The mechanics of solid-state nanofoaming

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Solid-state nanofoaming experiments are conducted on two polymethyl methacrylate (PMMA) grades of markedly different molecular weight using CO₂ as the blowing agent. The sensitivity of porosity to foaming time and foaming temperature is measured. Also, the microstructure of the PMMA nanofoams is characterized in terms of cell size and cell nucleation density. A one-dimensional numerical model is developed to predict the growth of spherical, gas-filled voids during the solid-state foaming process. Diffusion of CO₂ within the PMMA matrix is sufficiently rapid for the concentration of CO₂ to remain almost uniform spatially. The foaming model makes use of experimentally calibrated constitutive laws for the uniaxial stress versus strain response of the PMMA grades as a function of strain rate and temperature, and the effect of dissolved CO₂ is accounted for by a shift in the glass transition temperature of the PMMA. The maximum achievable porosity is interpreted in terms of cell wall tearing and comparisons are made between the predictions of the model and nanofoaming measurements; it is deduced that the failure strain of the cell walls is sensitive to cell wall thickness.

1. Introduction

Polymeric nanofoams are polymer foams with an average cell size below 1 µm [1]. This new class of porous solids has the potential to offer unique and attractive combinations of thermal, mechanical and optical properties [2–4]. For example, the thermal conductivity \( \lambda \) of polymeric nanofoams may be lower
than the value for air, \( \lambda = 0.025 \text{ W m}^{-1} \text{K}^{-1} \); when the average cell size is of the order of the mean free path of the gas molecules in the cells (close to 70 nm for air at standard conditions), the thermal conductivity of the gas in the foam is significantly reduced due to the Knudsen effect [5,6]. A polymeric nanofoam may have a thermal conductivity close to or below 0.025 W m\(^{-1}\) K\(^{-1}\) when the average cell size \( l \) is below 200 nm and the porosity \( f \) exceeds 0.85; see, for example, Wang et al. [7]. To achieve this morphology, the cell nucleation density \( N_d \) must exceed \( 10^{21} \text{ m}^{-3} \) [1].

A large number of experimental studies focus on the effect of processing conditions and the choice of polymer precursor upon the cell nucleation density \( N_d \), the void size \( l \) and the porosity \( f \) of polymeric nanofoams, as reviewed by Costeux [1]. Many of these studies employ the solid-state foaming method in which a physical blowing agent (e.g. CO\(_2\)) is used to nucleate and grow cells in a polymer matrix such as polymethyl methacrylate (PMMA) [8,9]. The available data on the cell size and porosity that have been achieved to date for high porosity (PMMA-based) polymeric nanofoams via solid-state foaming are summarized in figure 1. Data are retrieved from [4,9–17]. It is clear that the ideal combination of high porosity (\( f > 0.85 \)) and small cell size (\( l < 200 \text{ nm} \)) is yet to be achieved. Polymeric nanofoams of porosity of the order of 0.8–0.9 have been produced, but their cell size is above 200 nm (and \( N_d < 10^{21} \text{ m}^{-3} \)). By contrast, polymeric nanofoams of \( l < 200 \text{ nm} \) are reported for a nucleation density above \( 10^{21} \text{ m}^{-3} \), but their porosity is limited to close to 0.85. Recently, manufacturing techniques have evolved to combine solid-state nanofoaming and injection moulding in an attempt to improve the mechanical properties and surface properties of injection moulded foams, but these nanofoams have porosities well below 0.5 [18].

The observed porosity limit for nanofoams with a nucleation density above \( 10^{21} \text{ m}^{-3} \) may be due to the fact that the minimum wall thickness between nano-sized cells is dictated by the end-to-end distance of the individual polymer chains [1,12]. An aim of the present study is to gain scientific insight into this limiting behaviour, and thereby suggest ways of overcoming this barrier, if possible.

The final porosity and final cell size in solid-state nanofoaming requires a solid mechanics analysis of void growth. A substantial body of experimental work has now been performed on polymeric nanofoams produced via solid-state foaming (recall figure 1 and the review by Costeux [1]), and several analyses have been developed for cell growth in liquid-state foaming.
processes [19–21]. By contrast, theoretical studies on cell growth during solid-state nanofoaming are limited. Costeux and co-workers [16,22] have simulated void nucleation and void growth during the solid-state nanofoaming of acrylate co-polymers by making use of the model of Shafi et al. [23]. However, their model overestimates the final porosity of their nanofoams. The mismatch between the simulated and measured porosity of acrylic nanofoams may be due to (i) the assumption that cell growth continues until the foaming temperature attains the glass transition temperature of the polymer-gas solid and/or (ii) the assumption that the polymer-gas solid surrounding the cell is in a liquid (viscous) state throughout the solid-state foaming process. In reality, void growth occurs at temperatures close to the glass transition temperature of the solid surrounding the void, and significantly below the melting temperature. This is addressed in detail in the present study.

(a) Scope of study

Nanofoams are produced from two PMMA grades of widely different molecular weight; a solid-state foaming process is used with CO₂ as the blowing agent. We characterize the microstructure of the nanofoams in terms of porosity \( f \), cell size \( l \) and cell nucleation density \( N_d \). In addition, we develop a void growth model, based on the constitutive law of PMMA grades close to the glass transition temperature, by building on the recent study of Van Loock & Fleck [24]. Both predicted and measured final porosities are obtained as a function of foaming time and foaming temperature; also, cell wall tearing mechanisms are considered in order to account for the observed limit in final porosity.

2. Nanofoaming experiments

(a) Materials

Foaming experiments were conducted on two PMMA grades: pelletized PMMA (Altuglas V825T) of average molecular weight \( M_w = 92500 \text{ g mol}^{-1} \) and cast PMMA sheets (Altuglas CN with sheet thickness close to 3 mm) of high molecular weight \( M_w = 3580000 \text{ g mol}^{-1} \). We shall refer to the Altuglas V825T and Altuglas CN grades as ‘low \( M_w \) PMMA’ and ‘high \( M_w \) PMMA’, respectively. Both grades have a density \( \rho_p = 1190 \text{ kg m}^{-3} \) (as measured at 23°C and at 50% relative humidity). The glass transition temperatures \( T_g = 114.5°C \) of the low \( M_w \) PMMA, and \( T_g = 116.5°C \) of the high \( M_w \) PMMA, have been measured by differential scanning calorimetry (DSC) using a heating rate of 10°C min\(^{-1}\): the values are almost equal.

(b) Solid-state nanofoaming experiments

Foaming precursors of the low \( M_w \) and high \( M_w \) PMMA grades were made as follows. The low \( M_w \) PMMA pellets were heated to 250°C for 450 s and then compressed for 60 s between two heated plates at a pressure equal to 17 MPa. The resulting sheet was cooled to room temperature with the pressure of 17 MPa maintained. Cuboid precursors of dimension 20 × 10 × 3 \text{ mm}^3 were machined from the low \( M_w \) PMMA sheet and from the as-received high \( M_w \) PMMA sheet.

Foaming experiments were performed in a pressure vessel\(^2\) with feedback pressure controller\(^3\) and temperature controller.\(^4\) Medical grade CO₂ (greater than 99.9% purity) was used as the blowing agent for the foaming experiments. The solid-state foaming process involved a nucleation step and then a subsequent growth step, as detailed by Martin-de León et al. [9].

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1The average molecular weight was measured by gas permeation chromatography (GPC) with an Agilent Technologies PL GPC220 (USA) instrument with a nominal flow rate equal to \( 1.67 \times 10^{-5} \text{ l s}^{-1} \) at a test temperature equal to 30°C.
2Pressure vessel model PARR 4681 of Parr Instrument Company (USA).
3Pressure controller pump SFT-10 of Supercritical Fluid Technologies Inc (USA).
4Temperature controller CAL 3300 of CAL Controls Ltd (UK).
First, the precursor samples were held in the pressure vessel at a constant CO₂ saturation pressure equal to 31 MPa, and at a constant temperature equal to 25°C for 24 h in order to ensure saturation of the CO₂ into the PMMA. The mass concentration C, at equilibrium, is close to 24 wt% for both the low and high Mₚ PMMA, by making use of the measurement procedure of Martin-de León et al. [9]. Second, the pressure was released to atmospheric pressure at the rapid rate of 100 MPa s⁻¹; this is the nucleation step. Third, samples were foamed in a foaming bath at selected foaming temperatures (25°C, 40°C, 60°C, 80°C, 100°C) and selected foaming times (60 s, 180 s, 300 s, 600 s); this is the void growth step. It is assumed throughout the remainder of this study that the foaming times are sufficiently long for the temperature to be spatially uniform within the sample.

