of spherically symmetric bubbles with the diffusion of a foaming agent. They used a multimode Phan-Thien Tanner model to analyze the effect of viscoelastic characteristic on bubble growth. Xu [8] examined the growth of a spherical bubble with the cell model by using a finite-element-based numerical simulation method. A truncated power-law constitutive equation was used to describe the rheology of the melt. The effects of process parameters and the rheology of the melt on bubble growth were investigated. Ramesh [9] proposed a modified cell model. The model used the upper-Maxwell model to describe the viscoelastic of polymer/gas solutions. They studied the effects of dissolved gas content, temperature on rheology and other physical properties. Li [10] based on the cell model, a mathematical model for bubble growth was established under isothermal conditions. The established
model was used to predict the influence of the physical properties and rheological properties on bubble growth dynamics.

All the researches above analyzed the isothermal bubble growth. However, in the process of polymer foaming, bubbles usually grow under non-isothermal condition. The properties of materials have change greatly during the cooling process. Thus, the non-isothermal bubble growth differs much from the isothermal one. In the paper, a mathematical model based on the cell model was established to simulate the non-isothermal bubble growth. We assumed that the polystyrene/carbon dioxide system cooled at a set speed. In the simulation process, the effect of temperature on the rheological properties of the polymer-gas melt, Henry’s law constant, diffusion coefficient and surface tension were considered. The change of bubble growth behavior in non-isothermal was simulated with the model. In addition, CO$_2$ as blowing agent has been performed to study the effects of different cooling rates on final cell structures of foamed plastics. The batch foaming experiment was conducted to verify the simulation results.

2. Modeling of non-isothermal bubble growth

In this study, the cell model was used to establish the mathematic model. This model divided the polymer/gas melt into spherical unit cells composed of equal and finite amounts of dissolved gas and assumed that gas only diffuse in the unit cells. The following assumptions were made to model the non-isothermal bubble growth dynamics:

1. The bubble is spherically symmetric throughout the growth process.
2. The polymer/gas solution is incompressible.
3. The effects of inertial forces and gravity are negligible.
4. The initial dissolved gas distributes uniformly in the unit cell. The dissolved gas concentration at the polymer/gas solution interface obeys Henry’s Law [11]:

\[ c(R) = P_g K_h \]

where \( c(R) \) is the dissolved gas concentration at the polymer/gas solution interface and \( K_h \) is the Henry’s Law constant.

5. The initial stress around the bubble is zero.
6. Using the upper-convected Maxwell model to describe the viscoelastic properties of the polymer.

2.1. Bubble growth dynamics

Based on momentum equation, mass equation, diffusion equation and constitutive equation, a mathematical model can be established for the bubble growth. Considering the viscoelastic stress, surface tension, pressure in the bubble, and the ambient pressure, the momentum equation can be reduced to [11]

\[ P_g - \frac{2\sigma}{R} - P_f + 2\int_0^S \tau_{r}\theta - \tau_{\theta\theta} dr = 0 \]

where \( P_f \) is the ambient pressure, \( \sigma \) is the surface tension at the bubble surface, \( r \) is radial position. \( \tau_{rr} \) and \( \tau_{\theta\theta} \) are the stress in the \( r \) and \( \theta \) directions respectively, and \( S \) is the radius of the spherical unit cell, \( R \) is bubble radius.

Because the initial stress around the bubble is zero, the initial momentum equation can be expressed as

\[ P_g(t = 0) = P_f + \frac{2\sigma}{R} \]

where \( P_g(t = 0) \) is the initial pressure in the bubble.
To solve the momentum equation, the upper-convected Maxwell model was introduced to describe the viscoelastic properties of the polymer. The equations are expressed as follows [11]:

\[
\begin{align*}
\tau_{rr} + \lambda \left( \frac{\partial \tau_{rr}}{\partial t} + \frac{R^2 \dot{R}}{r^2} \frac{\partial \tau_{rr}}{\partial r} + \frac{4R^2 \dot{R}}{r^3} \tau_{rr} \right) &= -4\eta \frac{R^2 \dot{R}}{r^3} \\
\tau_{\theta\theta} + \lambda \left( \frac{\partial \tau_{\theta\theta}}{\partial t} + \frac{R^2 \dot{R}}{r^2} \frac{\partial \tau_{\theta\theta}}{\partial r} - \frac{2R^2 \dot{R}}{r^3} \tau_{\theta\theta} \right) &= 2\eta \frac{R^2 \dot{R}}{r^3}
\end{align*}
\]

where \( \lambda \) is the relaxation time of the polymer/gas solution and \( \eta \) is the zero-shear viscosity.

