Numerical simulation of polypropylene foaming process assisted by carbon dioxide: Bubble growth dynamics and stability

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Abstract

A mathematical model was established to simulate the bubble growth process during foaming of polypropylene (PP) by carbon dioxide, taking into account of a wide range of physical and rheological properties (solubility, diffusivity, surface tension, long-chain branching, zero shear viscosity, relaxation time, strain hardening), as well as processing conditions. By employing the Considere construction the possibility of growth instability and bubble rupture at later stage of bubble growth was predicted. The simulation revealed that the improvement of foamability of polypropylene by introducing long-chain branching was due to the well-defined viscoelastic characteristics of the melt. Rheological factors that impede bubble growth are beneficial in stabilizing the bubble growth. Stability during bubble growth is further facilitated by moderate strain hardening characteristics and elastic properties of the polymers. The diffusivity and solubility characteristics also have profound impact on the bubble growth stability, while the influence of the surface tension is negligible.

1. Introduction

With the progress of research work on high melt strength polypropylene (HMSPP) to address the foamability issue, there is increasing amount of interest in using polypropylene (PP) as a foams material. Melt strength may be improved by using polymers with broad or bimodal molecular weight distributions. However, this approach has been shown not effective for PP (Sugimoto et al., 2001). The main and efficient method to prepare HMSPP is to incorporate long-chain branch (LCB) by chemical modification (Auhl et al., 2004; Borsig et al., 2008; Cao et al., in press; Mabrouk et al., 2009; Yao et al., 2009; Ye et al., 2004). Many researchers have carried out experimental investigation on the effect of LCB on foamability of PP. Nam et al. (2005) modified PP by introducing the LCB onto the backbone and studied the effects on the performance of foaming process. They found that the LCB structure of PP was the main factor affecting the foam density. Stange and Munstedt (2006) investigated blends of a linear PP (L-PP) and a long-chain branched polypropylene (LCBPP). They found that a small amount of LCBPP into L-PP could significantly improve the foaming process. Spitael and Macosko (2004) studied the strain hardening in PP and its role in extrusion foaming. They reported that the strain hardening in LCBPP could retard cell coalescence. Recently, Zhai et al. (2008) investigated the foaming behavior of linear and branched PP. They pointed out that the LCBPP exhibited well-defined close cell structure comparing with L-PP due to the increased melt strength. These experimental studies demonstrate that the presence of LCB can improve the foamability of PP and the strain hardening plays an important role in stabilizing the cellular structure during the foaming process.

Furthermore, a great deal of numerical studies was also devoted to better understand the PP foaming process. Otsuki and Kanai (2005) carried out numerical simulations for five kinds of L-PP. They used the Phan-Thien Tanner (PTT) constitutive equation to describe the rheological characteristics of the polymers. The nonlinear parameter, on which the strain hardening property strongly depends, was varied to analyze the effects of the linear and nonlinear viscoelastic characteristics on bubble growth during isothermal extrusion foaming. It was found that the linear viscoelastic characteristics were more influential and
the strain hardening had little effect on bubble growth rate. Den Doelder et al. (2002) investigated the nonisothermal foaming process for a L-PP and a LCBPP. Contrary to Otsuki and Kanai (2005), they concluded that the strain hardening should be one of the most important factors that stabilized the bubble growth.

All previous numerical studies on bubble growth were based on the assumption that the bubbles could grow steadily until thermodynamic equilibrium was achieved between the bubbles and the melt (Mao et al., 2006). That was to say, the melt extension was always stable in bubble growth.

In this paper, extensional flow instability of the melt in bubble growth and bubble rupture were simulated. Rheological data of five different model PPs were first used in the simulation to investigate the influences of the macromolecular architecture (branch ratio) on the bubble growth and rupture in the foaming process. This was followed by extensive analysis of individual rheological parameters, and some additional physical properties of the polymer–gas system and processing conditions, and their effect of bubble growth dynamics and stability.

