Experimental observations and modelling relating to foaming and bubble growth from pentane loaded polystyrene melts

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Abstract

This paper is concerned with microstructure and kinetics relating to bubble growth within a pentane loaded molten polystyrene sample and the work is of relevance to the commercial foaming of polymers achieved by pressure release at the exit of an extruder. Optical experiments were carried out using a Multipass Rheometer to follow the time evolution for melting pentane loaded polystyrene beads. Two protocols were followed and one resulted in the formation of a single melt phase. With subsequent pressure release, the growth kinetics of bubbles were followed together with rheological measurements. A modified Newtonian model incorporating gas diffusion was developed and compared with the experimental data. Good matching of data could be achieved using realistic values of parameters and the model was able to predict early stage growth conditions. The model, as presented, still has many simplifications, however it does form the basis for further refinement.

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1. Background

Thermoplastic foams represent an important class of materials that have cost and weight effective properties particularly in the areas of impact strength, thermal and electrical insulation and light weight structures. Polymeric foams can be produced by wide variety of processes ranging from expandable beads to injection moulding and extrusion. Polymer foaming by extrusion processing involves the dissolution of a gas into the molten polymer to produce a supersaturated solution of the polymer and gas at elevated temperature and pressure. When the polymer exits from an extrusion die, sudden pressure and temperature changes occur, resulting in nucleation and growth of bubbles producing a foamed structure (Joshi et al., 1998). The bubbles which form, expand and the foam structure stabilises as the polymer matrix solidifies resulting in the final foam morphology. The type of foam and the final properties such as strength, density and insulating properties of the foam are determined by the chemistry, process parameters, such as extrusion rate, dissolved gas concentration, cooling rate and the foaming temperature and pressure. The final foam can be brittle, soft or resilient depending on the control of cell structure and induced orientation. Different foaming processes vary on the macroscopic level, in relation to the temperature, pressure and stabilising of the process. At a submicron level, thermodynamic fluctuations give rise to clusters of gas molecules forming, and these clusters grow or decay depending on whether their size is greater or less than a critical cluster size (Amon and Denson, 1984).

The foaming of thermoplastic polymers using physical blowing agents is a complex process. Many variables simultaneously influence the rheological and the microstructure of the product during the growth and its final stage. Investigations addressing the theoretical analysis of bubble growth in polymer foam have been reported (Shafi et al., 1996; Shafi...
and Flumerfelt, 1997; Koopmans et al., 2000; Den Doelder et al., 2002). Almost all previous work on polymer foaming involve the theoretical study of bubble growth and only few experiments were reported that address the dynamic behaviour of bubble growth in the molten polymer (Villamizar and Han, 1978a,b; Ramesh et al., 1991; Taki et al., 2003). Other experimental studies have mainly focused on the effect of polymer properties as well as operating conditions on the cellular structure in foams. The cellular structure has been mostly investigated from experiments after the foam has been formed (Ramesh et al., 1994a,b; Pallay et al., 2000; Elmoutaouakkil et al., 2003).

The bubble growth data for these foams are important for understanding the foam growth process and for testing the validity of models. This paper details an investigation into the controlled foaming of a commercial expandable polystyrene loaded with pentane. Visual and rheological experiments were performed using a Multipass Rheometer under closely controlled pressure and temperature conditions, allowing online observation of bubble growth and deformation to be made. Based on the existing literature, a bubble growth model has been developed to fit the experimental data and this helps in establishing parameter values for the foaming process and also aids understanding the early stage of the foaming process.

2. Experimental: apparatus and loading protocol

The MPR was used as a variable pressure device to follow foaming. The MPR was developed by Mackley et al. (1995) at the University of Cambridge and has proved to be a useful platform for foaming studies. In this paper the sample under test was constrained in a ‘test section’ which comprised of a heated optical section held between two barrels that contained servo-hydraulically controlled pistons, as shown in Fig. 1. The pistons are housed in two barrels (top and bottom sections), both of which are fitted with pressure transducers and thermocouples. The temperature of the sample was controlled by flowing heated silicon oil from a heater/circulator through the heated jackets around the bottom and top barrels and the test section. As the MPR is a closed system, it is possible to control the internal operating pressure precisely by adjusting the position of the servo-hydraulically controlled pistons. This allows a foam sample to be melted under pressure, inhibiting gas escape and immediate foam growth, then by subsequently reducing the internal pressure, initiating foaming in controlled manner. The optical arrangement includes a light source; collimating lenses to generate a parallel beam of light; quartz optic windows in the test section (Fig. 1a). The images transmitted through the sample were detected by CCD camera and captured using a video recorder. Images were analysed and processed using image-editing software Adobe® Premier Photoshop.

The MPR was also used in a more standard way to obtain rheological data of a single phase melt. Details of the MPR and its application to rheology processing are explained elsewhere (see e.g. Mackley et al., 1995; Ranganathan et al., 1999). The MPR was used as a double-piston capillary rheometer (Fig. 1b). The sample under study was driven back and forth through a capillary test-section by hydraulic pistons. This unique arrangement allowed rheological experiments to be carried out for molten polymer containing dissolved gas.

The foaming experiments were carried out using commercial expanded polystyrene (EPS) pellets provided by BASF and The DOW Chemical Company. EPS are produced through suspension polymerisation of styrene in the presence of pentane, nucleating agents, initiators, and stabiliser systems. In this paper, experimental data for BASF EPS is only presented. Qualitatively it was observed that the DOW EPS behaved in a similar way in relation to bubble growth kinetics. The changes in the rheology of EPS due the presence of pentane were compared with base polystyrene (PS).

2.1. Loading protocol

In order to contain the pentane of EPS, it was essential to keep the material enclosed when it was being heated from a solid state to the molten state in the MPR. The following loading protocol I was followed. The bottom barrel, test section and the top barrel were filled with EPS pellets at room temperature. The moveable bottom platform was then raised so that the top piston entered the top barrel to form fully enclosed system. The vacuum pump was attached through the bleed valve to evacuate entrapped air from the system. The bleed valve was then tightened to form a sealed assembly. The oil circulator pump was switched on to pump heated oil through MPR circuit. The piston positions were constantly adjusted to maintain the system pressure while the sample was continuously being heated up.