The amount of gas in the bubble increases with the expanding of the bubble. The rate of the change of the mass in the bubble should be equal to the rate of the mass diffusing into the bubble. The mass conservation equation can be expressed as [12]

\[
\frac{d}{dt} \left( 4\pi \frac{P_g R^3}{3 Z R_g T} \right) = 4\pi R^2 D \frac{\partial c}{\partial r} \bigg|_{r=R_g}
\]

where \( D \) is the diffusion coefficient, \( Z \) is the compressibility factor, \( T \) is melt temperature, \( c \) is the dissolved gas concentration, and \( R_g \) is the universal gas constant.

Considering the non-ideal behavior of the gas under high pressure, the Peng–Robinson cubic equation of state is introduced to describe the properties of the gas. The equations are as follows [13]:

\[
Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0
\]

where

\[
\begin{align*}
A &= 0.45724 \alpha \frac{P_r}{T_r^2} \\
B &= 0.0778 \frac{P_r}{T_r} \\
\alpha &= \left[ 1 + f (1 - T_r^{0.5}) \right]^2 \\
f &= 0.37464 + 1.54226 \omega - 0.2699 \omega^2
\end{align*}
\]

To solve the equation (6), the distribution of the gas concentration in the unit cell should be obtained. Many studies described the dissolved gas concentration distribution in the form of a polynomial [14, 15]. In this study, the diffusion equation is used to calculate the distribution of the gas concentration. The equation can be expressed as [16]

\[
\frac{\partial c}{\partial t} + V_r \frac{\partial c}{\partial r} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right)
\]

where \( V_r \) is the fluid velocity in the radial direction. According to the continuity equation for the flow around the bubble, \( V_r \) can be expressed as

\[
V_r = \frac{\dot{R} R^2}{r^3}
\]

The initial and boundary conditions are as follows:
where $c_0$ is the initial dissolved gas concentration.

### 2.2. The properties of PS/CO\textsubscript{2} solution

To analyze the non-isothermal bubble growth, we assumed that the temperature decreases with a set rate. During the cooling process, the properties of the PS/CO\textsubscript{2} solution change greatly. Several models were utilized to describe the properties of the PS/CO\textsubscript{2} solution as a function of the temperature.

The temperature dependence of gas diffusivity of the system was assumed to obey the Arrhenius relationship [17].

$$D = D_0 \exp \left( \frac{-E_a}{R_g T} \right)$$  \hspace{1cm} (13)

where $D_0$ is the pre-exponential factor and $E_a$ is the activation energy for the gas diffusion. The gas diffusivity at each temperature was calculated by the equation (13) with the experiment data by Sato [18].

The solubility of CO\textsubscript{2} in PS also changes with the decrease of temperature. The model for the solubility at each temperature is as follows [18]:

$$\ln K_h = 6.4 + 2.537 \left( \frac{T_c}{T} \right)^2$$  \hspace{1cm} (14)

where $T_c$ is the critical temperature of CO\textsubscript{2}.

Lee et al [19] proposed a generalized Arrhenius equation to estimate the zero-shear viscosity of PS/CO\textsubscript{2} system. The model took into account the effects of temperature, pressure, and CO\textsubscript{2} content. The equation is as follows:

$$\eta_0 = 0.8298 \exp \left( \frac{1272}{T - 341.1} \right) + 6.023P - 66.51c$$  \hspace{1cm} (15)

where $c$ is the dissolved gas concentration (wt/wt).