2. Bubble growth model

The simulation of bubble growth and stability is based on the well-known cell model (Arefmanesh and Advani, 1991; Leung et al., 2006; Shafi et al., 1996; Venerus et al., 1998; Venerus, 2001; Venerus, 2003; Tuladhar and Mackley, 2004). The cell model approximates the well-known cell model (Arefmanesh and Advani, 1991; Leung et al., 2006; Shafi et al., 1996; Venerus et al., 1998; Venerus, 2001; Venerus, 2003; Tuladhar and Mackley, 2004). The cell model approximates the situation in polymer foaming by considering the growth of a single bubble with a shell of polymer–gas solution. A schematic is shown in Fig. 1. The following assumptions are used in our model:

1. The system is isothermal.
2. The bubble is spherically symmetric.
3. The polymer melt is incompressible.
4. The inertial forces and gravity are neglected.
5. The gas concentration in the polymer–gas solution and the melt (Mao et al., 2006) is the most important factors that stabilized the bubble growth.
6. The effect of plasticization is ignored.
7. There is no loss of gas to the surroundings.

2.1. Mathematical formulations (governing equations)

Using the cell model, the bubble growth can be calculated by simultaneous solving the mass and momentum transfer between the bubbles and the surrounding polymer–gas shell, typically in a spherical coordinate.

From Arefmanesh and Advani (1991) and Amon and Denson (1984) the kinematics of spherical bubble growth are ideally described by a purely radial velocity field, which is obtained from the continuity equation as

\[ \n = \frac{R^2}{r^2} \frac{1}{3} \left( \frac{d \ln \rho}{dt} \right) \left( r - \frac{R^3}{r^2} \right) \]  

where \( r \) is the radial position, \( \nu_r \) is the radial velocity of the fluid at \( r \) position, \( R \) is the radial velocity at the interface between the gas and the melt. Assuming incompressible flow the above equation reduces to

\[ \n = \frac{R^2}{r^2} \]  

The deformation rate tensor derived from the above equation (Amon and Denson, 1984) indicates that it is a biaxial extensional flow:

\[ \mathbf{d} = \begin{pmatrix} -2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \frac{R^2}{r^2} \]  

Using this equation together with the assumption of negligible inertia and gravitational force (assumption (4)), the momentum equation is written as

\[ P_s - P_0 - \frac{2y}{R} + 2 \int \frac{\tau_{rr} + \tau_{zz}}{r} \, dr = 0 \]  

where \( y \) is the surface tension, \( P_s \) and \( P_0 \) are the bubble and system pressure, respectively, \( \tau_{rr} \) and \( \tau_{zz} \) are the stress components.

A more accurate calculation of the gas phase pressure is conducted to take into account the non-ideal behavior of the CO2 gas under elevated pressure during foaming. Thus the Peng–Robinson (PR) cubic equation of state is employed in polynomial form:

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

where

\[ Z = \frac{PV}{RT} \]  

\[ A = \frac{bP_s}{RT^2} \]  

\[ B = \frac{bP_s}{RT} \]  

\[ a = \frac{0.45724 \pi R^2 T^2 \alpha}{P_c} \]  

\[ b = \frac{0.07780 \pi T_c}{P_c} \]  

\[ \alpha = [1+k(1-T^{-0.5})]^2 \]  

\[ T_r = \frac{T}{T_c} \]  

\[ k = 0.3746 + 1.54226 \omega - 0.26992 \omega^2 \]  

Fig. 1. Schematic of the cell model.
The governing equation, initial and boundary conditions are
Mass balance for gas in the bubble:
\[
\frac{d}{dt} \left( c_g \frac{4}{3} \pi R^3 \right) = D \frac{\partial c_g}{\partial r} \bigg|_{r = R} (4 \pi R^2)
\]
(14)

where \( R \) is the bubble radius, \( c_g \) is the gas concentration in the bubble, \( c \) is the dissolved CO2 concentration in the shell, \( D \) is the diffusion coefficient and \( t \) is time. Given that \( c_g = P_g / 2 \pi R T \), the above equation is transformed to

\[
\frac{d}{dt} \left( \frac{P_g R^3}{2T} \right) = 3 \pi DR^2 \frac{\partial c}{\partial r} \bigg|_{r = R}
\]
(15)

And the associated initial and boundary conditions are as follows:

\[
c(0, r = 0) = c_0
\]
(16)

\[
\frac{\partial c}{\partial r} \bigg|_{r = 0} = 0
\]
(17)

\[
c \bigg|_{r = R} = K_g P_g
\]
(18)

Mass balance for gas in polymer–gas solution shell:

\[
\frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right)
\]
(19)