(c) Characterization of the PMMA nanofoams

(i) Porosity

The density ρₚ of the foamed samples was determined by the water-displacement method with a weight balance. A surface layer of depth 200 µm was removed by polishing to ensure that the solid skin (of thickness below 100 µm) was absent before the density measurements were made. The porosity f of the samples is obtained by

\[ f = 1 - \frac{\rho_f}{\rho_p}, \]

where \( \rho_p \) (= 1 190 kg m⁻³) is the density of solid PMMA.

(ii) Microstructure

Foamed samples were cooled in liquid nitrogen and then fractured. The fracture surfaces were coated with a layer of gold by sputtering and micrographs of the coated fracture surfaces were taken by a scanning electron microscope (SEM). The cellular structure of each material was characterized by analysing the micrographs with dedicated in-house software based on ImageJ/FIJI [26]. Microstructural parameters such as the average cell size \( l \), standard deviation \( s \) of the observed cell sizes, and cell nucleation density \( N_d \), using the method as suggested by Kumar & Suh [27], were obtained.

(iii) Open cell content

The open cell content of the foamed samples was measured by gas pycnometry with nitrogen in accordance with the ASTM D6226-15 standard [28]. The open cell content ratio \( O_v \) is defined

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5We define the mass concentration C of CO₂ in PMMA with respect to the total mass of the PMMA–CO₂ mixture. Note that the definition of CO₂ solubility (with respect to the mass of the PMMA absent CO₂) is used in the work of Martin-de León et al. [9].

6Thermal bath J.P. Selecta Model 6000685 of Grupo Selecta (Spain). The time between the pressure release and the start of foaming was close to 120 s.

7Samples were immersed in a water bath at a temperature close to 10°C at the end of the foaming time.

8The justification for this assumption is as follows. Immersion of the sample in water or oil provides excellent heat transfer at the surface of the sample. The time constant \( \tau = x^2/\kappa \approx 20 \text{s} \), where \( x = 1.5 \text{mm} \) is the half-thickness of the PMMA sample and \( \kappa = 1.1 \times 10^{-7} \text{m}^2 \text{s}^{-1} \) is the thermal diffusivity of PMMA at room temperature [25].

9Analytical balance AT261 of Mettler-Toledo (USA).

10 Grinding and polishing system LaboPOI2-LaboForce3 of Struers (USA).

11 Sputter coater SDC 005 of Balzers Union (Liechtenstein).

12 Scanning electron microscope QUANTA 200 FEG of Thermo Fisher Scientific (USA).

13 At least 200 cells were analysed from multiple micrographs per foamed sample.

14 Gas pycnometer (USA) AccuPyc II 1340 of Micromeritics (USA).
as the ratio of the volume of open pores to the total pore volume of a foam, and is obtained by

\[ O_v = \frac{V^s - V^p - V^s}{f V^s} \]  

(2.2)

where \( V^s \) is the geometric volume of the foam, \( V^p \) is the pycnometer volume and \( V^s \) is a penalty volume to account for the volume of the cells at the surface of the foam. The penalty volume \( V^s \) is assumed to be close to zero in the case of nanofoams. The geometric volume \( V^s \) is measured by the water-displacement method as detailed above. Foamed samples were subjected to a pressure scan from 0.02 to 0.13 MPa in the gas pycnometer. The pycnometer volume initially decreases as the gas pressure increases until the interconnected open cells are completely filled with gas and the pycnometer volume remains constant at increased pressures. We take this constant value of pycnometer volume \( V^p \) in order to calculate \( O_v \) via equation (2.2).

3. Results of the nanofoaming experiments

The measured porosity \( f \), average observed cell size \( l \), standard deviation \( s \) of observed cell sizes and cell nucleation density \( N_d \) of the nanofoams are reported in tables 1 and 2 for the low \( M_w \) and high \( M_w \) grades of PMMA, respectively. In addition, a representative series of SEM micrographs of the nanofoams is shown in figure 2. The low \( M_w \) and the high \( M_w \) nanofoams have contrasting microstructures and the cell nucleation density of the low \( M_w \) nanofoams \( (N_d \approx 2 \times 10^{20} \text{ m}^{-3}) \) is an order of magnitude less than that of the high \( M_w \) nanofoams \( (N_d \approx 2 \times 10^{21} \text{ m}^{-3}) \). The average cell size \( l \) of the high \( M_w \) nanofoams ranges from 20 to 50 nm, and is an order of magnitude smaller than the average cell size of the low \( M_w \) nanofoams (of size 200–350 nm). These values of \( l \) and \( N_d \) for the low \( M_w \) nanofoams are consistent with the results of Martin-de León et al. [9], who conducted solid-state foaming experiments with an identical low \( M_w \) PMMA grade. The measured average cell size \( l \) of the low \( M_w \) and the high \( M_w \) nanofoams, as a function of foaming time \( t_f \) for \( T_f = 60^\circ \text{C} \), is plotted in figure 3a. Void growth typically occurs over a foaming time period of 60–180 s, followed by arrest. There is a mild dependence of the foaming temperature \( T_f \) upon the final value for \( l \) (tables 1 and 2).

The measured porosity \( f \) of the nanofoams is plotted as a function of \( t_f \) in figure 3b for \( T_f = 60^\circ \text{C} \) and for \( T_f = 100^\circ \text{C} \). Consistent with the \( l \) versus \( t_f \) curves for \( T_f = 60^\circ \text{C} \), as presented in figure 3a, the porosity increases over a foaming period of 60–180 s until a stable (\( t_f \)-independent) value of final porosity is achieved. The highest observed porosity of the low \( M_w \) PMMA nanofoams (\( f_{\text{max}} = 0.75 \)) is approximately 25% higher than that of the high \( M_w \) PMMA nanofoams (\( f_{\text{max}} = 0.60 \)). At a foaming temperature of \( T_f = 100^\circ \text{C} \), the porosity decreases with increasing foaming time beyond \( t_f = 60 \text{ s} \), and this is due to collapse of the foamed structure. This behaviour is also illustrated in plots of \( f \) versus \( T_f \) over the explored range of foaming times; see figure 3c,d for the low \( M_w \) and high \( M_w \) PMMA nanofoams, respectively.

The measured open cell content \( O_v \) is plotted as a function of the measured porosity \( f \) in figure 4a (low \( M_w \)) and in figure 4b (high \( M_w \)) for \( 20^\circ \text{C} \leq T_f \leq 80^\circ \text{C} \). Nanofoams with porosities well below the highest observed porosity \( f_{\text{max}} \) are closed-cell in nature. An abrupt transition to an open-celled structure occurs close to \( f_{\text{max}} \). The observed collapse of the foam at \( T_f = 100^\circ \text{C} \) is preceded by cell wall rupture for the low \( M_w \) nanofoams (figure 2b) and by the formation of cracks interconnecting the nano-sized pores for the high \( M_w \) nanofoams (figure 2d).

