Supporting Information

Porosity-tunable structures with “fossilized” bubbles

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Section I. Prediction of the bubble’s volume when detached from the PTFE membrane

For a precise prediction, it is critical to determine the moment when the bubble gets detached from the porous membrane. Here, we choose a simple criterion that a bubble gets released when the buoyancy balances the resultant of the viscous drag and surface tension force. The gravity of the bubble is ignored here because it is negligible compared to buoyancy ($\rho/\rho_{vapor} \sim 1000$, $\rho$ is the precursor’s mass density and $\rho_{vapor}$ is the vapor’s mass density). Accordingly, the force balance equation of the submerged bubble is

$$F_b = F_v + F_s$$  \[S1\]

where $F_b$, $F_v$ and $F_s$ denote the buoyancy, viscous force and surface tension, respectively. The buoyancy is given by the classic hydrostatic formula $F_b = \rho g V$, where $g$ is the gravity constant and $V$ is the bubble’s volume. The shape of the generated bubble is approximately taken as a sphere\(^1,2\), of which the diameter is $d$. Since Reynolds number $Re$ is quite low due to the high viscosity of precursor (eq S2), the viscous force is expressed as Stokes dragging force (eq S3)

$$Re = \frac{\rho U d}{\mu} \sim \frac{1g/cm^3 \cdot 1mm/s \cdot 1mm}{1Pa \cdot s} \sim 10^{-3}$$ \[S2\]

$$F_v = c_f \pi \mu r U = 4\pi \mu r U = 4\pi \mu r \frac{dr}{dt}$$ \[S3\]

where $\mu$ is the viscosity of the precursor, $r$ is the bubble’s radius and $U$ is the translational velocity. The coefficient $c_f$ is taken as 4 here instead of 6 because of vapor-liquid interface between the bubble and the surrounding fluidic media\(^1\). The translational velocity is estimated as the velocity of the center of the bubble above the porous membrane $U = dr/dt$. The surface tension force is expressed as $F_s = 2\pi \sigma sin\theta$, where $\sigma$ is the surface tension coefficient of the uncured PDMS, $a$ is the radius of the micrometer-scaled pore of PTFE membrane and $\theta$ is the contacting angle. Balancing the above three terms together, we have the following governing equation:

$$\rho g V = 4\pi \mu r \frac{dr}{dt} + 2\pi \sigma sin\theta$$ \[S4\]
The balance equation (eq S4) can be rearranged in terms of the bubble’s radius \( r \) only, since:

\[
r = \left[ \frac{3}{4\pi} \right]^{1/3} V^{1/3}
\]

\[\text{S5}\]

\[
\frac{dr}{dt} = \frac{1}{3} \left[ \frac{3}{4\pi} \right]^{1/3} V^{-2/3} \frac{dV}{dt} = \frac{1}{3} \left[ \frac{3}{4\pi} \right]^{1/3} V^{-2/3} Q
\]

\[\text{S6}\]

where \( Q = dV/dt \) is the volume flow rate of the air or vapor. We estimate \( Q \) by using Darcy’s law for compressible fluid as

\[
Q = Au = \pi a^2 u
\]

\[\text{S7}\]

\[
u' = u\phi
\]

\[\text{S8}\]

\[
u' = \frac{\kappa}{\mu l} \frac{p_b^2 - p_a^2}{2p_a}
\]

\[\text{S9}\]

Where \( A \) is the area of one micrometer-scaled pore, \( u \) is the fluid flow velocity through the pore, \( u' \) is the superficial fluid velocity across the membrane, \( \phi \) is the porosity of PTFE membrane, \( l \) is the membrane’s thickness, \( \kappa \) is the permeability of PTFE membrane, \( \mu' \) is the viscosity of the vapor, \( p_b \) and \( p_a \) are the pressure value below and above the membrane, respectively.

Therefore, the force balance equation can be written as

\[
\frac{4}{3} \pi \rho g r^3 = \frac{\mu Q}{r} + 2\pi \sigma \sin \theta
\]

\[\text{S10}\]

The equation (eq S10) can be further non-dimensionalized by utilizing the expression of Fritz radius \( r_f \) that is defined as the radius of the spherical bubble whose buoyancy is balanced alone by the surface tension (eq S11)

\[
\frac{4}{3} \pi r_f^3 \rho g = 2\pi \sigma a
\]

\[\text{S11}\]

The dimensionless radius \( \tilde{r} \) is defined as \( r = \tilde{r}r_f \) and the equation (eq S10) is arranged as

\[
\tilde{r}^4 = \sin \theta \tilde{r} + Ca
\]

\[\text{S12}\]

where \( Ca = \mu Q / 2\pi \sigma a r_f \) is the capillary number that measures the ratio between the viscous force and surface tension.