In order to eliminate the convective term in Eq. (19) and reduce problems with large gradient near the bubble surface, we follow Arefmanesh and Advani (1991) and use the Lagrangian coordinate transformation:

\[
y = r^3 - R^3
\]
(20)

and define the concentration potential function \( c = c - c_0 \)
(21)

The governing equation is rewritten as

\[
\frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right)
\]
(22)

With the following initial and boundary conditions:

\[
c \bigg|_{t = 0} = 0
\]
(23)

\[
\frac{\partial c}{\partial r} \bigg|_{r = R_c \rightarrow R} = 0
\]
(24)

\[
c \bigg|_{t = 0} = K_g P_g - c_0
\]
(25)

Define the concentration potential function \( \Phi \) as

\[
\frac{\partial \Phi}{\partial y} = c = c - c_0
\]
(26)

The governing equation, initial and boundary conditions are rewritten as

\[
\frac{\partial \Phi}{\partial t} + v_r \frac{\partial \Phi}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Phi}{\partial r} \right)
\]
(27)

\[
\Phi(r, 0) = 0
\]
(28)

\[
\frac{\partial^2 \Phi}{\partial r^2} \bigg|_{r = R_c \rightarrow R} = 0
\]
(29)

\[
\frac{\partial \Phi}{\partial y} \bigg|_{y = 0} = K_g P_g - c_0
\]
(30)

To take into account the nonlinear viscoelastic characteristics of the polymer–gas system, Gotsis’s model was employed, which explicitly includes the effects of the macromolecular architecture, i.e., chain branching, on the rheological properties (Tsengoglou et al., 2006).

\[
\frac{d \tau_T}{d t} = -4 \dot{\gamma} (\tau_T + G) - \frac{\tau_T}{\lambda} - \dot{\gamma} n (\tau_T + G)
\]
(31)

\[
\frac{d \tau_0}{d t} = 2 \dot{\gamma} (\tau_0 + G) - \frac{\tau_0}{\lambda} - \dot{\gamma} n (\tau_0 + G)
\]
(32)

\[
\dot{\gamma} = \frac{\hat{R} R^2}{y + R^3}
\]
(33)

\[
\dot{\gamma} = \frac{\eta}{G}
\]
(34)

where \( \dot{\gamma} \) is the biaxial extension rate, \( G \) is the rigidity module, \( \lambda \) is the relaxation time, \( \eta \) is the zero shear viscosity, \( n \) is the viscoelastic nonlinearity exponent and has values in the range 0–2. Depending on the value of \( n \) used, the model is capable of describing either strain hardening or stress plasticity. \( n = 0 \) represents the case of rubber–like liquid corresponding to a high branching degree. At \( n = 2 \) limit, the polymer resembles the zero post-equilibration chain stretch case of the Doi-Edward model. Gotsis et al. (2004b) have shown that for biaxial extension a value of \( n \geq 1.8 \) corresponds to linear polymers devoid of branching.

The initial conditions are as follows:

\[
\tau_T \big|_{t = 0} = 0
\]
(35)

\[
\tau_0 \big|_{t = 0} = 0
\]
(36)

To simulate the stability during bubble growth, the Considère criterion is employed to predict the bubble interface rupture. The Considère construction is a thermodynamic relationship between the stress and strain that was originally developed for solid mechanics. It was later extended for the quantitative prediction of breaking up of polymer melts under extensional flow (McKinley and Hassager, 1999; Petrie, 2009; Yao et al., 2000) and more recently qualitatively description of interface rupture of polymer bubbles (Taki et al., 2006). To our knowledge, the current study is the first report on the investigation of the bubble growth stability using sophisticated growth model, which is capable of predicting various physical properties and processing conditions on bubble rupture.

The Considère criterion states that for stable bubble growth, the following criterion for thermodynamic stability needs to be satisfied (McKinley and Hassager, 1999; Petrie, 2009; Yao et al., 2000):

\[
d \tau_T/d \dot{\gamma} > \tau \]
(37)

\[
\tau = \frac{\eta}{\eta_0}
\]
(38)

\[
\eta_0 = \frac{\tau_0 - \tau_T}{\dot{\gamma}}
\]
(39)

where \( \tau \) is the transient Trouton ratio, \( \dot{\gamma} \) is the Hencky strain and \( \eta_0 \) is the transient biaxial elongational viscosity.