Using loading protocol I, it was not possible to achieve a single phase melt because there was not enough piston displacement available to compensate for compressible effects. A single phase of the melt is a prerequisite to study foaming similar to that experienced in certain commercial foaming processes. In order to achieve a single phase, it was essential to keep the pentane loaded polystyrene pellets under high pressure during the transition from the solid to melt. This was achieved by altering the loading protocol I to enable a greater volume of sample to be loaded into the MPR barrels. This protocol is named as loading protocol II. Based on the visual observations of the sample obtained using loading protocol I (discussed in Fig. 2), the samples were initially loaded at high temperature. The bottom and top barrel were filled with EPS pellets and heated to 80°C using the silicone oil heating circuit. At this temperature, the pellets expanded, but the identity of each pellets were preserved. The expanded samples were periodically compacted with a brass rod to minimise the amount of trapped air. The void space left from compaction was filled with more pellets.
until the barrels were full. The same procedure was repeated for the test section for rheological and decompression foaming experiments. For the visual observation of the heating sequence at high pressure, the bottom and top barrel were loaded using loading protocol II and the test section (with optical settings) was loaded using loading protocol I so that the original pellet structure is retained initially in the test section.

3. Results and discussion

3.1. Protocol I: Optical and microstructure observations

Experiments were carried out to visualise polymer melting at different stages of heating at 1 bar. Initially the EPS pellets were loaded into MPR using protocol I (Fig. 2a). Heating of EPS pellets at low pressure involves (i) swelling, (ii) space filling, (iii) cloudy phase formation and finally, (iv) bubble formation and growth. Initially EPS pellets swelled to form compact particles. The mechanism for swelling is either associated with an internal osmotic pressure within the polymer due to the presence of the solvent (see e.g. Gao and Mackley, 1994), or the presence of micro voidage gas phase. At 85°C, the swollen spherical pellets expanded further to polyhedral shapes filling up interstitial void spaces (Fig. 2b). With further heating, the MPR pressure started to rise slightly. The pressure was adjusted to 1 bar by moving the two pistons apart. At ca. 95°C, the expanded pellets started to lose their boundary and fuse together forming a white opaque “cloudy phase” (Fig. 2c). A further increase in temperature (>100°C) led to the emergence of microscopic bubbles from the cloudy phase. These microscopic bubbles subsequently grew in size and filled the entire test section (Fig. 2d). The overall appearance of the melt also changed from opaque cloudy structure to transparent polymer melt with bubble inclusions. Above 130°C, there was barely any change in bubble size.

Fig. 3 shows the corresponding micro-structure of EPS samples obtained in Fig. 2. The samples were obtained by “heat and quench technique” in the MPR. The sample was heated and held at a constant temperature for a prescribed period and then quenched to room temperature under the same loading pressure. One of the drawbacks of heat-and-quench technique is the effect of quenching on bubble size as compared to in situ optical observation. The quenched samples obtained from MPR barrel were cylindrical with a diameter of 12 mm. The samples were then sliced and viewed using a SEM. Fig. 3a shows unprocessed EPS spherical pellets at room temperature with an average size of 300–800 μm. The surface appears fairly smooth at higher magnification. At 65°C, a slight dent is visible on the sample where it was in contact with the neighbouring pellets (Fig. 3b). At this temperature, the sample is loosely held together and can be easily dispersed with a small force. Crazing, 2–5 μm in width, appear on inter-granular contact points (Fig. 3b2). Crazing may be a starting point from where cracks start to grow and finally lose their boundary structure to fuse with the neighbouring samples as the heating proceeds further. At 85°C, the structure of each spherical pellets change to form polyhedral structure filling up the inter-granular void spaces (Fig. 3c). Though the surface of each pellet is in contact with the neighbouring sample, it still retains its structure and has not fused.

The appearance of cloudy phase as seen in Fig. 2c is assumed to consist of clusters of sub-micron bubbles which are not optically resolvable. We were not able to see the presence of any bubbles using the SEM and the heat and quench technique. Disruption of these sub-micron bubbles may have occurred during SEM sample preparation or may be some way related to the extended cooling protocol used.
We were however, able to observe micro-bubbles using a different but related preparation method. Solid single phase thin EPS discs samples (\( \sim 200 \) \( \mu \)m) were prepared by placing EPS pellets between two aluminium sheets in the heated press and was heated at 90 °C with a force of 20 tons (measured on a 4 in diameter ram) for 30 min. The sample was subsequently cooled under the same loading condition. The sample was then removed and heated in a control oven at around 95 °C (\( \pm 1 \) °C) in ambient pressure resulting in change from transparent to white cloudy phase. SEM image of such cloudy phase at low magnification shows a smooth surface (Fig. 3d1). However, the samples consists of cluster of tiny bubbles in sub-micron domains (Fig. 3d2) when viewed at higher magnifications.

Above 100 °C, many small bubbles less than 100 \( \mu \)m in diameter were visible. With increasing temperature, more bubbles appear (Fig. 3e1). Each bubble was separated from the neighbouring bubble by thin film of polystyrene (Fig. 3e2).

### 3.2. Protocol II: Optical observations

The heating of EPS pellets at high pressure was carried out using loading protocol II in order to achieve a single phase melt of PS and pentane (Fig. 4). The heating sequence at high pressure involves (i) swelling, (ii) space filling and finally (iii) single phase melt. Initial stages were similar to that of Fig. 2 where EPS spherical pellets expanded to form polyhedral structures and filled up the void spaces (Fig. 4b). The pressure increased significantly to ca. 60 bar at this stage as compared to 5–10 bar with the loading protocol I. At 90 °C, the pressure in the system increased to ca. 110 bar. At this point, the EPS pellets started to lose their boundary to form a
single phase melt as shown in Fig. 4c where the melt is forming from the top. With further melting, the pressure started to drop. At this point, the sample was compressed by moving both pistons inward to increase the pressure within the system above 100 bar. The entire test section then formed a transparent single phase melt at 100 °C (Fig. 4d). No bubbles were observed during the entire process. SEM observation of the sample also did not show the presence of bubbles.

The above sequence shows that a single phase melt of the polystyrene loaded with pentane can be obtained in MPR when heated under high pressure. This was necessary in order to study the nucleation and bubble growth of polymer foams by subsequent decompression.