The model by Park [20] was introduced to calculate the temperature dependence of surface tension at the interface. The equation can be expressed as

$$\sigma = 38.7032 - 0.0559P - 0.01P + 2.596 \times 10^{-5}TP$$  \hspace{1cm} (16)

Because the unavailability of the relaxation time of PS/CO\textsubscript{2} system, the corresponding value for pure PS was used. The relaxation time of pure PS was estimated with the experiment data by Venerus [21].

### 2.3. Numerical simulation algorithm

A Lagrangian coordinate transformation [11] was used to reduce the governing equations for convenient of calculation. At early stage of bubble growth, the change in state was sharply near the bubble surface, so a non-uniform mesh, denser as the location got closer to the bubble interface, was used to discrete the governing equations. The finite volume method and the fourth-order Runge-Kutta method were employed to solve the governing equations and simulate the bubble growth dynamics. The diffusion equation was discrete with the finite volume method to form the implicit differential
equation on the non-uniform mesh. In every time step, we calculated the rheological properties of the polymer-gas melt, Henry’s law constant, diffusion coefficient and surface tension firstly. Then the viscoelastic stress was obtained with the equations (4) and (5). Lastly solve the equations (2), (6) and (8) to acquire the radius of the expanding bubble. The parameters for bubble growth simulation were obtained by Leung [12] and Lee [19]. The parameters were listed in table 1.

| Table 1. Parameters for bubble growth simulation. |
|-----------------------------------------------|
| Ambient pressure | 5MPa |
| Initial unit cell radius | 50μm |
| Initial bubble radius | 1μm |
| Initial temperature | 200℃ |
| Initial dissolved gas concentration | 0.04wt/wt |
| The rate of cooling | 50℃/s |

3. Experiment
Materials: The PS used in the experiment was purchased from Petrochina Daqing Petrochemical Company in the form of pellets. The PS pellets were compression molded to 1 mm-thick sheets by pressing at 180℃; the sheets were cut into 2×2 mm pieces. The physical blowing agent was 99% pure carbon dioxide.

Foaming process: A depressurization batch foaming process was used to foam the PS. Foams were prepared in a 2L stainless steel hexagonal high-pressure autoclave purchased from Dalian Automatic Control Equipment Plant. The samples were placed in the autoclave. The vessel was preheated to a set temperature and then filled with CO₂ to the desired pressure. The sample was maintained for a prescribed period of time until saturation conditions were reached. Then the vessel was depressurized to ambient pressure to induce bubble nucleation and growth. At last the foamed sample was cooled and stabilization. In all the experiments, samples were saturated under 10 MPa of ScCO₂ for 6 h at 100℃ and the depressurization time is 10s. To investigate the effects of different cooling rates on foam process, three cooling methods were utilized to cooling the samples. In the first approach, once the pressure was completely released the 20℃ water was quickly injected into the vessel to cool the sample. In the second approach, the sample was maintained in the vessel for 3 minutes after depressurization and then was removed from the autoclave and cooled in the air. In the third approach, the sample was cooled to room temperature in the autoclave.

Characterization: The foams were characterized to determine the cell sizes and densities. All foamed samples were immersed in liquid nitrogen for 10 min and then fractured to assure that the microstructure remained intact. The cellular structures of the samples were characterized by scanning electron microscope.

4. Results and discussion

4.1. The effect of temperature on bubble growth
During the cooling process, the bubble growth behavior changes greatly. To analyze the non-isothermal bubble growth in detail, the influences of the change of the zero-shear viscosity, Henry’s law constant, diffusion coefficient and surface tension on bubble growth dynamics were investigated respectively.

The zero-shear viscosity, varying with the temperature, is one of the retarding forces that affect the bubble growth behavior. Figure 1 illustrates the effect of the change of zero-shear viscosity on bubble growth. In the early process of bubble growth (0-0.7s), the effect of zero-shear viscosity on bubble growth is almost negligible. It probably resulted that the melt temperature is still high in the process, the resistance produced by zero-shear viscosity is small. In the later growing process (0.7-1s), with the decrease of the temperature, zero-shear viscosity increases greatly, and viscoelastic stress around the bubble gradually accumulates. Therefore, the bubble growth rate under non-isothermal conditions will be reduced. In general, the effect of zero-shear viscosity is not pronounced.
Figure 2 indicates that the effect of Henry’s constant on non-isothermal bubble growth. From 0 to 0.2s, the effect of Henry’s constant on bubble growth is almost negligible. From 0.2 to 1s, the bubble radius increases slowly under non-isothermal conditions, and the difference between the two conditions increases gradually. It probably resulted that the increase of Henry’s constant with the decrease of the temperature means the polymer has a higher capability of dissolving gas. The gas concentration of the bubble interface decrease faster and the diffusion of CO$_2$ gets slower. Therefore, the bubble expands slowly in non-isothermal condition.