2.2. Numerical algorithm

An implicit finite difference method is employed to solve the model equations. At early stage of bubble growth, it is challenging to obtain stable numerical solution due to the large concentration gradient near the bubble interface. To overcome this difficulty, the potential function described earlier (Arefmanesh and Advani, 1991) and nonuniform grid method (Proussevitch and Sahagian, 1998; Tannehill et al., 1997) were used.
3. Results and discussion

3.1. Model validation

Initial simulation was conducted to test the validity of the bubble growth model and the effectiveness of the numerical algorithms. The simulated results were compared with experimental data from Taki et al.'s (2003) work on the bubbles growth in batch foaming of polypropylene with supercritical CO2. The physical and processing parameters used in the simulation are listed in Table 1. As shown in Fig. 2, the model prediction is in good agreement with the experimental results.

3.2. Effect of branch ratio on the bubble growth

To investigate the effect of long-chain branch ratio of PPs on the bubble growth, the foaming behavior of five model PPs used by Gotsis et al. (2004b) are simulated. Among the five PPs, one is a linear PP and the other four are LCBPPs with different degree of branching by modifying the linear PP. The branch ratio and rheological parameters for these PPs are shown in Table 2. Table 3 summarizes the foaming process conditions and other material properties used in the simulation of bubble growth.

The evolution of the bubble size was simulated and the results are shown in Fig. 3a. The rate of bubble growth decreases slightly with the increase of the branch ratio. Fig. 3b shows the development of both Tr and dTr/dt as a function of t for different PPs during bubble growth. Recall the Considere criterion requires that for stable bubble growth, dTr/dt must be larger than Tr. And the intersection of the two curves (dTr/dt and Tr) represents the onset of unstable extension that leads to eventual bubble rupture. For polymers with a higher branch ratio, the model predicts that the time for stable bubble growth before rupture is longer (see Fig. 3b). Compared with the linear PP, the LCBP with a degree of branching of 0.8 has an increase of stable growth time of more than 20%. The model prediction agrees well with the observation that the presence of long-chain branch is beneficial for the improvement of foamability of PPs. Note that the increase of branching ratio may result in changes of a variety of rheological properties, e.g., zero shear viscosity, relaxation time, strain hardening behavior, etc. The increased stability for bubble growth, therefore, results from these collectively changes. An investigation of the properties individually will facilitate de-convoluting these compounded effects and identifying the critical properties that affect the bubble growth stability. Simulation study presented in the next section is focused on this.

3.3. Rheological properties on bubble growth stability

3.3.1. Zero shear viscosity

The effect of zero shear viscosity on the bubble growth was simulated and the results are shown in Fig. 4. The viscosity was changed in the range of 2 × 10^5 to 1.6 × 10^8 Pa s. For a higher viscosity melt, the bubbles growth rate is lower and the stable growth time is longer. This is readily conceivable as the viscosity is a retarding force during bubble growth. The influence of viscosity, however, is highly nonlinear. Whereas quadrupling the viscosity from 2 × 10^5 to 8 × 10^7 Pa s only resulted in a moderate increase in the stable growth time (from 0.61 to 1.0 s), these values increase significantly (to 12.0 s) when the viscosity was further doubled.

3.3.2. Relaxation time

The relaxation time measures the duration time over which the stresses accumulate after initiation of flow or relax after cessation of flow (Arefmanesh and Advani, 1991). During bubble growth, a shorter relaxation time results in more rapid accumulation of the stresses around the bubbles and a lower bubble growth rate (Fig. 5a). This is in agreement with reports from other works (Leung et al., 2006; Otsuki and Kanai, 2005). On the other hand, a longer relaxation time indicates a larger elasticity of the material. The stability for bubble growth is affected to a great extent by the change of relaxation time (Fig. 5b). As the relaxation time