3.3. The evolution and growth of bubbles during decompression

Having established a single phase melt, the evolution of nucleation and bubble growth during decompression of the EPS melt is shown in Fig. 5. The decompression process of the melt involves a phase transition of the dissolved gas from solution in the melt to a gaseous phase. This transition is caused by a change in volume and corresponding pressure of the system. Fig. 5a shows a photograph of a single phase melt at 140 °C at 190 bar. The pressure is then reduced by moving both pistons apart by 7.7 mm on each side at a speed of 1 mm/s, hence increasing the overall MPR chamber volume by 21%. There was a lag period of few seconds before the first bubble was optically visible (Fig. 5d). As the pressure drops, nucleation appears to occur randomly leading to subsequent bubble growth from these sites. With time, more bubbles nucleate and grow. During the initial growth phase, all the bubbles are spherical, however, after reaching a critical diameter, the bubble becomes elliptical with the vertical axis of the MPR forming a major axis (Fig. 5h). For most conditions studied, the growth appears to be a slow process taking more than 1 min for the bubbles to reach their maximum limiting size.

Fig. 6a follows the time evolution of a single bubble (obtained from Fig. 5) during decompression. The figure also shows the effect of change in MPR piston position on the overall pressure of the system, hence leading to subsequent bubble formation and growth. For clarity only the bottom pressure and bottom piston position are shown as both the top and bottom pressures and pistons profiles were identical. The increase in overall chamber height is represented by a reduction in pistons position. Most of the pressure drop occurs for a very small piston displacement (<2 mm) shown by two vertical dotted lines XX’ and YY’ which gives the initial pressure release rate of ca. 75 bar/s. There is then a lag period of few seconds before the bubble becomes visible. After the lag period, the bubble formation and growth is spontaneous. Initially a microscopic dot appears within the melt and spherical bubble growth occurs. In the next 20–30 s, the bubble reaches its maximum spherical size having a diameter of ca. 400–500 µm. After this critical spherical size, the bubble then tends to grow more along the vertical axis than the horizontal axis as shown on the figure (defined as height and width, respectively). In less than 2 min, the bubble has reached its maximum size after which there is no further growth. The width of the barrel is fixed and during decompression, the piston is moved apart from each other creating
extra free space in the vertical sections of the barrel. This may be the reason for elliptical bubble with major extension in the vertical direction. Gravity acting on the bubble could be another reason for elliptical bubble formation. The growth of other bubbles were also studied. For all the bubbles, the critical spherical size were found to be ca. 400–500 μm in diameter after which they grew as ellipses. The maximum bubble size were found to be in the range 1200–1850 μm in height and 700–850 μm in width. This gives an equivalent bubble radius (assuming \( \pi R^2 = \frac{1}{4\pi} \times \text{width} \times \text{height} \)) of 450–650 μm for all bubbles. Though the lag time varied between the bubbles, once the nucleation process initiated, growth profile followed a similar profile as shown here (Fig. 6b).

From Fig. 5(l), the number of bubbles formed was found to be 55 bubbles per cm² with 53% void fraction. Assuming an isotropic distribution of bubbles with an average bubble radius of 550 μm, the number of bubbles formed per unit volume was determined to be ca. 7.6 × 10² cm⁻³. This is much less than compared to that obtained in a commercial extrusion foamed product ∼2.3 × 10⁵ cm⁻³ with 98% void fraction and an average bubble radius of 100 μm. In the case of the MPR, decompression involves piston movement from one volume to another resulting in pressure reduction within MPR. The pressure within the MPR decreases as shown for example in Fig. 6b. Subsequently as the bubble nucleate and grow, the pressure within the MPR can rise (Fig. 6b). By contrast extrusion foaming involves the sudden release of molten polymer from the die with the emergence of a free surface that allows the unrestricted expansion of the material.

3.4. Dissolution of bubble under compression

Fig. 7 illustrates the dissolution of bubbles from the polymer melt into a single phase melt when the pressure of the system is raised. Fig. 7a shows a two-phase mixture of
Fig. 5. Nucleation and bubble formation from a EPS single phase melt with a rapid release of pressure from 190 to 1 bar in an isothermal condition of 140 °C within the MPR. Decompressed at a piston speed of 1 mm/s with a 7.7 mm total displacement of the top and bottom pistons corresponding to 21% increase in the sample volume: (a) $t = 0$ s, $P = 190$ bar; (b) $t = 6.8$ s, $P = 70$ bar; (c) $t = 13.0$ s, $P = 0.2$ bar; (d) $t = 15.0$ s, $P = 0.2$ bar; (e) $t = 18.0$ s, $P = 0.2$ bar; (f) $t = 23.0$ s, $P = 0.2$ bar; (g) $t = 30.0$ s, $P = 0.2$ bar; (h) $t = 40.0$ s, $P = 0.3$ bar; (i) $t = 50.0$ s, $P = 0.6$ bar; (j) $t = 70.0$ s, $P = 1$ bar; (k) $t = 130.0$ s, $P = 2.1$ bar; (l) $t = 245.0$ s, $P = 2.5$ bar.
This shows that the sample is highly compressible. This is equivalent to a 4% reduction in the sample volume. During this stage, the bubble size drops rapidly and they subsequently dissolve. The rapid increase in pressure for a small displacement $(XX' \to YY')$ towards the end of piston displacement is analogous to the rapid drop in pressure in the early stage of decompression test (Fig. 6). These results illustrate the high compressibility of the sample. The bubble–polymer sample has to be initially compressed above a critical value before a significant increase in pressure is obtained and hence dissolution of the bubble is achieved.

4. The rheology of PS and EPS

In order to model the observed bubble growth kinetics, it is necessary to know the rheological behaviour of the pentane loaded PS samples and series of ‘standard’ MPR experiments were carried out to establish the materials flow curve. The MPR was operated in multi-pass mode where the two pistons in tandem and are used to drive the fluid sample through a capillary insert. Piston velocities ranging from 0.01 to 80 mm/s were used to cover a large range of apparent wall shear rates. The experiments at different temperatures and shear rates were tested using the same loaded sample. The pressure difference across the capillary of length was calculated from the output of two pressure transducers mounted on the top and bottom section of the MPR, and an estimate of apparent viscosity, $\eta_{\text{app}}$, obtained as (Mackley et al., 1995)

$$\eta_{\text{app}} = \frac{\Delta P a^4}{8 L R_b^2 V_P},$$

where $\Delta P$ is the measure pressure difference across a capillary of length $L$ and radius $a$. $R_b$ is the radius of the barrel and $V_P$ is the piston velocity.