4. Void growth model

A void growth model is now developed to predict porosity as a function of foaming time and foaming temperature for the PMMA nanofoams. The expansion of a pre-existing as-nucleated spherical cavity during solid-state nanofoaming is simulated by means of a one-dimensional single-cell growth model [20,29]. A finite shell surrounds the spherical void in order to account for void–void interaction in an approximate manner. More sophisticated models of an array of voids
by incompressibility. For later use, this relation is rearranged to the form

$$r^3 - a^3 = R^3 - a_0^3$$  \hspace{1cm} (4.1)

and outer radius \(b_0\), along with the adopted spherical coordinate system \((r, \theta, \phi)\), is shown in figure 5. Assume that the initial gas pressure \(p_0\) in the as-nucleated void equals the saturation pressure during the saturation phase prior to nucleation of the voids. The deformed configuration for the void of inner radius \(a\) and outer radius \(b\) at time \(t\) is shown in figure 5.

| \(t_f\) (s) | \(T_f\) (°C) | \(f\) | \(l\) (nm) | \(s\) (nm) | \(N_d\) (10^35 m^-3) | \(O_v\) |
|---|---|---|---|---|---|---|
| 60 | 25 | 0.45 | 219 | 87 | 1.50 | 0.12 |
| 180 | 25 | 0.47 | 228 | 79 | 1.50 | 0.08 |
| 300 | 25 | 0.51 | 283 | 112 | 0.91 | 0.08 |
| 600 | 25 | 0.51 | 235 | 85 | 1.48 | 0.08 |
| 60 | 40 | 0.52 | 262 | 102 | 1.22 | 0.07 |
| 180 | 40 | 0.61 | 250 | 125 | 1.70 | 0.02 |
| 300 | 40 | 0.64 | 254 | 105 | 1.27 | 0.15 |
| 600 | 40 | 0.66 | 233 | 103 | 2.11 | 0.14 |
| 60 | 60 | 0.56 | 234 | 89 | 2.34 | 0.07 |
| 180 | 60 | 0.66 | 297 | 111 | 1.72 | 0.33 |
| 300 | 60 | 0.68 | 279 | 122 | 1.76 | 0.40 |
| 600 | 60 | 0.68 | 284 | 109 | 1.66 | 0.36 |
| 60 | 80 | 0.72 | 333 | 134 | 1.16 | 0.63 |
| 180 | 80 | 0.74 | 288 | 138 | 1.83 | 0.90 |
| 300 | 80 | 0.75 | 297 | 125 | 1.75 | 0.78 |
| 600 | 80 | 0.73 | 274 | 109 | 2.08 | 0.93 |
| 60 | 100 | 0.64 | 297 | 122 | 1.21 | — |
| 180 | 100 | 0.68 | 253 | 110 | 1.81 | — |
| 300 | 100 | 0.62 | 246 | 103 | 1.75 | — |
| 600 | 100 | 0.51 | 291 | 125 | 0.76 | — |

| Table 1. Measured porosity \(f\), average cell size \(l\), standard deviation of observed cell size \(s\), cell nucleation density \(N_d\) and open cell content \(O_v\) of the low \(M_w\) PMMA nanofoams as a function of foaming time \(t_f\) and foaming temperature \(T_f\). Foams collapsed at \(T_f = 100^\circ C\), and so no open cell content values are reported for nanofoams produced at \(T_f = 100^\circ C\). |

(such as periodic cell models) could be adopted but the intent here is to emphasize the strong role of the evolving constitutive response of the cell wall.

Consider a polymer-gas solid with equi-sized spherical voids. A cross section of the undeformed (reference) configuration of the spherical void, with initial radius \(a_0\) and initial outer radius \(b_0\), along with the adopted spherical coordinate system \((r, \theta, \phi)\), is shown in figure 5. Assume that the initial gas pressure \(p_0\) in the as-nucleated void equals the saturation pressure during the saturation phase prior to nucleation of the voids. The deformed configuration for the void of inner radius \(a\) and outer radius \(b\) at time \(t\) is shown in figure 5.

(a) Kinematics

Assume that the void remains spherical during growth and that the solid surrounding the void is incompressible. Then a material point within the cell wall, initially at radius \(R\), is displaced to a radius \(r\) such that

$$r^3 - a^3 = R^3 - a_0^3$$

by incompressibility. For later use, this relation is rearranged to the form

$$\left(\frac{r}{R}\right)^3 = 1 + \left(\frac{a_0}{R}\right)^3 \left[\left(\frac{a}{a_0}\right)^3 - 1\right].$$  \hspace{1cm} (4.2)
Table 2. Measured values for the porosity $f$, the average observed cell size $l$, the standard deviation of the observed cell size $s$, the cell nucleation density $N_a$, and the open cell content $O_o$ of the high $M_w$ PMMA nanofoams as a function of foaming time $t_f$ and foaming temperature $T_f$. Foams collapsed at $T_f = 100^\circ$C, and so no open cell content values are reported for the nanofoams produced at $T_f = 100^\circ$C.

| $t_f$ (s) | $T_f$ (°C) | $f$  | $l$ (nm) | $s$ (nm) | $N_a$ ($10^{20}$ m$^{-3}$) | $O_o$ |
|----------|-------------|------|----------|----------|-----------------------------|------|
| 60       | 25          | 0.22 | 36       | 14       | 14.9                        | 0.30 |
| 180      | 25          | 0.28 | 23       | 10       | 40.0                        | 0.22 |
| 300      | 25          | 0.29 | 30       | 12       | 9.0                         | 0.28 |
| 600      | 25          | 0.31 | 36       | 18       | 6.9                         | 0.21 |
| 60       | 40          | 0.33 | 28       | 13       | 54.2                        | 0.19 |
| 180      | 40          | 0.42 | 32       | 16       | 32.3                        | 0.07 |
| 300      | 40          | 0.45 | 37       | 14       | 7.8                         | 0.08 |
| 60       | 40          | 0.47 | 45       | 29       | 26.0                        | 0.09 |
| 180      | 60          | 0.55 | 39       | 17       | 24.0                        | 0.03 |
| 300      | 60          | 0.57 | 40       | 17       | 31.8                        | 0.28 |
| 600      | 60          | 0.57 | 41       | 19       | 25.8                        | 0.03 |
| 60       | 80          | 0.58 | 39       | 20       | 21.8                        | 0.51 |
| 180      | 80          | 0.60 | 39       | 19       | 27.8                        | 0.73 |
| 300      | 80          | 0.60 | 38       | 19       | 36.6                        | 0.95 |
| 600      | 80          | 0.59 | 44       | 22       | 46.6                        | 0.88 |
| 60       | 100         | 0.59 | 34       | 15       | 35.4                        | —    |
| 180      | 100         | 0.53 | 27       | 14       | 80.4                        | —    |
| 300      | 100         | 0.50 | 37       | 18       | 24.9                        | —    |
| 600      | 100         | 0.45 | 34       | 12       | 32.6                        | —    |

Note that $r/R$ is a function of the time-like variable $(a/a_0)$ and of the Lagrangian position variable $R/a_0$. The von Mises effective strain $\varepsilon_e$ is defined in the usual manner as $\varepsilon_e^2 = (2/3)\varepsilon_{ij}\varepsilon_{ij}$, giving

$$\varepsilon_e = |2\varepsilon_{\theta\theta}| = 2 \ln \left( \frac{r}{R} \right), \quad (4.3)$$

where $\varepsilon_{\theta\theta}$ is the hoop strain. Now insert equation (4.2) into equation (4.3) to obtain

$$\varepsilon_e = \frac{2}{3} \ln \left[ 1 + \left( \frac{a_0}{R} \right)^3 \left( \left( \frac{a}{a_0} \right)^3 - 1 \right) \right] \quad (4.4)$$

and take the time derivative of $r$ in equation (4.1) to give

$$\dot{r} = v_r = \left( \frac{a}{r} \right)^2 \dot{a} \quad (4.5)$$

where $v_r$ is the radial velocity of a material element at $r$. Consequently, the effective strain rate $\dot{\varepsilon}_e$ reads

$$\dot{\varepsilon}_e = \left| \frac{\partial v_r}{\partial r} \right| = \frac{2a^2}{R^3} \left( \frac{r}{R} \right)^{-3} \dot{a}. \quad (4.6)$$
Figure 2. SEM micrographs of the low $M_w$ nanofoams at (a) $T_f = 60^\circ C$, (b) $T_f = 100^\circ C$ and of the high $M_w$ nanofoams at (c) $T_f = 60^\circ C$ and (d) $T_f = 100^\circ C$.