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**Table 1** Parameters for bubble growth simulation in batch foaming process.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere pressure (Pa)</td>
<td>1.0 × 10^5</td>
<td>Estimated</td>
</tr>
<tr>
<td>Melt temperature (°C)</td>
<td>170</td>
<td>Otsuki and Kanai (2005)</td>
</tr>
<tr>
<td>Melt density (kg/m^3)</td>
<td>1.0 × 10^3</td>
<td>Venerus (2003)</td>
</tr>
<tr>
<td>Rigidity module of melt (Pa)</td>
<td>100</td>
<td>Estimated</td>
</tr>
<tr>
<td>Relaxation time of melt (s)</td>
<td>10</td>
<td>Estimated</td>
</tr>
<tr>
<td>Surface tension (J/m^2)</td>
<td>1.3 × 10^{-2}</td>
<td>Estimated</td>
</tr>
<tr>
<td>Henry constant (Pa^{-1})</td>
<td>7.9 × 10^{-2}</td>
<td>Venerus (2003)</td>
</tr>
<tr>
<td>Diffusion coefficient (m²/s)</td>
<td>4.0 × 10^{-9}</td>
<td>Estimated</td>
</tr>
<tr>
<td>Initial CO₂ concentration (wt/wt)</td>
<td>3.4 × 10^{-3}</td>
<td>Venerus (2003)</td>
</tr>
<tr>
<td>Initial bubble radius (µm)</td>
<td>1.0</td>
<td>Venerus (2003)</td>
</tr>
<tr>
<td>Initial shell radius (mm)</td>
<td>0.075</td>
<td>Otsuki and Kanai (2005)</td>
</tr>
<tr>
<td>Rate of pressure release (MPa/s)</td>
<td>0.354</td>
<td>Otsuki and Kanai (2005)</td>
</tr>
</tbody>
</table>

**Table 2** Relaxation times and modulus used for numerical analysis (190°C) (Tsenoglou et al., 2006).

<table>
<thead>
<tr>
<th>Samples</th>
<th>B_n</th>
<th>n</th>
<th>G (Pa)</th>
<th>λ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-A</td>
<td>0</td>
<td>1.8</td>
<td>2000</td>
<td>8</td>
</tr>
<tr>
<td>PP-B</td>
<td>0.4</td>
<td>0.63</td>
<td>2000</td>
<td>11</td>
</tr>
<tr>
<td>PP-C</td>
<td>0.6</td>
<td>0.36</td>
<td>2000</td>
<td>18</td>
</tr>
<tr>
<td>PP-D</td>
<td>0.7</td>
<td>0.18</td>
<td>2000</td>
<td>22</td>
</tr>
<tr>
<td>PP-E</td>
<td>0.8</td>
<td>0</td>
<td>5000</td>
<td>30</td>
</tr>
</tbody>
</table>

**Table 3** Input data for bubble growth simulation (Otsuki and Kanai, 2005).

<table>
<thead>
<tr>
<th>Atmosphere pressure (Pa)</th>
<th>1.0 × 10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt temperature (°C)</td>
<td>190</td>
</tr>
<tr>
<td>Surface tension (J/m^2)</td>
<td>1.32 × 10^{-2}</td>
</tr>
<tr>
<td>Henry constant (Pa^{-1})</td>
<td>5.38 × 10^{-9}</td>
</tr>
<tr>
<td>Diffusion coefficient (m²/s)</td>
<td>8.0 × 10^{-9}</td>
</tr>
<tr>
<td>Initial CO₂ concentration (wt/wt)</td>
<td>3.4 × 10^{-3}</td>
</tr>
<tr>
<td>Initial bubble radius (µm)</td>
<td>0.1</td>
</tr>
<tr>
<td>Initial shell radius (mm)</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Fig. 2. Comparison of the bubble growth between numerical results and Taki et al.’s experiment data.
Fig. 3. (a) Effect of branching degree on the bubble growth. (b) The generalized Considère stability criterion for various PPs.

Fig. 4. (a) Effect of zero shear viscosity on the bubble growth. (b) The generalized Considère stability criterion. $\eta = 10^{5}$ Pa s, $n = 1$ and other parameters are the same as in Table 3.

Fig. 5. (a) Effect of relaxation time on the bubble growth. (b) The generalized Considère stability criterion. $\eta = 8.0 \times 10^4$ Pa s, $n = 1$ and other parameters are the same as in Table 3.
increases over the range from 0.2 to 2 s, the interface rupture occurs at much later stage from 2.6 to 6.6 s. Thus the melt elasticity enhances the stability during bubble growth process. It shall be noted, however, a reversed trend was observed when the relaxation time was further increased to 10 s, and the stable growth time decrease to 1.0 s. This could be readily understood from the following arguments. As discussed earlier, for stable growth, stress accumulation around the bubble is critical. With a longer relaxation time, the accumulation of stress is retarded during bubble growth and it may not attain needed levels. Consequently instability incurs.