Fig. 9 shows the pressure difference and piston displacement data obtained from multi-pass experiments for pure PS melt and EPS single phase melt containing 6 wt% pentane at a mean pressure of 100 bar and a piston speed of 0.1 mm/s. This corresponds to a wall shear rate of $15 \text{s}^{-1}$. Both shows the general trend where the pressure difference increases as the piston is displaced and reaches a steady state. EPS single phase, however, has lower $\Delta P$ values than the PS sample indicating a lower viscosity. When the flow is stopped, the PS sample takes longer time to relax as compared to EPS single phase melt. Similar profiles were obtained at other shear rates.

Fig. 10 compares the apparent viscosity of pure polystyrene and EPS single phase melt at 190°C and 100 bar melt pressure obtained from multi-pass experiments in MPR. In general, it can be seen that the apparent viscosities of the EPS (with pentane additives) follows a similar
Fig. 7. Dissolution of bubbles during compression at 150°C. Compressed at the piston speed of 1 mm/s with 7.8 mm total displacement of top and bottom pistons corresponding to 17% reduction in the sample volume: (a) $t = 0$ s; (b) $t = 1.0$ s; (c) $t = 2.0$ s; (d) $t = 3.0$ s; (e) $t = 4.0$ s; (f) $t = 5.0$ s; (g) $t = 5.24$ s; (h) $t = 5.40$ s; (i) $t = 5.56$ s; (j) $t = 5.64$ s; (k) $t = 5.84$ s; (l) $t = 6.52$ s.
Dissolution of a bubble was obtained following the reduction of an individual bubble shown in Fig. 7.

Fig. 8. Time evolution of pressure, piston position and bubble size during compression.

Fig. 9. Piston displacement and differential pressure using multipass steady experiments at high pressure (> 100 bar) for PS and EPS single phase containing 6 wt% pentane at 190 °C. Capillary diameter 2 mm, length 12 mm, piston displacement 10 mm, piston speed 0.1 mm/s (apparent wall shear rate = 15 s⁻¹).

Fig. 10. Apparent viscosity as a function of apparent shear rate for PS and EPS single phase melt (containing 6 wt% pentane) at 190 °C. Capillary: diameter 2 mm, length 12 mm, barrel diameter = 12 mm.

Fig. 11. The effect of temperature on the apparent viscosity of a EPS single phase melt (containing 6 wt% pentane) above 100 bar. Capillary: diameter 2 mm, length 12 mm, barrel diameter = 12 mm.

Trend to that of PS, however, the PS with 6 wt% pentane consistently exhibits a lower apparent viscosities compared to pure PS. The effect of gas on apparent viscosity is slightly higher at lower shear rates. Detailed investigation of viscosity reduction in polymers due to the presence of a dissolved gas has been reported earlier (Lee et al., 2000; Chong et al., 2003). Chong et al. (2003) found the viscosity of polymer decreased with increasing gas concentration during the manufacture of microcellular plastics.

Fig. 11 shows the temperature effect on the apparent viscosities for EPS single phase melt. The steady shear viscosity data appears to be well behaved and covers a range of shear rates from 1 to 10,000 s⁻¹ at 150–190 °C. The temperature dependence is compatible with the one for standard polystyrene melts. Additives such as pentane may act as plasticisers, hence an analogous formalism for the change in the viscosity holds for melts with additives. In general, as the temperature reduces the apparent viscosity of the melt increases and each new flow curve obtained therefore lies above the previous ones.

5. Bubble growth modelling

Having established both the bubble growth kinetics and rheology of the system, a model was developed to describe the process. The first two stages in foaming involve nucleation and bubble growth. The classical theory of nucleation is based on Gibbs free energy required for creating a void in a liquid and assumes that the critical bubble is in mechanical and thermodynamic equilibrium with the surrounding liquid (Jones et al., 1999). Bubbles larger than the critical bubble has a tendency to grow while smaller one collapse. Although many theories have been proposed for nucleation, there is no single theory that is able to predict events accurately. Recently, Feng and Bertelo (2004) developed a nucleation model based on the concept of heterogeneous nucleation originating from pre-existing micro-voids on solid particles. Joshi et al. (1998) attempted to derive an initial condition that corresponds to the upper bound of critical state where thermal fluctuation cannot drive a supercritical bubble to subcritical state. Han and Han (1990) included the effect of supersaturation on bubble nucleation in determining the minimum work for critical bubble formation. The nucleation process is difficult to predict, but once the nucleation
occurs, bubble growth is controlled by the classical laws. The pressure of the gas within the bubble provides a driving force to expand bubble while the viscosity of the polymer and surface tension of the bubble wall provide resistance to bubble growth (Barlow and Langlois, 1962). There is a scientific literature on bubble growth of gas laden melts (see e.g. Barlow and Langlois, 1962; Patel, 1980; Han and Yoo, 1981; Shafi et al., 1996; Shafi and Flumerfelt, 1997; for a bubble growth in an infinite melt and Amon and Denson, 1984; Ramesh et al., 1991, 1994a; Prousevitch et al., 1993; Prousevitch and Sahagian, 1998; Koopmans et al., 2000; for a bubble growth in finite melt).

In terms of bubble growth, in this paper the fluid is assumed to be Newtonian and governed by equations first proposed by Barlow and Langlois (1962). An important aspect of the model is bubble growth modified by the diffusion of gas from the surrounding melt. During a foaming process, a number of bubbles grow in close proximity, hence, the dissolved gas available for diffusive bubble growth in the foaming process is limited to the gas in solution surrounding a bubble. The modelling used in this paper is based on a bubble growing in liquid of finite volume. A schematic diagram (Fig. 12) shows the key aspect of the model. Each bubble is assumed to be surrounded by a finite volume of melt (with dissolved gas) represented by an “influence cell”. The influence cell is assumed spherical having an initial radius of \( r_0 \) with a bubble nucleus at its centre. The bubble growth is assumed spherical when it is nucleated and remains so for the entire period of growth. This approximation simplifies the numerical formulation reducing the three-dimensional problem to a single dimensional parameter in spherical coordinate. It is also assumed that the gas pressure in the bubble, \( P_G(t) \) is always at equilibrium with the dissolved gas concentration at the bubble gas/melt interface, \( c_R(t) \). As the polymer is highly viscous, inertial and gravity effect are neglected.

5.1. Governing equations for a single bubble growth

The governing equation for a single bubble growth in a polymer melt solution can be represented by three equations (2–4) (for derivations see Barlow and Langlois, 1962; Ramesh et al., 1991; Prousevitch et al., 1993) based on the overall force balance on the melt, mass balance of the gas in the polymer melt and the mass balance on the bubble, respectively.

