Manufacturing polymeric capsules for CO2 capture using microfluidic emulsification and on-the-fly photopolymerisation

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1. INTRODUCTION

In this work, novel monodispersed polymeric core/shell microcapsules of controllable size and shell thickness have been developed and produced using continuous microfluidic emulsification and “on-the-fly” photopolymerisation. The process can be used for gas capture or sensing and allows encapsulation of CO$_2$ selective liquid with 100% efficiency inside a semipermeable shell. Conventional methods for fabrication of core/shell capsules such as internal phase separation, interfacial polymerization, complex coacervation and layer-by-layer electrostatic deposition require multi-stage processing and do not permit precise control over the shell thickness and capsule size.

The process was used to encapsulate aqueous solutions of K$_2$CO$_3$ of various concentrations in the presence of the pH-sensitive dye m-cresol purple, so that CO$_2$ adsorption can be visualised (Fig. 1a). Post-combustion amine scrubbing, mainly using monoethanolamine (MEA), is the most established commercial technology for CO$_2$ capture from large point sources. Although MEA exhibits a high CO$_2$ selectivity and capture capacity, it is a corrosive and volatile liquid, and requires a high regeneration energy [1]. On the other hand, solid adsorbents, such as zeolites, metal-organic frameworks, and activated carbons are non-volatile, noncorrosive materials and have the lower regeneration energy than amines. However, they suffer from low CO$_2$ capture capacity and selectivity, especially at low pressures [2]. Our core/shell capsules are hybrid liquid/solid materials that keep all benefits of liquid absorbents, such as high CO$_2$ capture capacity and selectivity, while providing protection against evaporation and a high surface area to volume ratio of solid adsorbents, up to 100 times higher than in a typical packed-bed column [3].

2. EXPERIMENTAL

Core/shell droplets have been produced using a glass capillary microfluidic device that combines co-flow and counter-current flow focusing [4] (Fig. 1b) placed on the stage of an inverted microscope with a high-speed camera attached to it. The microfluidic device was consisted of two round inner capillaries inserted inside a square outer capillary. The orifice sizes of the injection and collection capillary were 50 and 430 µm, respectively. The droplet shells were polymerised by exposure to UV-A radiation with an irradiance of 0.7-38.1 mW·cm$^{-2}$ after droplet generation. The inner phase was 5-30 wt% aqueous solution of K$_2$CO$_3$.
containing small amounts of the pH indicator m-cresol purple. The middle phase was a UV-curable liquid silicon rubber (Semicosil® 949) containing 0-2 wt% Dow Corning 749 Fluid added to stabilise the inner liquid-liquid interface. The outer phase was 60-70 wt% aqueous solution of glycerol containing 0-2 wt% PVA, Tween 20 or Pluronic® F-127 added to stabilise the outer interface. The capsules were cut using a microtome and the images of cross-sectioned capsules were taken using a Scanning Electron Microscope (SEM) (Fig. 1c.3).

3. RESULTS AND DISCUSSION

The capsule diameter and the shell thickness were precisely adjusted over the range of 200-400 and 20-30 µm, respectively by controlling the flow rate of the three fluid streams in the microfluidic device. By increasing the outer phase flow rate from 5 to 35 mL/h at the constant inner and middle phase flow rates of 1.5 mL/h, a reduction in the droplet size from 324 to 228 µm was achieved, while the shell thickness remained unchanged at 30 µm. The same behaviour was predicted numerically by Nabavi et al. [5]. The coefficient of variation of droplet diameters was less than 2.6%. An increase in the concentration of K₂CO₃ in the core solution from 5 to 30 wt% at the outer phase flow rate of 5-10 mL/h caused a slight increase in the droplet diameter which could be attributed to the corresponding increase in the viscosity of the compound jet formed in the collection capillary and its higher resistance to pinch off. For inner phase containing 5-15 wt% K₂CO₃ solution, the presence of 0.5-2 wt% PVA (poly(vinyl alcohol), 0.5-2 wt% Tween 20, or 0.5-1 wt% Pluronic F127 in the outer phase provided a good drop formation stability. However, in the case of 30 wt% K₂CO₃ solution in the core, only 0.5 wt% Pluronic F127 could provide a successful long-term drop formation stability.