(b) Equilibrium

Write $(\sigma_{rr}, \sigma_{\theta\theta}, \sigma_{\phi\phi})$ as the active stress components in the spherical coordinate system. Radial equilibrium dictates that [30]

$$\frac{\partial \sigma_{rr}}{\partial r} + \frac{1}{r}(2\sigma_{rr} - \sigma_{\theta\theta} - \sigma_{\phi\phi}) = 0. \quad (4.7)$$

Due to symmetry, $\sigma_{\phi\phi} = \sigma_{\theta\theta}$ and equation (4.7) simplifies to

$$\frac{\partial \sigma_{rr}}{\partial r} = \frac{2(\sigma_{\theta\theta} - \sigma_{rr})}{r} = \frac{2\sigma_e}{r}, \quad (4.8)$$

where $\sigma_e = \sigma_{\theta\theta} - \sigma_{rr}$ is the von Mises effective stress [31]. Integration of equation (4.8) provides the gas pressure $p$ inside the cavity as an implicit function of current void radius $a$, and ambient pressure $p_a$ such that

$$p - p_a = \int_{r=b}^{r=a} \frac{2\sigma_e}{r} dr. \quad (4.9)$$
Figure 3. Nanofoaming experiments on the low $M_w$ and high $M_w$ PMMA grades: (a) measured average cell size $l$ versus foaming time $t_f$ for $T_f = 60^\circ$C, (b) measured porosity $f$ versus foaming time $t_f$ for $T_f = 60^\circ$C and $T_f = 100^\circ$C, (c) measured porosity $f$ versus foaming temperature $T_f$ for the range of explored foaming times ($t_f = 60–600$ s) for the low $M_w$ nanofoams and (d) measured $f$ versus $T_f$ for the range of explored foaming times ($t_f = 60–600$ s) for the high $M_w$ nanofoams.

Now make use of equation (4.1) to re-express the above integral in the form

$$p - p_a = \int_{R=a_0}^{R=b_0} 2 \left( \frac{R}{r} \right) \sigma_e dR.$$  

(4.10)

The effective stress $\sigma_e$ is a function of the effective strain $\varepsilon_e$, the effective strain rate $\dot{\varepsilon}_e$, as given by equation (4.6) and the normalized temperature $T/T_g$ via the constitutive law for the PMMA–CO$_2$ solid, of general functional form $F$ where

$$\sigma_e = F \left( \varepsilon_e, \dot{\varepsilon}_e, \frac{T}{T_g} \right).$$  

(4.11)

The choice of $F$ is given below. We show in appendix A that the concentration $C$ of CO$_2$ can be taken to be spatially uniform throughout the spherical shell at any instant of time, but the magnitude of $C$ depends upon the current size of the void by a mass conservation argument as detailed below. This leads to a major simplification of the analysis. The glass transition temperature $T_g$ of the PMMA is taken to be a function of CO$_2$ concentration $C$, and is also given below.
Figure 4. Measured open cell content $O_v$ as a function of porosity $f$ for (a) the low $M_w$ PMMA nanofoam and (b) high $M_w$ PMMA nanofoam.

Figure 5. Spherical void in (a) undeformed configuration with initial radius $a_0$ and initial outer radius $b_0$ and (b) deformed configuration at time $t$ of the void with radius $a$, outer radius $b$ and gas pressure $p$. (Online version in colour.)

(c) The solution strategy

Substitute equation (4.11) into (4.10), and integrate over the thickness of the spherical shell in order to obtain an expression for the gas pressure $p$ within the cavity as a function of $\dot{a}$ (via equation (4.6)), and the current state, as parametrized by the current value of $a/a_0$. It remains to obtain an expression for $p$ as a function of $a/a_0$ by considering the gas law for the void and mass conservation of CO$_2$ in the void and solid PMMA. Once we have obtained $p$ as a function of $a/a_0$, we can re-express equation (4.10) as $\dot{a}$ as a function of $a/a_0$; integration of $\dot{a}$ then gives the time evolution of $a/a_0$.

(d) Gas laws

The equilibrium concentration $C$ of CO$_2$ in PMMA is a function of CO$_2$ pressure $p$ and of temperature. Here, we assume that Henry’s Law suffices such that [32–35]

$$ C = K_H p, $$

(4.12)

where Henry’s Law coefficient $K_H$ is assumed to be independent of both temperature and pressure. Assume that the concentration of CO$_2$ at the surface of the cavity ($R = a_0$) is in equilibrium with the CO$_2$ pressure within the void via equation (4.12).
Take \( K_H = 7.8 \times 10^{-9} \text{Pa}^{-1} \) for both the low \( M_w \) and the \( M_w \) PMMA grades, based on the measured \( C = 0.24 \) equilibrium concentration of CO\(_2\) in PMMA at a pressure \( p = 31 \text{ MPa} \) and temperature \( T = 25^{\circ}C \), as detailed in §2b. Also, assume that the CO\(_2\) gas in the void satisfies the ideal gas law

\[
p = \frac{\rho^g \text{RT}}{M^g_w},
\]

where \( R \) is the universal gas constant.

It is recognized that the use of Henry’s Law and the ideal gas law have a somewhat limited range of validity and the current analysis can be embellished by employing alternative laws such as the lattice-based theory equation of state of Sanchez & Lacombe \[36–39\] or empirical non-ideal equation of states for CO\(_2\) \[40,41\]. However, the use of a number of such laws is considered to lie beyond the scope of the present study.

**(e) Mass conservation**

We shall assume that the total mass of gas molecules in the voids and in the surrounding solid is constant; leakage of gas molecules to neighbouring voids or the sample’s environment is neglected. Also, assume that the concentration \( C \) of dissolved CO\(_2\) in the PMMA spherical shell is independent of radius, as justified in appendix A. The resulting mass conservation statement for CO\(_2\) reads

\[
C_0 \rho^p (b^3 - a^3) + \rho^g a^3 = C \rho^p (b^3_0 - a^3_0) + \rho^g_0 a^3_0,
\]

where \( \rho^p \) is the density\(^{15}\) of the PMMA–CO\(_2\) solid and \( \rho^g \) is the density of the CO\(_2\) in the voids. Substitution of equation (4.13) into equation (4.14) gives \( p \) as a function of cavity size \( a/a_0 \).

**(f) Dependence of the glass transition temperature of PMMA upon CO\(_2\) content**

The dissolution of CO\(_2\) into a linear, amorphous polymer such as PMMA reduces the glass transition temperature \( T_g \) of the PMMA–CO\(_2\) solid. This plasticization effect is attributed to the increased mobility of PMMA chains due to lubrication by the CO\(_2\) molecules, and the decrease of the intermolecular bond strength as the CO\(_2\) molecules increase the spacing between the PMMA chains \[42,43\]. A range of experimental techniques has been used in the literature to determine the glass transition temperature \( T_g \) of PMMA as a function of CO\(_2\) mass concentration \( C \). Chiou \textit{et al.} \[44\] made use of DSC to measure \( T_g/T_g^0 \) as a function of \( C \), where \( T_g^0 = T_g(C = 0) \). Likewise, Wissinger & Paulaitis \[45\] measured the dependence of \( T_g/T_g^0 \) upon \( C \) via creep compliance measurements. Guo & Kumar \[46\] made use of solid-state foaming experiments to observe the relationship between \( T_g/T_g^0 \) and CO\(_2\) for a PMMA–CO\(_2\) mixture. The measured \( T_g/T_g^0 \) versus \( C \) data, for PMMA–CO\(_2\), as reported by Chiou \textit{et al.} \[44\], Wissinger & Paulaitis \[45\] and Guo & Kumar \[46\] are shown in figure 6. Chow \[47\] used statistical thermodynamics to predict \( T_g/T_g^0 \) as a function of \( C \) and introduced a parameter \( \theta \) where

\[
\theta = \frac{M^p_w}{z M^g_w} \frac{C}{1 - C}.
\]