Combined equation of momentum and continuity of the melt surrounding the bubble in the radial component (\( r \)) of spherical coordinate gives

\[
P_G = P_L + \frac{2\pi}{R} + 4\pi R^2 \int_{z(S)} \eta(z) \, dz, \tag{2a}
\]

where \( \bullet \) is the bubble radius growth rate, \( P_L \) is the ambient pressure, \( \sigma \) is the surface tension, \( \varepsilon = 1/r^3 \), \( \eta \) is the melt viscosity that may depend on gas concentration, \( R \) and \( S \) are the bubble and melt radius at time \( t \). The integration above takes account of the effect of variable viscosity within the melt radius. Polystyrene melts are viscoelastic, however in this paper they are treated purely as being Newtonian. Clearly this is a great simplification and issues such as shear thinning, non-linear viscoelasticity and solvent concentration effect of viscosity could, with benefit, be included into the modelling, however at this preliminary stage it was felt their inclusion would be a over complication. If the viscosity within the melt is assumed constant, Eq. (2a) gives,

\[
P_G = P_L + \frac{2\pi}{R} + 4\pi R^2 \left( \frac{1}{R} - \frac{R^2}{S^3} \right). \tag{2b}
\]

Eq. (2b) can be represented as

\[
P_G = P_L + P_o + P_V, \tag{2c}
\]

where \( P_g \) and \( P_V \) are surface tension and dynamic pressure contribution, respectively.

Mass balance of the bubble requires that rate of mass added to the bubble by pentane diffusion equals the rate that the gas diffuses in through the bubble surface. Thus, diffusive mass balance at the bubble surface relates bubble pressure to the concentration gradient at the surface,

\[
\frac{d}{dr} \left( \frac{4\pi R^2}{3} \frac{P_G M}{RT} \right) = 4\pi R^2 D \rho \left( \frac{\partial c}{\partial r} \right)_{r=R}, \tag{3}
\]

where \( c \) is the dissolved gas concentration (wt. fraction) in the melt, \( D \) is the binary diffusion coefficient, \( \rho \) is the
melt density, \( M \) is the molecular weight of the gas, \( T \) is the temperature and \( R \) gas constant. The left-hand side of Eq. (3) implicitly contains the bubble growth velocity term.

Diffusion of gas in the melt is assumed to obey Fick’s law defined as

\[
\frac{\partial c}{\partial t} + \frac{R}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) = 0 \quad r \geq R. \tag{4}
\]

Eq. (4) describes the concentration profile in the melt. It is necessary to know the concentration gradient at the bubble-melt interface for Eq. (3). Bubble growth is initiated by an unspecified nucleation process. The prediction of nucleation is difficult area and this paper has only been addressed in relation to model initial condition. In terms of the modelling, this is represented by an initial bubble radius, \( R_0 \), and an initial pressure, \( P_{G0} \). The concentration profile of the gas across the bubble wall and \( R_0 \) value have strong influence on the bubble growth. An arbitrary choice of these can lead to considerable error. The actual initial bubble pressure is likely to be between ambient pressure and the saturation pressure and the initial concentration may be non uniform leading to different internal bubble pressure.

Initially the gas is assumed to be uniformly distributed throughout the melt with a concentration equal to \( c_0 \). Instability of the bubble physical state causes development of a concentration gradient in the influence cell which activates the diffusion of the gas into the bubble. This initial instability is induced by disequilibrium between gas pressure inside the bubble and saturation pressure for \( c_0 \) (Prousevitch et al., 1993). The outer surface of the influence cell is considered to be impermeable for the gas, and therefore the gas flux is zero. The corresponding initial and boundary conditions for Eq. (4) are

\[
c_r(0) = c_0(r) \quad \text{at} \quad r > R \quad \text{and} \quad t = 0, \tag{5a}
\]

\[
\left( \frac{\partial c}{\partial r} \right)_{r=R} = 0 \quad \text{at} \quad t \geq 0. \tag{5b}
\]

The concentration of the gas in the nucleated bubble is assumed to be related to the concentration of the melt at the interface through Henry’s law

\[
c_R(t) = K_H P_G(t), \tag{5c}
\]

where \( K_H \) is the Henry’s solubility coefficient and is a complex function of temperature and pressure for a given polymer melt with dissolved gas system (Lee and Flumerfelt, 1995).

The sample is initially loaded above its saturation pressure (\( P_{sat} \)) to form a single phase melt of gas and polymer. For the bubble to grow during decompression after the onset of nucleation, \( P_{G0} \) must overcome \( P_L \) and \( P_G \) and must be less than the \( P_{sat} \) to prevent transfer of gas from the bubble into the melt giving

\[
P_L + \frac{2\sigma}{R_0} < P_{G0} < P_{sat}, \tag{6a}
\]

\[
R_0 > R_{cr} = \frac{2\sigma}{(P_{sat} - P_L)} = \frac{2\sigma}{(K_H P_{sat} - P_L)} \tag{6b}
\]

Hence a cluster of bubbles smaller than the critical radius, \( R_{cr} \), has a tendency to collapse. On the other hand, if the cluster is sufficiently large compared to \( R_{cr} \), the cluster will grow spontaneously to a macroscopic bubble.

The governing equations (2–4) are non linear, stiff and cannot be solved analytically. The equations are also very sensitive to time steps and a very small step change is required. Several numerical methods have been developed to predict bubble growth dynamics. We have used the numerical approach taken by Prousevitch et al. (1993). In this approach, the diffusion equation is transformed using Lagrangian co-ordinates which eliminate the convection terms and the whole sets of equations are non-dimensionalised.

The integration problem for initial stiff concentration gradient is solved using a non-uniform grid which clusters the computational domain to very fine intervals near bubble interface.

Fig. 13a shows a model prediction of bubble growth and the associated change in influence cell radius (S) as the bubble grows. Arbitrary parameter values used for the prediction are given in Table 1. The shape of the calculated
growth profile of a bubble fits qualitatively with experimental growth curve (Fig. 6). The nature of the evolution of the concentration profile through the melt wall around a bubble provides insight into the way the gas concentration changes near the bubble. Fig. 13b shows the evolution of gas concentration profile across the normalised bubble wall as the bubble grows. In the early stage, there is a steep concentration gradient near the bubble wall. The dynamics of bubble growth initially resembles that of an infinite melt as the gas concentration far from the bubble surface remains almost constant. The dynamics of bubble growth diverges from the case of infinite melt when a bubble reaches above 60% of its final equilibrium size at which point the gas the concentration starts to decrease at the outer boundary.