The minimum UV light irradiance and energy density of 13.8 mW·cm⁻² and 2 J·cm⁻² respectively, corresponding to the minimum exposure time of 144 s were required to achieve a complete shell polymerisation. The core-shell drops made without any lipophilic stabiliser (Dow Corning 749 Fluid) were unstable and released the inner droplet before they had time to polymerise. Adding at least 0.5 wt% Dow Corning 749 Fluid in the organic phase was essential to stabilise the core/shell structure prior to polymerisation. The shells containing 0.5 wt% Dow Corning 749 Fluid were fully solidified ~30 min after UV exposure. However, for 2 wt% Dow Corning 749 Fluid in the shell, the curing time was more than one hour which was attributed to accumulation of the stabiliser at the outer interface of the shell and the reduction in intensity of the incident UV light. When placed in hypotonic solutions, the capsules became swollen due to diffusion of water to the interior of the capsules. For the capsules containing initially 30 wt% K₂CO₃, a particle diameter became 4 times larger than the initial diameter, when they were stored in pure water until the osmotic equilibrium was established. An analytical model was developed to estimate the size of the core, D₁,eq at equilibrium:

\[
(KC_{out})\beta^4 + (1 - KC_{in})\beta - 1 = 0
\]
where $\beta = \frac{D_{1,\text{eq}}}{D_1}$, $C_{out}$ and $C_{in}$ are the equilibrium expansion ratio of the core, and the molarity of storage and core solutions before equilibrium, respectively, $D_1$ is the initial diameter of the core and $K$ is

$$K = \frac{D_1 RT_i}{8t_E}$$

where $R$ is the gas constant, $T$ is the temperature, $i$ is the van 't Hoff factor, $E$ is the elastic modulus, and $t$ is the initial shell thickness.

Prior to CO$_2$ uptake, the capsule interiors were purple because the pH was above 11 (Fig. 1c.1). After exposure to CO$_2$, the colour of the core liquid turned yellow (Fig. 1c.2), due to decrease in pH below 8 caused by the chemical reaction: $K_2CO_3 + H_2O + CO_2 \rightarrow 2KHCO_3$. The capsule can be regenerated by heating, which can cause the reaction to proceed in the opposite direction and a pure stream of CO$_2$ is released: $2KHCO_3 \rightarrow CO_2 + K_2CO_3 + H_2O$. Based on the stoichiometry of the CO$_2$ uptake by potassium carbonate solution, the equilibrium capture capacity of 30 wt% $K_2CO_3$ solution is 2.17 mmol/g. However, due to the volume of the shell, a correction factor of $rac{\rho_c D_1}{6\rho_s t + \rho_c D_1}$ should be taken into the account, where $\rho_c$ is the density of core liquid, and $\rho_s$ is the density of cured shell. Therefore, the actual CO$_2$ capture capacity of 30 wt% $K_2CO_3$ capsules was 1.6-2 mmol/g and the
exact value was dependant on the size and shell thickness of the capsules. The capsules were thermally stable up to 450°C, as confirmed by thermogravimetric analysis (TGA). The drop fabrication process was stable over a period of at least one hour with a maximum deviation of droplet sizes of 4.3%.

4. CONCLUSIONS

A novel process for the production of highly uniform elastic capsules filled with aqueous K2CO3 solutions was developed consisting of generation of core/shell drops in a microfluidic device and “on-the-fly” photopolymerisation of the shell initiated by UV irradiation. The size of the capsules and their shell thickness were precisely tuned by controlling the flow rate of the three fluid streams in the microfluidic device. The minimum UV light irradiance, energy density and exposure time for a complete shell polymerisation were 13.8 mW·cm⁻², 2 J·cm⁻², and 144 s, respectively. An analytical model was developed to estimate the morphological changes of the capsules during storage caused by the osmotic stress. The optimum hydrophobic stabilizer for continuous production of capsules with 30 wt% K2CO3 in the core was 0.5 wt% Pluronic® F-127. The capture of CO2 by the capsules was visualised using a dye indicator, m-cresol purple. The CO2 storage capacity of the capsules containing 30 wt% K2CO3 in the core was found to be 1.6-2 mmol/g based on their size and shell thickness. The shell has a high thermal stability with the onset temperature of degradation at around 450°C, implying that the microcapsules are suitable for high temperature applications.

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6. REFERENCES