Another factor that will affect the bubble growth rate is diffusion coefficient. A higher diffusion coefficient means a faster diffusion of gas molecule into the bubble. So the bubble growth rate increases. As shown in figure 3, at the later stage of bubble growth (0.3-1s), the bubble growth rate will reduce under non-isothermal condition because of the decreasing of diffusion coefficient. As the diffusion coefficient decreases, the difference between the two conditions becomes larger.

Figure 4 illustrates the effect of surface tension on non-isothermal bubble growth. The surface tension increases with the decreasing of the temperature. However, the bubble growth states in the two different conditions are almost the same. This indicated that the surface tension has little effect on bubble growth.

From the discussion above, it’s clear that the bubble growth rate in non-isothermal condition gets
slower than the isothermal situation. The increasing of Henry’s constant and the reduction of diffusion coefficient are the main reasons for the decreasing of bubble growth rate during the cooling process. The effects of viscosity and surface tension are negligible.

4.2. The effect of cooling rate on bubble growth

The reduction of temperature has significant effect on the bubble growth dynamics. The effect of cooling rate on bubble growth is analyzed in detail. As shown in figure 5, the bubble growth rate decreases with the increasing of cooling rate. A higher cooling rate leads to Henry’s constant increasing faster and diffusion coefficient decreasing more rapidly. So the bubble growth rate get slower and the final cell size will be finer. In order to investigate the effect of cooling rate on the cellular structures of the foams, a series of experiments was carried out in which the cooling rate was varied while holding the other conditions constant. Figure 6a, 6b and 6c show the microstructures of PS foams prepared with three different cooling approaches respectively. It is observed that the final cell size of the foam decreases with the increasing of cooling rate while the final cell density increases. Stabilized at a fast cooling speed can suppress bubble growth, so the final cell size of the foam cooled by water is smallest compared the other two foams. On the other hand, immediately cooling the foam after bubble nucleation can prevent cell coalescence which is an important cause for reduction of cell density. Cell coalescence can be observed in the foam by furnace cooling, the bubble surface is rough, and the phenomenon of bubble coalescence is serious. This resulted that the interface strength of the bubble-polymer melt is low, and the stability of the bubble nuclei is weakened, which is disadvantageous for microcellular foaming. This shows that increasing the cooling rate can effectively suppress the expansion of the bubble, and obtain high density and small size cell structure.

![Figure 5. Effect of cooling rate on bubble growth.](image)

![Figure 6. SEM micrographs showing cellular structures in polystyrene foams prepared with different cooling methods: (a) water cooling (fast speed); (b) air cooling (intermediate speed); (c) furnace cooling (slow speed).](image)
5. Conclusion
A mathematics model was established to simulate the non-isothermal bubble growth. The model took into account the changes of the rheological properties of the polymer/gas solution, Henry’s law constant, diffusion coefficient and surface tension during the cooling process. A PS foam experiment with different cooling methods was conducted to verify the simulation results. The results show that Henry’s constant and diffusion coefficient have a significant effect on bubble growth. With the decrease of the temperature, the increasing of Henry’s constant and the reduction of diffusion coefficient can reduce the bubble growth rate compared with the isothermal condition. Zero-shear viscosity changes greatly during the cooling process. At the later bubble-growth process, the increase of zero-shear viscosity will suppress the bubble growth. However, surface tension has no significant effects on bubble growth. Increasing the cooling rate can increase the cell density and reduce the cell size. So adopting a more rapid cooling approach is an effective way to produce foamed plastics with high bubble density and finer bubble size.

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