5.2. Sensitivity of parametric values on bubble growth profiles

Many variables simultaneously influence the model and the model was used to test the sensitivity to variations or uncertainties in the values of relevant foaming parameters such as initial bubble radius, influence cell radius, melt viscosity, diffusion coefficient and initial gas concentration on the bubble growth dynamics (Fig. 14). In the test, the values of all physical properties of the melt including viscosity and density of the melt are held constant during decompression and bubble growth. The time dependence of the concentration in the melt is only varied. The base parameters used in the sensitivity tests are listed in Table 1. The model was run for sets of condition with a variation in a single parameter, while all others were left constant.

5.2.1. Initial bubble radius, \( R_0 \)

Initial bubble radius, \( R_0 \), was varied from 0.1 to 100 \( \mu m \) (Fig. 14a). The growth curves of smaller bubbles depart from that of larger initial radius due to surface tension and dynamic pressure effect. This departure reflects change in initial growth rate, and is referred to as delay time. The delay time is qualitatively defined as the time before the steep part of the growth curve in the plot. The delay time increase with increasing \( R_0 \). Surface tension has a greater retarding effect on the smaller values of \( R_0 \) (Eq. (3)). As the bubble size gets larger, the effect of surface tension pressure gets less significant. The size of the final bubble is not affected by the initial value of \( R_0 \).

5.2.2. Influence cell radius, \( S_0 \)

This effect of the influence cell was investigated by varying the values of \( S_0 \) over a range of 0.05–2.0 mm (Fig. 14b). All curves overlap because the dynamics of growth do not depend on the influence volume until later stages of the growth. Increasing \( S_0 \) leads to larger final bubble size due to increase in the total mass of dissolved gas in the influence cell. Time for final growth also increase with increasing \( S_0 \).

5.2.3. Diffusivity, \( D \)

Diffusion of the gas through the melt toward a bubble is affected by various factors such as temperature, pressure and concentration. The effect of diffusivity was investigated by varying the diffusion coefficient from \( 10^{-10} \) to \( 10^{-14} \) m\(^2\)/s and the result is plotted in Fig. 14c. Higher diffusivity decreases the time to complete growth and time delay. In reality, the concentrations of additives also strongly influence the diffusivity.

5.2.4. Melt viscosity, \( \eta \)

Viscosity is dependent on both melt composition and temperature and controls the dynamic pressure inside the bubble (Eq. (2)). Fig. 14d shows that the bubble growth is almost independent of viscosity for low viscous material (<10 Pa s) suggesting that the growth is controlled by diffusion rates at these conditions. The time delay was also negligible. However, high viscosity melts (>10 Pa s) have a significant influence on the growth dynamics and increase time delay. Longer delay time would be favourable in controlling the bubble size during the post-foaming process.

5.2.5. Initial gas concentration in the melt, \( c_0 \)

Initial pentane concentration profoundly affects the growth dynamics (Fig. 14e). An increase in \( c_0 \) in the melt increases the final bubble size but takes less time to reach that size. This is due to a higher concentration gradient at the bubble interface leading to a very rapid initial growth rate for high gas concentration. In reality, changes in \( c_0 \) will have a stronger influence on growth dynamics as viscosity is lower and diffusivity is greater for melts with higher gas concentrations.

5.2.6. Henry’s solubility constant, \( K_H \)

Concentration profile across the bubble wall, \( c_0 \), play an important role in diffusive bubble growth. The effect of \( K_H \) on growth kinetics is complex affecting both \( c_0 \) and bubble pressure, \( P_G \). Though \( P_G \) is inversely proportional to \( K_H \)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>( T )</td>
<td>150 degC</td>
</tr>
<tr>
<td>Ambient pressure</td>
<td>( P_L )</td>
<td>1 bar</td>
</tr>
<tr>
<td>Polymer: Polystyrene</td>
<td>( \rho )</td>
<td>1200 kg/m(^3)</td>
</tr>
<tr>
<td>Surface tension</td>
<td>( \sigma )</td>
<td>0.05 N/m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Base conditions:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial bubble radius</td>
<td>( R_0 )</td>
</tr>
<tr>
<td>Initial influence cell radius</td>
<td>( S_0 )</td>
</tr>
<tr>
<td>Initial gas concentration</td>
<td>( c_0 )</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>( D )</td>
</tr>
<tr>
<td>Viscosity</td>
<td>( \eta )</td>
</tr>
<tr>
<td>Henry’s solubility constant</td>
<td>( K_H )</td>
</tr>
</tbody>
</table>
Fig. 14. The effect of variable parameters on bubble growth kinetics: (a) $R_0$; (b) $S_0$; (c) $D$; (d) $\eta$; (e) $c_0$ and (f) $K_H$.

6. Comparison of experimental data with bubble growth model

Experimental bubble growth data were compared with the calculated bubble growth curve. The list of variables and their values used in predicting the bubble growth of PS-pentane system are shown in Table 2. For the model prediction, most of the values were either provided or measured experimentally. The initial gas concentration, melt density were supplied by the manufacturer. In a compressed state, the EPS melt was maintained at around 190 bar, much above the saturation vapour pressure of pentane. During decompression, for the bubble to grow, the initial bubble radius, $R_0$, has to be greater than the critical bubble radius, $R_{cr}$ (Eq. (6)). The $R_{cr}$ was estimated to be $\sim 35$ nm, assuming the initial bubble pressure, $P_{G,0}$, to be pentane saturation pressure of ca 30 bar. SEM micrograph showed the existence of the bubble in sub-micron size, hence $R_0$ can be anywhere between $R_{cr}$ and 1 µm. The surface tension of PS is temperature dependent and is obtained from the literature. Solubility coefficient for PS-pentane is assumed to be $10^{-8}$ Pa$^{-1}$. 