Here, \( M^p_w \) is the molecular weight of the polymer repeat unit (\( M^p_w = 100.12 \text{ g mol}^{-1} \) for a methyl methacrylate monomer), \( M^g_w \) is the molecular weight of the gas (\( M^g_w = 44.01 \text{ g mol}^{-1} \) for CO\(_2\)), and \( z \) is a lattice coordination number equal to 2, as suggested by Chow \[47\]. In addition, Chow \[47\] defined a parameter \( \beta \)

\[
\beta = \frac{zR}{M^g_w \Delta C_p},
\]

where \( \Delta C_p \) is the change in specific heat capacity of the polymer at the glass transition temperature at constant pressure. The normalized glass transition temperature is then predicted

\(^{15}\)We assume that the density of the PMMA–CO\(_2\) solid is equal to the density of PMMA absent CO\(_2\) at standard conditions (i.e. \( \rho = 1190 \text{ kg m}^{-3} \)) based on the measurements of Pantoula & Panayiotou \[33\] and Pantoula \textit{et al.} \[34\] who observed that the relative increase in volume of a PMMA–CO\(_2\) mixture is close to the relative increase of the mass of a PMMA–CO\(_2\) mixture for a CO\(_2\) pressure up to 30 MPa.
Figure 6. The normalized glass transition temperature $T_g/T_0^g$ of PMMA as a function of CO$_2$ mass concentration $C$, as reported by Chiou et al. [44], Wissinger & Paulaitis [45] and Guo & Kumar [46]. The $T_g/T_0^g$ versus $C$ curve is given by the calibrated version of equation (4.17).

by

$$\frac{T_g}{T_0^g} = \exp[\beta((1 - \theta) \ln(1 - \theta) + \theta \ln \theta)].$$

(4.17)

The above equation is curve fitted to the measured $T_g/T_0^g$ versus $C$ data shown in figure 6 by a suitable choice of $\Delta C_p$. The fitted value for $\Delta C_p = 355$ J kg$^{-1}$K$^{-1}$ which is slightly higher than the value of $\Delta C_p$ for PMMA as measured by DSC [44,48]. We note in passing that the value of $\Delta C_p = 355$ J kg$^{-1}$K$^{-1}$ gives a good fit to the data of Guo & Kumar [46] in addition to the data of by Chiou et al. [44] and Wissinger & Paulaitis [45] (figure 6). This is consistent with the observation by Guo & Kumar [46] that a value of $\Delta C_p = 265$ J kg$^{-1}$K$^{-1}$ (assuming $z = 2$) gives a relatively poor fit to their data.

(g) Constitutive model for the PMMA–CO$_2$ solid

We assume that the effective stress $\sigma_e$ of the PMMA–CO$_2$ solid at a given strain $\varepsilon_e$, strain rate $\dot{\varepsilon}_e$ and normalized temperature $T/T_g$ is the same as that given by PMMA in the absence of CO$_2$: the effect of CO$_2$ is accounted for by a shift in the value for $T_g$. The deformation mechanisms for PMMA in uniaxial tension close to the glass transition temperature have been reviewed recently by Van Loock & Fleck [24] and deformation mechanism maps were constructed by performing a series of uniaxial tension tests on the high $M_w$ PMMA over a range of temperatures near the glass transition and over two decades of strain rate. The operative deformation mechanism depends upon the temperature $T/T_g$, the strain rate $\dot{\varepsilon}_e$ and strain $\varepsilon_e$. We shall make use of the constitutive models as calibrated by Van Loock & Fleck [24] for the high $M_w$ PMMA: the Ree–Eyring equation and a rubbery-flow model. For the low $M_w$ PMMA, it is necessary to construct an alternative deformation mechanism map. This is reported in appendix B. For this grade, the relevant deformation mechanisms are Ree–Eyring and viscous flow.

The Ree–Eyring equation relates $\sigma_e$ in the glassy and glass transition regime to temperature $T/T_g$ and strain rate $\dot{\varepsilon}_e$

$$\frac{\dot{\varepsilon}_e}{\dot{\varepsilon}_0} = \sinh\left(\frac{\sigma_e v}{kT}\right) \exp\left(-\frac{q}{kT}\right),$$

(4.18)

where $\dot{\varepsilon}_0$ is a reference strain rate, $q$ is an activation energy, $v$ is an activation volume and $k$ is Boltzmann’s constant. Visco-elastic effects are neglected in this finite strain regime. Van Loock &
relatively low molecular weight, i.e. $M_w$ in terms of a reference viscosity can be used to describe the constitutive behaviour of a low $M_w$ PMMA. An additional series of tensile tests have been performed on the low $M_w$ PMMA grades of relatively low molecular weight, i.e. $M_w < 150$ kg mol$^{-1}$ [49]. Instead, a linear, viscous flow rule can be used to describe the constitutive behaviour of a low $M_w$ PMMA for $T/T_g \gg 1$

$$\sigma_e = E_0 \left(1 - \alpha_R \frac{T}{T_g}\right) \left(\frac{\dot{\epsilon}_e}{\dot{\varepsilon}_R}\right)^n \varepsilon_e,$$  

(4.19)

where $E_0$ is a reference modulus, $\alpha_R$ is a temperature sensitivity coefficient, $\dot{\varepsilon}_R$ a reference strain rate, and $n$ a strain rate sensitivity coefficient.

Table 3. Fitted parameters for the constitutive laws for the low $M_w$ PMMA (equations (4.18) and (4.20)) and the high $M_w$ PMMA obtained from Van Loock & Fleck [24], see equations (4.18) and (4.19).

|                  | low $M_w$ PMMA | high $M_w$ PMMA |
|------------------|----------------|-----------------|
| $\nu$ (nm$^{-3}$) | 2.5            | 1.8             |
| $q$ (J)          | $7.31 \times 10^{-19}$ | $7.31 \times 10^{-19}$ |
| $\dot{\varepsilon}_0$ (s$^{-1}$) | $1.5 \times 10^{56}$ | $1.5 \times 10^{56}$ |
| $\eta_0$ (Pa s)  | $2.8 \times 10^5$ | —              |
| $C_1$            | 3.2            | —               |
| $C_2$ (K)        | 17.3           | —               |
| $E_R^0$ (MPa)    | —              | 65.8            |
| $\alpha_R$       | —              | 0.8             |
| $\dot{\varepsilon}_R$ (s$^{-1}$) | — | 1.58 |
| $n$              | —              | 0.173           |

Fleck [24] also fitted an empirical equation to relate $\sigma_e$ to $T/T_g$, $\varepsilon_e$ and $\dot{\varepsilon}_e$ in the rubbery regime for the high $M_w$ PMMA

$$\sigma_e = E_0 \left(1 - \alpha_R \frac{T}{T_g}\right) \left(\frac{\dot{\varepsilon}_e}{\dot{\varepsilon}_R}\right)^n \varepsilon_e,$$  

(4.20)

where $E_0$ is a reference modulus, $\alpha_R$ is a temperature sensitivity coefficient, $\dot{\varepsilon}_R$ a reference strain rate, and $n$ a strain rate sensitivity coefficient.

Note that the rubbery regime above the glass transition is absent for PMMA grades of relatively low molecular weight, i.e. $M_w < 150$ kg mol$^{-1}$ [49]. Instead, a linear, viscous flow rule can be used to describe the constitutive behaviour of a low $M_w$ PMMA for $T/T_g \gg 1$

$$\sigma_e = 3\eta \dot{\varepsilon}_e,$$  

(4.20)

where $\eta$ is a temperature-dependent viscosity [50,51]

$$\eta = \eta_0 \exp\left(-\frac{C_1 (T/T_g - 1)}{C_2/T_g + T/T_g - 1}\right).$$  

(4.21)

in terms of a reference viscosity $\eta_0$ at $T/T_g = 1$; $C_1$ and $C_2$ are fitting constants.