Inserting the parameters \( \mu' = 0.018 \text{mPa} \cdot \text{s} \), \( p_b \approx 169 \text{kPa} \), \( p_a = 75 \text{kPa} \), \( \mu = 8.45 \text{Pa} \cdot \text{s} \), \( \sigma = 19.8 \text{mN/m} \), \( l = 130 \mu m \), \( \kappa = 2 \times 10^{-9} \text{mm}^2 \), we have \( Ca \approx 0.93 \), \( r_f \approx 0.25 \text{mm} \) and \( \tilde{r} \approx \frac{3}{3} \).
The results show that the viscous force and surface tension have relatively the same magnitude and hence the radius of the detached bubble is slightly bigger than the Fritz radius. In the experiments, the pressure value below the PTFE membrane $p_b$ is estimated as the equilibrium pressure of the vapor at the curing temperature. As for the pressure above the PTFE membrane $p_a$, it depends on the pressure value inside the vacuum oven $p_v$ as

$$p_a = p_v + \rho gh + \frac{2\sigma}{r}$$  \[S13\]

where $h$ is the depth of the PDMS precursor. The hydrostatic pressure from the precursor is estimated as $\rho gh = 0.97g/cm^3 \times 9.8m/s^2 \times 4mm = 38Pa$ while the capillary pressure coming from the bubble’s curvature is estimated as $2\sigma/r \approx 2 \times 19.8mN \cdot m^{-1}/0.3mm = 132Pa$. Both terms are much smaller than the pressure value in vacuum oven. Hence, a good approximation is given as $p_a \approx p_v$.

**Section II. Transition time after the bubble’s detachment and the critical bubble’s diameter**

After the bubble gets detached, its velocity $U$ is controlled by Newton’s second law as

$$\rho_{vapor} V \frac{du}{dt} = \rho V g - 4\pi \mu r U$$  \[S14\]

This ordinary differential equation can be easily solved as

$$U = U_0 e^{-t/t_c} + U_\infty \left(1 - e^{-t/t_c}\right)$$  \[S15\]

where $U_0$ is the initial velocity when the bubble gets pinched off, $U_\infty$ is the steady velocity when buoyancy balances the Stokes dragging force and $t_c = \rho_{vapor} V / 4\pi \mu r \approx 4 \times 10^{-8}s$ is the characteristic time scale if the system reaches the steady velocity. Since $t_c \ll 1s$, the transition time before the bubble reaches this stable velocity is ignored. Therefore, the time of rising through the uncured PDMS is given as

$$t = \frac{h}{U_\infty} = \frac{4\pi \mu r h}{\rho V} = 12\mu h \rho^{-1} g^{-1} d^{-2}$$  \[S16\]
When $t$ is smaller than the time left before solidification $\Delta t$, the bubble will stay in the PDMS membrane at last. Therefore, a critical diameter is yield as:

$$d_c = \sqrt{\frac{12\mu h}{\rho g \Delta t}} \quad [S17]$$

**Section III. Additional figures and results**

**Figure S1.** Experiment setup of preparing porous material by pumping air with an air compressor. This device contains a trilayer structure in which a porous PTFE membrane is sandwiched between two PMMA sheets and a gas-guide tube underneath the lower PMMA. Above the PTFE membrane lies the uncured PDMS, while below the PTFE membrane is the air pumped from the air compressor. Bubbles can be generated and trapped in PDMS medium when appropriate air flow is provided.

**Figure S2.** Experiment setup of preparing porous material by heating up the solutions in the container to generate vapor. Placing the device into the oven at 70 °C, liquid vapor can evaporate from the solution contained in the cuvette and bubbles can be produced in PDMS medium when the vapor goes through the porous PTFE membrane.
**Figure S3.** The time-dependent viscosity of the uncured PDMS at 70 °C.

**Figure S4.** The schematic illustration of preparing porous material with different pressure values above the PTFE membrane. Placing the device into a vacuum oven at 70 °C, porous structures with different pore sizes can be prepared by controlling the absolute pressure value in the vacuum oven.

**Figure S5.** Strain-stress curves of porous material under compression and tensile tests. Porous samples are prepared from the water/ethanol vapor with different water/ethanol ratios.
Figure S6. Porous PDMS with intricate patterns such as (a) small circle, (b) large circle, (c) letter “l” and (d) letter “H” shapes can be obtained by designing proper templates. First row: template design, second row: porous PDMS from the top view, third row: porous PDMS from the side view.

Figure S7. The thermal properties of the porous structures with non-interconnected pores (left) and interconnected pores (right). The thickness is 5 mm.

References