(Eq. (5c)), $c_0$ at any time increased with $K_H$. Fig. 14f shows the effect of $K_H$ on the bubble growth dynamics. The influence on the growth dynamics, time delay, final bubble size and growth time is minimal at low $K_H$ values ($10^{-8} - 10^{-13}$). However, both growth dynamics and time delay change at high $K_H$ value ($\geq 10^{-7}$).
Table 2
The list of variables and their values used in predicting the bubble growth of PS-pentane system

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
<th>References/Relations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial gas concentration in melt, $c_0$</td>
<td>6 wt%</td>
<td>supplied</td>
</tr>
<tr>
<td>Initial melt temperature, $T$</td>
<td>140–150 °C</td>
<td>measured</td>
</tr>
<tr>
<td>Loading pressure, $P_L$</td>
<td>190 bar</td>
<td>measured</td>
</tr>
<tr>
<td>Melt density, $\rho$</td>
<td>1200 kg/m$^3$</td>
<td>supplied</td>
</tr>
<tr>
<td>Surface tension of PS, $\sigma$</td>
<td>0.05 N/m</td>
<td>$40.7 - 0.072(T - 293)$ mN/m</td>
</tr>
<tr>
<td>Henry’s solubility constant, $K_H$</td>
<td>$10^{-8}$/Pa</td>
<td>$PS - N_0 \sim 5.1 \times 10^{-9}$/Pa (Ramesh et al., 1991)</td>
</tr>
<tr>
<td>Initial bubble radius, $R_0$ (&gt; $R_{crit}$)</td>
<td>$\sim 5 \times 10^{-8}$–$10^{-6}$ m</td>
<td>$LDPE - N_0 \sim 10^{-9}$/Pa (Shafi et al., 1996)</td>
</tr>
<tr>
<td>Initial radius of influence volume, $S_0$</td>
<td>$(1 - 10) \times 10^{-4}$ m</td>
<td>approximated from experiment</td>
</tr>
<tr>
<td>Zero shear viscosity, $\eta_0$</td>
<td>$10^{3}$–$10^{5}$ Pa s</td>
<td>experimentally determined: $\eta_0$ PS $\leq \eta_0$ PS $PS - N_0 = 6.0 \times 10^{-12}$ m$^2$/s at 25 °C (Ramesh et al., 1994a)</td>
</tr>
<tr>
<td>Diffusion coefficient, $D$</td>
<td>$10^{-12}$–$10^{-9}$ m$^2$/s</td>
<td>$PS - CO_2 = 1.3 \times 10^{-9}$ m$^2$/s at 200 °C (Park and Suh, 1996)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$LDPE - N_0 \sim 4 \times 10^{-9}$ m$^2$/s (Shafi et al., 1996)</td>
</tr>
</tbody>
</table>

Table 3
Extrapolated values of zero shear viscosity of PS and EPS (containing 6 wt% pentane) from rheological experiments

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Apparent zero shear viscosity, $\eta_0$ (Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PS</td>
</tr>
<tr>
<td>140</td>
<td>$1 \times 10^5$</td>
</tr>
<tr>
<td>150</td>
<td>$7 \times 10^4$</td>
</tr>
<tr>
<td>170</td>
<td>$3 \times 10^4$</td>
</tr>
<tr>
<td>190</td>
<td>$2 \times 10^4$</td>
</tr>
</tbody>
</table>

slightly higher than for $N_2$ in PS (see Table 2). Diffusion coefficient and viscosity of the single phase melt would be concentration dependent and hence time dependent during growth. In the model, these values are considered constant throughout the growth process.

Sensitivity test shows that a final bubble size is dependent on $c_0$ and $S_0$. The initial gas concentration is known, therefore, the final bubble radius is fitted by adjusting $S_0$. Sensitivity test also show that the growth profile is influenced by the diffusion coefficient and viscosity. During the growth stage, the concentration of the gas at the bubble surface varies from the initial loading concentration to almost zero towards the end (Fig. 13b) suggesting that both $\eta$ and $D$ are time dependent. In this paper however, the value of $\eta$ and $D$ are assumed to be constant throughout the growth process and were varied to fit the growth profiles. Hence, the only variable parameters for the model were $S_0$, $\eta$ and $D$. The values of $S_0$, $\eta$ and $D$ obtained from the model were tested with the experimental data and literature values respectively so that it lies within the estimated range. The model value of $S_0$ was compared with the approximations obtained from experimental final bubble size. The model value of $\eta$ was compared against $\eta_0$ values of Table 3 and was expected to lie between the PS and EPS melt values. The model value of $D$ was compared with the experimental values of self diffusion coefficient (calculated by the free volume theory) of the PS-pentane melt.

Fig. 15a shows the model prediction of the bubble growth profile of Fig. 6a obtained at 140 °C. As indicated, the
symbols with lines represent the bubble height and width. As the model takes account of spherical bubble, the equivalent radius is determined from the above size represented by the circles. During decompression experiment, there was a lag period of few seconds before the bubble formed and grew. Hence in the model, onset of nucleation is taken as time zero. The model in Fig. 15a was fitted with \( S_0 = 0.15 \text{ mm}, \eta = 1 \times 10^5 \text{ Pa.s} \) and \( D = 1 \times 10^{-12} \text{ m}^2/\text{s} \). These values appear reasonable. The value of \( S_0 \) is less than the final bubble size obtained experimentally (0.5 mm). The model shows good prediction with the viscosity data close to that of pure PS than that of EPS. This is consistent with the concentration profile shown in Fig. 13b, where the gas concentration at the bubble surface is much less than the initial gas concentration in the melt. Diffusivity of \( 1 \times 10^{-12} \text{ m}^2/\text{s} \) appears slightly lower than the experimental data. Diffusivity of 6 wt% pentane dissolved in PS at 100 and 150 °C were reported to be \( 7.2 \times 10^{-12} \) and \( 1.8 \times 10^{-10} \text{ m}^2/\text{s} \). The initial size of the bubble is very important for strain and strain rate determination during expansion and to predict earlier growth profiles. Experimental data starts only from 10 µm bubble radius due to the limitation in optical observation. Three different values of \( R_0 \) are assumed which give different early growth profiles. Hence from the model, one can now predict the missing data especially the early stage of bubble growth and the associated change in the bubble pressure, strain rates during the growth. The model in Fig. 15a does not completely fit the earlier growth data. Complete match of the experimental data was not obtained by varying viscosity (Fig. 15b). There was always some partial deviation either in the early or the final growth stage. The deviations in simulation results with the growth data suggest that other parameters such as time dependent variation in the viscosity, diffusivity and the interaction between the bubbles should be considered along with the non-spherical nature of growing bubbles in the model.

Fig. 16 compares the model prediction for experimental data obtained at two different temperatures. All other conditions are kept constant including the decompression rate. Change in temperature would lead to a change in material properties. Experimental results show that increasing temperature changes the growth profiles and the final bubble size which may be due to increase in diffusivity and decrease in viscosity. The model also shows sensitivity to all these parameters and is consistent with what one would expect with increase in temperature. The fittings parameter values are shown in figures. The values of \( \eta \) is within the experimental zero shear viscosity of PS and EPS.