The dependence of the effective stress $\sigma_e$ upon normalized temperature $T/T_g$ and strain rate $\dot{\varepsilon}_e$ is assumed to be governed by equations (4.18) and (4.19) for the high $M_w$ PMMA and by equations (4.18) and (4.20) for the low $M_w$ PMMA. The fitted parameters for the constitutive laws for the high $M_w$ PMMA are taken from Van Loock & Fleck [24] and are summarized in Table 3. An additional series of tensile tests have been performed on the low $M_w$ PMMA at temperatures close to the glass transition in order to calibrate equations (4.18) and (4.20) for the low $M_w$ PMMA as detailed in appendix B. The resulting calibrated parameters for equations (4.18) and (4.20) for the low $M_w$ PMMA are included in Table 3.

(h) Temperature-time profile during void growth

During the rapid release of pressure at the end of the saturation phase, the samples cool down from the saturation temperature equal to 25°C to a temperature $T_0 = -15°C$ due to adiabatic

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16 We assume that the dependence of the effective stress $\sigma_e$ of the PMMA–CO$_2$ solid upon pressure is small as a first-order approximation for the void growth problem.

17 Measured by placing a thermocouple on the sample after pressure release at the end of the saturation phase.
cooling of the expanding gas. The samples are subsequently placed in a thermal bath at a maintained foaming temperature $T_f$. Upon submersion in the foaming bath, assume that the temperature profile $T(t)$ is of the form

$$T = T_0 + (T_f - T_0) \left( 1 - \exp \left( \frac{-t}{\tau} \right) \right),$$

where $\tau$ is a time constant associated with the heat conduction into the PMMA, as measured by a thermocouple. The direct measurement of the temperature history by an in situ thermocouple supports this simple relation. This expression also agrees with the dominant, leading-order term in the series expansion of the temperature dependence for a cuboid with a sudden jump in surface temperature; see, for example, Carslaw & Jaeger [52].

(i) Void growth simulations

Void growth during solid-state foaming is simulated by solving the equilibrium equation, equation (4.10), and the mass conservation statement, equation (4.14), simultaneously, with due account of the dependence of $T_g$ upon $C$ via equation (4.17), the dependence of the effective stress $\sigma_e$ of the PMMA–CO$_2$ solid upon $\dot{\varepsilon}_e$, $\dot{\varepsilon}_e$ and $T/T_g$ via equations (4.18)–(4.20), the gas laws via equations (4.12) and (4.13), and the time-temperature profile as captured by equation (4.22). The resulting system of equations is solved by numerical integration. The values of the processing parameters and the material properties are summarized in Table 4. Note that the initial porosity $f_0$ is

$$f_0 = \left( \frac{a_0}{b_0} \right)^3,$$

and is estimated to equal $10^{-3}$ for both the low $M_w$ and high $M_w$ PMMA nanofoams. The initial void radius $a_0$ is estimated by

$$a_0 \approx \left( \frac{3f_0}{4\pi N_d} \right)^{1/3},$$

where the cell nucleation density $N_d = 2 \times 10^{20}$ m$^{-3}$ for the low $M_w$ PMMA nanofoams (Table 1) and $N_d = 20 \times 10^{20}$ m$^{-3}$ for the high $M_w$ PMMA nanofoams (Table 2).

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**Table 4. Summary of the assumed processing parameters and material properties for the void growth predictions.**

| Parameter       | low $M_w$ PMMA | high $M_w$ PMMA |
|-----------------|----------------|-----------------|
| $\rho_0$ (MPa)  | 31             | 31              |
| $\rho_s$ (MPa)  | 0.1            | 0.1             |
| $\tau$ (s)      | 20             | 20              |
| $\rho_p$ (kg m$^{-3}$) | 1190         | 1190           |
| $T_g$ (°C)      | 114.5          | 116.5           |
| $f_0$           | $10^{-3}$      | $10^{-3}$       |
| $a_0$ (nm)      | 10.5           | 5               |
5. Results and discussion of the void growth predictions

Consider the deformation mechanism maps for the low \( M_w \) PMMA (figure 7a) and for the high \( M_w \) PMMA (figure 7b). We superpose the predicted trajectory of the effective stress at the surface of the cavity \( \sigma_e \) by the void growth model as a function of \( T/T_g \) for foaming temperatures \( T_f = 25^\circ C \) and \( T_f = 80^\circ C \), and for a foaming time up to 600 s. Note that both the temperature \( T \) and glass transition temperature \( T_g \) evolve in time during foaming. For both the low \( M_w \) and high \( M_w \) PMMA, at the start of foaming, \( T = T_0 \) and \( T/T_g \) is close to 0.9; at this instant \( \sigma_e \) is close to 0.8 MPa for the low \( M_w \) PMMA and \( \sigma_e \) is close to 0.3 MPa for the high \( M_w \) PMMA. When the temperature increases from \( T = T_0 \) to \( T = T_f \), \( T/T_g \) rises to almost unity and \( \sigma_e \) rises steeply. The void growth simulations suggest that during solid-state foaming of PMMA, the normalized temperature \( T/T_g \) remains between 0.9 and 1 and consequently void growth does not occur within either the viscous regime (low \( M_w \) PMMA) or within the rubbery regime (high \( M_w \) PMMA).

The measured porosity \( f \) is plotted as a function of foaming time \( t_f \) for \( T_f = 25^\circ C \) to \( T_f = 80^\circ C \), and compared with the predicted \( f \) versus \( t_f \) curves for the low \( M_w \) and high \( M_w \) nanofoams, in figure 8a,b, respectively. There is reasonably good agreement between the measured and the predicted \( f-t_f \) curves for \( T_f = 25^\circ C \) and \( T_f = 40^\circ C \). The void growth model overestimates the porosity at \( T_f = 60^\circ C \) and at \( T_f = 80^\circ C \), where porosities close to \( f_{\text{max}} \) are observed. Observations of SEM micrographs suggest that cell walls tear, leading to open-celled microstructures. This is confirmed by open cell content measurements using gas pycnometry: nanofoams with the highest observed porosities have predominantly open-celled microstructures (figure 4). At increased foaming temperatures (i.e. \( T_f = 100^\circ C \)) collapse of the foamed open-celled microstructure is observed leading to measured porosities below the maximum observed porosities at \( T_f = 80^\circ C \), as shown in figure 2c,d.

We proceed to explore two alternative hypotheses for cell wall failure which could lead to open-celled microstructures as observed for the PMMA nanofoams: (i) achievement of a critical hoop strain at the void at a critical value of porosity \( f_t \) or (ii) achievement of a minimum (critical) value of ligament thickness between neighbouring voids at a critical value of porosity \( f_c \). A comparison of predictions with measured values of porosity is now given.

(a) Critical hoop strain

Assume that tearing of the cell wall occurs when the true (that is, logarithmic) value of hoop strain \( \varepsilon_s \) equals the \( T/T_g \)-dependent\(^{20}\) true tensile failure strain \( \varepsilon_f \). Recall that the solid surrounding the expanding void is incompressible. Then, by equation (4.1),

\[
b^2 - a^2 = b_0^2 - a_0^2. \tag{5.1}
\]

The initial (as-nucleated) porosity \( f_0 \) equals \( (a_0/b_0)^3 \) as defined in equation (4.23) and the current porosity \( f \) equals \( (a/b)^3 \). Now, rearrange equation (5.1), to express \( f \) as a function of \( f_0 \) and the true hoop strain \( \varepsilon_s \) at the surface of the void, where \( \varepsilon_s = \varepsilon_{\theta\theta}(r = a) = \ln(a/a_0) \)

\[
f^{-1} = 1 + \exp(-3\varepsilon_s)(f_0^{-1} - 1). \tag{5.2}
\]

Rupture of the cell wall occurs when \( \varepsilon_s = \varepsilon_f \). The critical porosity \( f_t \) corresponding to this ductility-governed failure criterion reads

\[
f_t^{-1} = 1 + \exp(-3\varepsilon_f)(f_0^{-1} - 1). \tag{5.3}
\]

(b) Critical ligament size

The alternative failure hypothesis assumes that there is a minimum number of confined polymer chains separating individual cells to prevent rupture of the solid between the cells. Write \( h_c \) as the critical cell wall thickness, and assume that it is independent of \( T/T_g \). Assume that the cell wall

\(^{20}\)We assume \( \varepsilon_f \) to be insensitive to strain rate [24,53].
Figure 7. Deformation mechanism maps for (a) low $M_w$ PMMA and (b) high $M_w$ PMMA (for a reference strain $\varepsilon_{\text{ref}} = 0.05$), for contours of effective strain rate $\dot{\varepsilon}_e$. The predicted effective stress at the surface of the cavity $\sigma_e$ is plotted as a function of $T/T_g$ for foaming temperatures $T_f = 25^\circ C$ and $T_f = 80^\circ C$ and for a foaming time up to 600 s.