### 3.3.3. Strain hardening

Fig. 6a shows the influence of strain hardening on the bubble growth by varying the viscoelastic nonlinearity exponent from 2 to 0. Strain hardening has negligible effect on the rate of growth and equilibrium size of the bubbles, similar to observations made by others (Otsuki and Kanai, 2005; Venerus et al., 1998). On the other hand, the strain hardening has moderate impact on the bubble growth stability, as shown in Fig. 6b and c. While bubble rupture occurs at early stage (0.81 s) of bubble growth for the linear PP \( n = 2 \), the stability is improved (1.0 s) as the nonlinearity exponent decreases to 1. The trend is, however, reversed as \( n \) is further decreased to 0 (elastic rubber), and the time for stable growth decreases to 0.6 s. This is probably due to the decreased strain at break for polymer melts exhibiting strong strain hardening behavior (Aloku and Yuan, 2010; Gotsis et al., 2004a).

The simulation results hitherto suggest that among the three factors considered hereof (zero shear viscosity, relaxation time and strain hardening), the change of which would result from change of the degree of branching, a good compromise between relaxation time and strain hardening may provide improved stability of bubble growth. In addition, the stability of bubble growth increases monotonously with the increase of viscosity. It is also noteworthy that our model could qualitatively capture the bubble rupture phenomenon and provide a useful tool to investigate the effects of a variety of physical chemical properties on the bubble growth stability. While previous numerical studies on bubble growth assumed that the bubbles would grow steadily until thermodynamic equilibrium was achieved (Mao et al., 2006), or the melt extension was always stable, our simulation suggests that this assumption is not always valid. Even at later stage of bubble growth, instability may still occur because a slower increase in bubble radius does not always warrant a stable extension flow field. This would result in cell opening and in the extreme, collapse of the cellular structure.

### 3.4. Analysis of other factors on bubble growth stability

In addition to the rheological properties, other physical properties of the polymers and processing parameters may also

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**Fig. 6.** (a) Effect of strain hardening on the bubble growth. (b) The generalized Considère stability criterion. (c) The time for the stable growth of bubble. \( \lambda = 10 \text{ s}, \eta = 8.0 \times 10^4 \text{ Pa s} \) and other parameters are the same as in Table 3.
impact the bubble growth process, and they are simulated using the established model.

3.4.1. Initial CO₂ concentration

The effect of initial CO₂ concentration on bubble growth and rupture was simulated and results are shown in Fig. 7. It is observed that initial CO₂ concentration has a remarkable effect on bubble growth. Both the rate of bubble growth and the equilibrium bubble size increase as the initial gas concentration in polymers is increased. At higher initial gas concentration, larger concentration gradient (thus higher diffusion rate) exists across the bubble polymer interface, leading to more rapid bubble growth. In addition, more gas is available to support the bubble growth and therefore a larger equilibrium bubble size. Note, however, in order to realize the equilibrium bubble size, growth stability is necessary, which is influenced by the initial gas concentration. Shown in Fig. 7b are the predicted stability using the Considère criterion. At higher gas concentration, the bubble growth instability occurs earlier. The reduced stability window may pose significant challenge to achieve stable foaming operations. For example, at gas concentration of $8.0 \times 10^{-3}$, the bubble size begins to slowly approach the equilibrium value in $\sim 0.05$ s and the instability occurs at $\sim 0.2$ s. The difficulty associated with narrow foaming window will need to be taken into account in foaming process development. On the other hand, the stability window can be significantly expanded by reducing the gas concentration. However, this would negatively impact the attainable cell size and overall porosity. As predicted by the model, decreasing the gas concentration to $2.0 \times 10^{-3}$ would lead to a stable growth time longer than 8.5 s, but this is accompanied by the reduction of achievable cell size of 42% and expansion ratio of 32%.

3.4.2. Gas diffusion

The effect of gas diffusivity on the bubble growth and rupture was modeled and shown in Fig. 8, in which the diffusion coefficients were varied from $2 \times 10^{-9}$ to $8 \times 10^{-9}$ m²/s. Diffusion primarily influences the foaming dynamics and has negligible effects on the equilibrium cell size (Fig. 8a). A reduction of the diffusion coefficient from $8 \times 10^{-9}$ to $2 \times 10^{-9}$ m²/s leads to a slight increase in time to reach the same cell size, while expanding the window for stable growth considerably. As shown in Fig. 8b, the stable growth time increases to 2.4 s from initially less than 1 s. Slower diffusion leads to slower bubble growth.