From the model, it is also possible to predict bubble pressure, strain rates. Fig. 17 shows the time evolution of the internal bubble pressure, bubble surface strain rates for a case study of Fig. 15a with \( R_0 = 1 \mu m \). The total bubble pressure, \( P_G \), is the sum of ambient, surface tension and dynamic pressures. The ambient pressure is held constant throughout the growth while the surface tension pressure depends on the bubble radius, decreasing as the bubble grows and the dynamic pressure is dependent on diffusion rate. Hence the total pressure depends on various factors including melt viscosity, rate of gas flux into the bubble and other time dependent parameters. Total pressure profile shows a pressure rising to a maximum to ca. 20 bar in the very early stage of the growth for a very short duration (<0.1 s) and then drops subsequently. Presumably, due to the technical limitations of the pressure transducer used, the model prediction of pressure increment was not observed experimentally. This increment in pressure corresponds to rapid increase in growth rate which leads to increase in the radial strain rate. The corresponding strain rate for maximum pressure is \( \sim 4 \text{ s}^{-1} \). As the radial strain rate is greater than 1 s\(^{-1}\) in the early stage of growth, viscoelastic terms may need to be taken into account. At higher strain rates, the polymer behaves as a non-Newtonian fluid, and hence the viscoelastic model may be better at predicting the growth rate.

**Fig. 16.** Effect of temperature on bubble growth and on sensitivity of the model parameters.

**Fig. 17.** Time evolution of radial strain rate at the bubble surface, bubble pressure and bubble radius for case study given in Fig. 15a.
7. Pressure release rate dependent

The above simplified model predicts time evolution of bubble growth after the onset of nucleation and does not take account of several factors. Taki et al. (2003) reported that pressure release rate is crucial to achieve final bubble size and cell density. Fig. 18 shows our own data on the effect of initial pressure release rate on the growth kinetics. All other conditions and parameters were kept constant apart from pressure release rate. Pressure release rates were varied by displacing pistons at different speed. The figure shows that both growth profiles and bubble size are very sensitive to pressure release rate. Initially, increase in pressure release rate increase final bubble size. However, above the optimum rate, the final bubble size reduces. The effect of pressure release rate needs further investigations in future to be incorporated in the growth model.

8. Conclusions

In this paper heating protocols for PS-pentane system have been reported. For a low pressure, protocol I method, the EPS pellets were seen to initially expand and space fill at a temperature near to the glass transition temperature of the material. Then a ‘cloudy phase’ was observed that we associate with the formation of sub-micron bubbles. At higher temperatures, the cloudy phase was seen to be replaced by the presence of individual micro-bubbles. By applying a pressure during heating stages, it was possible, using protocol II, to move directly into a high temperature melt phase. Subsequent decompression would lead to the controlled evolution of foam bubbles from an initially isotropic melt. The protocol enabled a systematic series of experiments to be carried out for different temperatures, loading and pressure release rates.

The rheology of the PS-pentane melt was established and this and other data were used to develop a model that could be matched with the experimental data. The model includes the effect of gas diffusion in the melt, the hydrodynamics of the melt surrounding the evolving bubble and the interactions between hydrodynamics and diffusion. The model enabled a sensitivity analysis to be carried out to establish the effect of each of the physical parameters used. Key observations relating to sensitivity test show that many variables simultaneously influence growth dynamics and time delay. The dissolved gas concentration and influence cell effect the final bubble size. It was found that by using physically realistic values for all the parameters used, it was possible to get a reasonable match between model and data. From this we were able to obtain the model predictions at early times in the bubble evolution to establish growth rates and initial nucleation conditions. From the results it would appear that growth rates are sufficiently large for visco-elastic effects to be important and these need to be investigated in future modelling. At this stage, no account is taken into the model in relation to pressure release rate, and this factor needs to be incorporated as the experimental data shows there is a strong effect. From the data presented in this paper, it appears that modelling of the bubble growth kinetic is satisfactory however, prediction and modelling of exact nucleation conditions remains elusive.

Notation

- $a$: capillary radius, m
- $c$: gas concentration in the melt (wt. fraction), dimensionless
- $c_0$: initial gas concentration in the melt (wt. fraction), dimensionless
- $c_R$: gas concentration at the bubble surface (wt. fraction), dimensionless
- $c_t$: gas concentration along the influence cell (wt. fraction), dimensionless
- $D$: diffusion coefficient, m$^2$/s
- $K_H$: Henry’s solubility coefficient, Pa$^{-1}$
- $L$: capillary length, m
- $M$: molecular weight of the gas, kg/mol
- $P$: melt pressure in MPR, Pa
- $P_G$: surface tension pressure, Pa
- $P_{G,0}$: initial bubble pressure, Pa
- $P_L$: ambient pressure, Pa
- $P_{sat}$: saturation pressure, Pa
- $P_{top}, P_{bottom}$: top and bottom pressure in MPR, Pa
- $P_V$: dynamic pressure, Pa
- $r$: radial distance, m
- $R$: bubble radius, m
- $R_0$: initial bubble radius, m
- $R_b$: barrel radius, m
- $R_{cr}$: critical bubble radius, m
- $R$: bubble radius growth rate, m/s
- $\mathfrak{R}$: gas constant, 8.3145 J/mol K
- $S$: influence cell radius, m
\( S_0 \) \hspace{1cm} \text{initial influence cell radius, m}
\( t \) \hspace{1cm} \text{time, s}
\( T \) \hspace{1cm} \text{melt temperature, K}
\( V_p \) \hspace{1cm} \text{piston speed, m/s}
\( X_t, X_b \) \hspace{1cm} \text{top and bottom piston position in MPR, m}
\( z \) \hspace{1cm} \text{1/r}^3

**Greek letters**

\( \eta \) \hspace{1cm} \text{melt viscosity, Pa s}
\( \eta_0 \) \hspace{1cm} \text{zero shear viscosity, Pa s}
\( \eta_{app} \) \hspace{1cm} \text{apparent melt viscosity, Pa s}
\( \Delta P \) \hspace{1cm} \text{pressure difference, Pa}
\( \rho \) \hspace{1cm} \text{density, kg/m}^3
\( \sigma \) \hspace{1cm} \text{surface tension, N m}

**Acknowledgements**

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**References**