Figure 8. Predicted and measured porosity $f$ versus foaming time $t_f$, for $T_f = 25^\circ C$ to $T_f = 80^\circ C$ for (a) the low $M_w$ PMMA nanofoams and (b) the high $M_w$ PMMA nanofoams. The ductility-governed porosity limit $f_f$ is plotted via equation (5.3) for an initial porosity $f_0 = 10^{-3}$. The minimum cell wall thickness-governed porosity limit $f_c$ is plotted via equation (5.5) for $f_0 = 10^{-3}$ and $h_c/a_0 = 3$ (low $M_w$ PMMA) and $h_c/a_0 = 4.2$ (high $M_w$ PMMA).

fails when the cell wall thickness reduces to this critical value, $h_c$. Define the smallest distance between two neighbouring cells $h$ as

$$h = 2(b - a). \quad (5.4)$$

Then, upon making use of the expressions $f_0 = (a_0/b_0)^3$, $f = (a/b)^3$ and equation (5.2), we obtain

$$\frac{h}{a_0} = 2(f^{-1/3} - 1) \left(\frac{f_0^{-1} - 1}{f^{-1} - 1}\right)^{1/3}. \quad (5.5)$$

The corresponding critical value of porosity $f_c$ is given by equation (5.5) with $h = h_c$. 
The ductility-governed porosity limit $f_1$ as given by equation (5.3) is plotted in figure 7 based on the predicted hoop strain $\varepsilon_s$ during void growth. Note that we make use of the measured response of $\varepsilon_s$ versus $T/T_g$ (equation (B2) for the low $M_w$ PMMA and equation (B1) for the high $M_w$ PMMA as detailed in appendix B) and assume that the initial porosity $f_0 = 10^{-3}$. The measured values of final porosity $f$ and the predictions of the void growth model exceed the porosity limit as given by $f_1$.

We now plot the porosity limit $f_c$ in figure 7 via equation (5.5) for $f_0 = 10^{-3}$ by taking $h_c/a_0 = 3$ (low $M_w$ PMMA) and $h_c/a_0 = 4.2$ (high $M_w$ PMMA) in order to match to observed values of the maximum observed porosity $f_{\text{max}}$ of the nanofoams. Recall that the initial void size $a_0$ of the low $M_w$ PMMA nanofoams is estimated to be close to 10.5 nm, whereas $a_0$ is close to 5 nm for the high $M_w$ PMMA nanofoams. Consequently, the estimated corresponding critical cell wall dimension $h_c = 32$ nm for the low $M_w$ PMMA nanofoams, whereas $h_c = 21$ nm for the high $M_w$ PMMA. These values for $h_c$ are of the same order of magnitude as root-mean-square end-to-end distance $R_{ee}$ of the PMMA chains, i.e. $R_{ee} \approx 20$ nm for the low $M_w$ PMMA and $R_{ee} \approx 110$ nm for the high $M_w$ PMMA based on an idealized equivalent freely jointed chain calculation [54]. This is in agreement with the results of Crosby and co-workers who conducted a series of uniaxial tensile tests on thin polystyrene (PS) films with $M_w = 136\,000$ g mol$^{-1}$ [55,56]. They found that the tensile failure strain $\varepsilon_f$ decreases with decreasing film thickness $t$ in the regime $t = 15$–$77$ nm; these values are close to the estimated value for $R_{ee} = 25$ nm of the PS chains.

6. Concluding remarks

Solid-state nanofoaming experiments are performed on two grades of PMMA of markedly different molecular weight ($M_w = 92\,500$ g mol$^{-1}$ and $M_w = 3\,580\,000$ g mol$^{-1}$). It was found that the molecular weight of the PMMA has a profound effect upon the microstructure of the PMMA nanofoams. When subjected to identical foaming conditions, the observed cell size $l \approx 35$ nm of the high molecular weight PMMA nanofoams is an order of magnitude less than that of the low molecular weight PMMA nanofoams, $l \approx 250$ nm. This is consistent with the observation that the nucleation density, $N_d \approx 20 \times 10^{20}$ m$^{-3}$ of the high molecular weight PMMA nanofoams is an order of magnitude higher than that of the low molecular weight PMMA nanofoams $N_d \approx 2 \times 10^{20}$ m$^{-3}$. In addition, a limit in attainable porosity $f_{\text{max}}$ was observed: $f_{\text{max}} = 0.65$ for the high molecular weight PMMA and $f_{\text{max}} = 0.75$ for the low molecular weight PMMA. The microstructure of the PMMA nanofoams transitions from closed-celled to open-celled at a porosity close to $f_{\text{max}}$.

A void growth model has been developed to simulate cavity expansion during solid-state nanofoaming of PMMA by CO$_2$. Experimentally calibrated constitutive laws for the PMMA grades close to the glass transition are used in the simulations. The predicted porosity of the nanofoams versus foaming time, at selected foaming temperatures, are in good agreement with the measured responses for porosities well below the maximum observed porosity. There is also close agreement between the predicted and observed sensitivity to molecular weight. This suggests that the observed difference in constitutive response close to the glass transition between the two PMMA grades leads to the measured difference in porosity. Moreover, cell wall tearing accounts for the observed limit in final porosity. Our analysis suggests the existence of a limiting minimum cell wall thickness of magnitude close to that of the end-to-end distance of the polymer chains. When the cell wall thickness approaches this minimum value during foaming, rupture of the cell walls occurs; this leads to an open-celled structure, and to a limit on foam expansion.

Data accessibility. Measurement data and code are available at the Cambridge University Apollo repository via https://doi.org/10.17863/CAM.43166.

Authors’ contributions. V.B. and M.A.R.P. designed the foaming experiments. F.V.L. and V.B. conducted the foaming tests. F.V.L. and N.A.F. developed the void growth model. F.V.L. conducted the uniaxial tensile tests and drafted the manuscript. All other authors critically revised the manuscript. All authors gave final approval for publication.

Competing interests. We declare we have no competing interests.
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**Appendix A. The assumption of uniform concentration of dissolved CO₂ within the spherical shell**

At the start of the foaming process, the chemical potential of the CO₂ molecules in the nucleated voids is lower than the chemical potential of CO₂ molecules in the PMMA–CO₂ solid. Consequently, CO₂ gas molecules migrate from the PMMA–CO₂ solid into the voids. The concentration of CO₂ gas molecules \( C(r, t) \) within the solid at time \( t \) and position \( r \) (for \( a < r < b \)) can be obtained by solving Fick’s second law of diffusion [57]

\[
\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial C}{\partial r} \right],
\]

in the deformed configuration, where \( D \) is the diffusion coefficient for CO₂ in PMMA. Measurements of \( D \) at temperatures and pressures typical for solid-state nanofoaming of PMMA by CO₂ are available in the literature as follows. Guo & Kumar [46] measured \( D \) based on desorption measurements and found that \( D \) ranges from \( D = 2.5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1} \) to \( D = 3.65 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \) for temperatures ranging from \(-30°C\) to \(100°C\) at a CO₂ pressure equal to \(5 \text{ MPa}\). Li et al. [58] measured \( D \) by a sorption technique and found that \( D \) lies in the range of \(6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}\) to \(9.5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}\) for temperatures between \(30°C\) and \(70°C\), and pressures between \(6 \text{ MPa}\) and \(18 \text{ MPa}\). Now, introduce a characteristic diffusion time \( \tau_D \)

\[
\tau_D = \frac{(L_D)^2}{D},
\]

where \( L_D \) is a diffusion length which is approximated for the void growth problem by

\[
L_D \approx b_0 \approx \left( \frac{3}{4\pi N_d} \right)^{1/3}.
\]

