Supplementary Information

Effect of additives on the pore structure of polymer foams obtained from Pickering HIPE templates

Various routes were investigated to create pore throats in closed-celled poly-Pickering-HIPEs; we tried to dissolve the silica particles used as emulsifiers out of the thin films separating individual pores by adding NaOH into the aqueous phase, which resulted indeed in the formation of interconnects of the size of the silica particles (from about 5-10 μm). We also explored the incorporation of 1 wt.-% degradable CaCO₃ particles, 25 μm in size, into the polymer (walls) followed by their degradation using HCl but the particles were too well dispersed to form interconnects (leaving just a rough pore surface after etching). Furthermore, we investigated the addition of additives such as methanol and polypropylene oxide to the emulsion template, however interestingly enough the emulsion templates remained stable but no pore throats were observed in the poly-Pickering-HIPEs afterwards.

1. Poly-Pickering-HIPE made from emulsion template containing 0.5 M NaOH as internal phase, in order to leach out silica particles from the areas of neighbouring pore walls. The poly-Pickering-HIPE also shrunk during polymerization.
2. Poly-Pickering-HIPE made from an emulsion template containing 1 wt.-% CaCO₃ particles (25 μm). The particles were dissolved by Soxhlet extraction in 5 M HCl to create pore throats.

3. Poly-Pickering-HIPEs synthesized from emulsion templates containing a) 4 vol.-% methanol in the aqueous internal phase and b) 10 wt-% Polypropylene oxide in the monomer phase
Estimation of the excess particle concentration in the continuous phase of Pickering emulsion templates

The number of excess particles in a Pickering emulsion, \( N_{ex} \), equals to the difference between the total number of particles, \( N \), and the number of particles attached to the o/w interface, \( N_s \), hence \( N_{ex} = N - N_s \). Assuming that the particles do not migrate into the internal phase, the concentration of the excess particles in the continuous phase, \( C_{ex} \) (in w/v % i.e. grams per 100 cm\(^3\)) is given by the equation

\[
C_{ex} = \frac{(N - N_s) m_p}{V (1 - \phi_i)} \times 100
\]

(1)

where \( m_p = (\pi/6) \rho_p d^3 \) is the mass of a spherical particle with density \( \rho_p \) and diameter \( d \), \( V \) is the emulsion volume and \( \phi_i \) is the internal phase volume fraction. The total number of particles added to the continuous phase at a concentration of \( C_p \) w/v % is

\[
N = \frac{C_p V (1 - \phi_i)}{100 m_p}
\]

(2)

The number of particles attached to the droplet surface is

\[
N_s = A_i \Gamma
\]

(3)

where \( A_i \) is the total area of the o/w interface and \( \Gamma \) is the number of attached particles per unit interfacial area. When the particle diameter is much smaller than the droplet diameter, it is reasonable to assume a hexagonal close-packing in the particle monolayer at the droplet surface,\(^1\) hence

\[
\Gamma = \frac{2}{(\sqrt{3} d^2)}
\]

(4)

The total area of the o/w interface in an emulsion with spherical droplets is given by

\[
A_i = 6 V \phi_i / d_i
\]

(5)

where \( d_i \) is the mean droplet diameter and \( \phi_i \) is not bigger than some critical internal phase volume fraction \( \phi_0 \), corresponding to touching spherical drops (\( \phi_0 = 0.74 \) for monodisperse droplets, but tends to be somewhat smaller for polydisperse systems\(^2\)). In the case of concentrated emulsions, \( A_i \) can be calculated by the empirical equation\(^2\) given below that takes into account the increase of the interfacial area due to droplet deformations at \( 0.715 \leq \phi_i < 0.9 \).

\[
A_i = A_0 \left[ 1 + \frac{1}{3} \left( \frac{0.084}{\phi_i} - \frac{0.068}{\phi_i} \ln(1 - \phi_i) - 0.237 \right) \right]
\]

(6)
Here $A_0$ is the total interfacial area of the emulsion with spherical droplets calculated by eq.(5) at $\phi = \phi_0$.

The table below shows the estimated concentration of the excess particles in the continuous phase of Pickering emulsion templates studied by us. They are calculated by eqs (1) - (4) and (5) at $\phi_i \leq 0.715$ or (6) at $\phi_i > 0.715$ with $C_p = 3 \text{ w/v } \%$, $d = 20 \text{ nm}$, $\rho_p = 2.2 \text{ g cm}^{-3}$, $V = 50 \text{ cm}^3$, $d_i = 200 \mu\text{m}$. It is seen that significant amounts of excess particles should remain in the continuous phase of all systems studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\phi_i^a$</th>
<th>$C_{ex}$ $(\text{w/v }%)^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-Pickering-HIPE 3</td>
<td>0.75 (0.74)</td>
<td>2.77 (2.56)</td>
</tr>
<tr>
<td>Poly-Pickering-MIPE 4</td>
<td>0.70 (0.69)</td>
<td>2.81 (2.64)</td>
</tr>
<tr>
<td>Poly-Pickering-HIPE 5</td>
<td>0.80 (0.79)</td>
<td>2.71 (2.46)</td>
</tr>
<tr>
<td>Poly-Pickering-HIPE 6</td>
<td>0.85 (0.84)</td>
<td>2.62 (2.28)</td>
</tr>
</tbody>
</table>

$^a$The numbers in brackets correspond to the systems with added surfactant (Hypermer 2296) where $d_i = 100 \mu\text{m}$.

References