![Fig. 7.](image)

(a) Effect of initial CO₂ concentration on the bubble growth. (b) The generalized Considère stability criterion. The concentrations were varied between $2.0 \times 10^{-3}$ and $8.0 \times 10^{-3}$; $\lambda = 10$ s, $\eta = 8.0 \times 10^4$ Pa s, $n = 1$ and other parameters are the same as in Table 3.

![Fig. 8.](image)

(a) Effect of diffusivity on the bubble growth. (b) The generalized Considère stability criterion. $\lambda = 10$ s, $\eta = 8 \times 10^4$ Pa s, $n = 1$ and other parameters are the same as in Table 3.
(expansion), which appears to substantially reduce the rate of strain hardening and saturation of the extension viscosity. Both contribute to the improvement of bubble growth stability. It shall be noted that the model is capable of capturing the essence of one well-known challenge in CO2 foaming technology. In spite of the many attractive features CO2 possesses, the potential of its application in foaming is yet to be achieved. One of the most prominent difficulties is the much higher diffusivity of CO2 compared to the traditional physical blowing agents such as fluoro-containing compounds and hydrocarbons. This difficulty is well depicted by the model, which predicts higher diffusivity of the blowing agent results in violent bubble expansion and extremely narrow stable operation window. In fact, effective strategies for slowing down CO2 diffusion are highly sought to address this challenge and improve the industrial applicability of CO2 foaming technology.

3.4.3. Henry constant

The influence of Henry constant on the bubble growth and rupture is shown in Fig. 9. With the same initial gas concentration, an increase in Henry constant leads to a smaller bubble size. This is conceivable as larger amount of gas is retained in the polymer–gas solution due to the higher gas solubility; the amount of gas available for bubble growth is reduced. The higher gas concentration in the polymer–gas solution shell and in particular at the gas bubble interface (Fig. 9c) also results in a reduced concentration gradient (Fig. 9d) and slower mass transfer into the bubble. Consequently the rate of bubble growth is lower. Furthermore, the slower accumulation of gas in the bubble and pressure buildup may lead to lower stress around the bubble interface. Thus the increased stable growth time at higher Henry constant (Fig. 9b) is the result of the synergistic effects of slower mass transfer and low stress during bubble growth. It shall be noted that these effects are highly nonlinear.

3.4.4. Interfacial tension

Fig. 10 illustrates the effect of interfacial tension on bubble growth and rupture, by varying surface tension values from $1.0 \times 10^{-2}$ to $2.0 \times 10^{-2}$ J/m$^2$. Neither the rate of bubble growth and equilibrium bubble size, nor the stability during growth is sensitive to the surface tension. This might result from the fact in our simulation the viscoelasticity of the materials dominates and the role of surface tension is negligible.

4. Conclusions

The isothermal bubble growth and rupture during foaming of polypropylenes by carbon dioxide were simulated by using the cell model. Gotsis’s model, which connects rheological characteristics with macromolecular architecture, was used to describe the
viscoelastic properties of the melt, and the Considère construction was used to predict the onset of bubble rupture. The established model is able to predict the effects of a wide range of physical and rheological properties on the foaming dynamics and occurrence of instability. The results indicate that higher viscosity facilitates stable bubble growth and delay the onset of bubble instability. The bubble growth stability is enhanced by moderate relaxation time and strain hardening. However, strong strain hardening and high elasticity are detrimental to the stability and bubble rupture may occur at an earlier stage. In addition, bubble growth stability is generally improved by reducing the bubble growth rate. This may be realized by change of the physical properties of the polymer–gas system, e.g., reduction in diffusivity and enhancement of solubility; or processing conditions, e.g., use of lower gas concentration. Some of these changes, however, will also influence the foam morphology (cell size) and porosity. Surface tension has negligible effect on the bubble growth.

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References

Fig. 10. (a) Effect of interfacial tension on the bubble growth. (b) The generalized Considère stability criterion. λ = 10 s, η = 8 × 10^6 Pa s, n = 1 and other parameters are the same as in Table 3.