Observations of cell nucleation densities of PMMA nanofoams (\( N_d > 10^{20} \text{ m}^{-3} \)) suggest that \( L_D < 133 \text{ nm} \) [1]. Upon assuming \( D = 10^{-12} \text{ m}^2 \text{ s}^{-1} \), we obtain \( \tau_D \approx 20 \text{ ms} \) via equation (A 2), which is two orders of magnitude lower than typical observed foaming times for solid-state nanofoaming of PMMA by CO₂ as reported by Martín-de León et al. [9]. We conclude that the CO₂ concentration profile \( C(R, t) \) is spatially uniform at all times: \( C(R, t) = C(t) \). Consequently, we do not need to solve the diffusion equation to predict void growth during solid-state nanofoaming of PMMA by CO₂.

**Appendix B. Calibration of the constitutive laws for PMMA**

Constitutive laws are calibrated for the low \( M_w \) PMMA grade\(^{21}\) close to its glass transition temperature. We follow the procedure of Van Lock & Fleck [24], who constructed deformation and failure maps for the high \( M_w \) PMMA grade\(^{22}\) in uniaxial tension close to the glass transition temperature. A series of uniaxial tensile tests were performed on the low \( M_w \) PMMA grade for a range of temperatures \((T = 90°C–170°C)\) and at a nominal strain rate \( \dot{\varepsilon} = 5.9 \times 10^{-2} \text{ s}^{-1} \). The dogbone specimen geometry and the measurement procedures are detailed in Van Lock & Fleck [24]. Note that the low \( M_w \) PMMA dogbone specimens are machined from the foaming precursor sheets. The true stress versus true strain responses of the low \( M_w \) PMMA dogbone

\(^{21}\)Altuglas V825T with \( T_g = 114.5°C \) and \( M_w = 92 500 \text{ g mol}^{-1} \).

\(^{22}\)Altuglas CN with \( T_g = 116.5°C \) and \( M_w = 3 580 000 \text{ g mol}^{-1} \).
specimens are plotted in figure 9a for 0.94 < \( T / T_g < 1.01 \) and in figure 9b for 1.04 < \( T / T_g < 1.14 \). The true stress versus true strain curves of the high \( M_w \) PMMA grade are included in figure 9a, b.

Loading–unloading uniaxial stress versus strain curves for the low \( M_w \) PMMA and high \( M_w \) PMMA are shown in figure 10. At \( T / T_g = 0.93 \), the elastic unloading of the low \( M_w \) and the high \( M_w \) PMMA occurs in the manner of an elasto-viscoplastic solid, with a remnant finite strain at zero load. The qualitative stress versus strain response of the low \( M_w \) PMMA and the unloading curve is almost coincidental with the loading curve; there is negligible hysteresis and negligible remnant strain. No rubbery regime is observed for the low \( M_w \) PMMA above the glass transition. At \( T / T_g = 1.06 \) and \( T / T_g = 1.12 \), the stress versus strain response of the low \( M_w \) PMMA in uniaxial tension is linear viscous. Unloading is accompanied by a finite remnant strain. The high \( M_w \) PMMA transitions from the rubbery regime to a viscous regime at \( T / T_g = 1.16 \).

First, consider the elasto-viscoplastic regime. The dependence of the measured flow strength \( \sigma_Y \) of the low \( M_w \) and high \( M_w \) PMMA grades upon \( T / T_g \) is shown in figure 11 for \( \dot{\varepsilon} = 5.9 \times 10^{-2} \text{s}^{-1} \). A single transition Ree–Eyring equation, equation (4.18), is fitted to the \( \sigma_Y \) versus \( T / T_g \) response of the low \( M_w \) PMMA in the glassy and glass transition regime (corresponding to \( 0.94 \leq T / T_g \leq 1.04 \)). We assume that \( q = 7.31 \times 10^{-19} \text{J} \) and \( \varepsilon_0 = 1.5 \times 10^{56} \text{s}^{-1} \) for both the low \( M_w \) and the high \( M_w \) PMMA, as reported by Van Loock & Fleck [24]. The activation volume \( v = 2.5 \text{nm}^{-3} \) for the low \( M_w \) PMMA, and \( v = 1.8 \text{nm}^{-3} \) for the high \( M_w \) PMMA [24]. The resulting curve fits are included in figure 11. Second, consider the viscous regime for the low \( M_w \) PMMA. We fit a linear, viscous constitutive law, equations (4.20) and (4.21), to the measured \( \sigma_Y \) versus \( T / T_g \) curves of the low \( M_w \) PMMA in the regime of 1.06 < \( T / T_g \) < 1.14 and \( \dot{\varepsilon} = 5.9 \times 10^{-2} \text{s}^{-1} \). The fitting values are \( \eta_0 = 2.8 \times 10^6 \text{Pa s} \), \( C_1 = 3.2 \) and \( C_2 = 17.3 \text{K} \). The resulting curve fit is adequate, see figure 11. Third, consider the rubbery regime of the high \( M_w \) PMMA. The constitutive description, equation (4.19), is adequate upon making use of previously measured values (\( \alpha_R = 65.8 \text{MPa}, \alpha_R = 0.80, \dot{\varepsilon}_R = 1.58 \text{s}^{-1} \) and \( n = 0.173 \) [24]), as shown in figure 11.

(a) Tensile ductility of the low \( M_w \) and high \( M_w \) PMMA

Van Loock & Fleck [24] measured the true tensile failure strain, that is ductility, \( \varepsilon_f \) of the high \( M_w \) PMMA grade by testing a dogbone geometry at \( T / T_g < 1 \) and an hourglass-shaped specimen geometry at \( T / T_g \geq 1 \). The measured values for \( \varepsilon_f \) of the high \( M_w \) PMMA grade are plotted as
Figure 10. Loading–unloading true stress versus true strain curves for the low $M_w$ PMMA and high $M_w$ PMMA grades in uniaxial tension, at selected values of $T/T_g$, for a nominal strain rate $\dot{\varepsilon} = 5.9 \times 10^{-4} \text{s}^{-1}$. 

Figure 11. Deformation mechanism maps of the low $M_w$ and high $M_w$ PMMA grades. Flow strength $\sigma_f (=\sigma_e)$ versus $T/T_g$ is plotted, with the curve fits of the constitutive models included for a reference strain $\varepsilon_{\text{ref}} = 0.05$. 

a function of the normalized temperature $T/T_g$ for a nominal strain rate $\dot{\varepsilon} = 5.9 \times 10^{-2} \text{s}^{-1}$ in figure 12. The $\varepsilon_f$ versus $T/T_g$ failure envelope is adequately fitted by a linear relation [24]

$$\varepsilon_f = 7.3 \frac{T}{T_g} - 6.3. \quad (B1)$$

An additional series of uniaxial tensile tests has been conducted on the low $M_w$ PMMA grade by using the same measurement methods as that detailed in the work of Van Loock &
Figure 12. The measured true tensile failure strain $\varepsilon_f$ as a function of normalized testing temperature $T/T_g$ for the low $M_w$ and high $M_w$ PMMA grades, at a nominal strain rate $\dot{\varepsilon} = 5.9 \times 10^{-2}$ s$^{-1}$.

No failure was observed at $T \geq 145^\circ$C prior to the attainment of the maximum cross-head extension. The measured $\varepsilon_f$ versus $T/T_g$ curve is shown in figure 12. The failure envelope of the low $M_w$ PMMA grade close to the glass transition is also fitted by a linear relation

$$\varepsilon_f = 13.3 \frac{T}{T_g} - 11.7.$$  

(B2)

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