Synthesis and characterization of acrylate microcapsules using microfluidics for self-healing in cementitious materials

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ABSTRACT

Capsule based self-healing is an effective method to obtain autonomic healing in concrete, releasing healing agent to seal cracks and in some cases, obtaining partial regain in mechanical properties. Currently, the production of microcapsules containing liquid healing agent is achieved via emulsification and interfacial polymerization, even though this method presents challenges associated with the reactive nature of the chosen core material. Thus, in this work we propose the use of a new technology to create microcapsules for self-healing concrete, based on the production of double emulsion template using microfluidic device. Due to the small dimensions of the device, the fluids present a laminar flow and reduced reactivity, enabling encapsulation of a wide range of core material. Moreover, this methodology of synthesis uses non-toxic substances and maximizes the incorporation of all materials used in the process, decreasing generation of by-products and therefore leading to a greener chemistry. The production of microcapsules is comprised of two steps: firstly, water-in-oil-in-water droplets are produced followed by photopolymerization of the middle oil phase creating a solid shell and resulting in the formation of capsules. The shell material is comprised of a mixture of acrylates encapsulating an aqueous core, which can further be used as a carrier phase for the healing agent.

1. INTRODUCTION

The capsule based self-healing of cementitious materials offers the advantage of simple addition of capsules during the mixing process, without any additional steps or reduction in the workability of concrete. Currently, the microcapsules are produced to be chemically resistant and to be able to release the cargo material after a specific triggering event (e.g., crack) [1–3]. In this context, microfluidics technology can be used in the production of microcapsules with narrow size distribution, precise control over the shell thickness and tunable mechanical properties[4]. Although promising, to the best of our knowledge, this is the first time this technology is used for the production of microcapsules for the self-healing concrete.

2. EXPERIMENTAL METHODOLOGY

a. Production of microcapsules

A flow-focusing microfluidic device (Dolomite Microfluidics, United Kingdom) was used for the production of the double emulsion. As the inner and outer fluids, we use 2 wt % aqueous solutions of poly(vinyl alcohol) (PVA, M_W 31000-50000, 87-89% hydrolyzed, Sigma Aldrich). For the middle phase, we use a solution of 40 wt % isobornyl acrylate (Sigma Aldrich), 10 wt % 1,6-hexanediol diacrylate (Sigma Aldrich) and 50 wt % bisphenol A glycerolate dimethacrylate (Sigma Aldrich). After the homogenization of the acrylate solution, 1 wt% of of photoinitiator hydroxy-2-methylpropiophenone was added to solution. We found that higher concentrations of photoinitiator could decrease the Young's Modulus of the hardened shell. The double emulsion is formed by continuous feed of the fluids through the microfluidic device, using pressure pumps (Dolomite Microfluidics, United Kingdom). Subsequently, the capsules are produced through the polymerization of the acrylates using a UV-lamp (Sylvania, BL350) and filtered. The whole process is schematically shown in Figure 1.

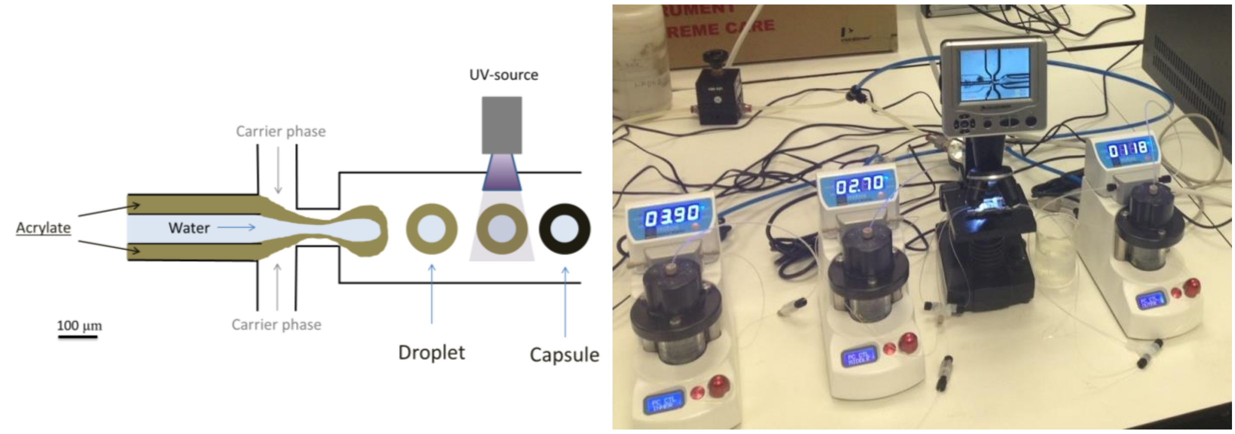

Figure 1 - Schematic representation of the production of microcapsules using microfluidics (left) and set-up of the experiments (right).

b. Characterization of the materials

We investigate the double emulsions with an optical microscope (OM) DM 2700 M (Leica, Germany) and the microcapsules formation with a scanning electronic microscopy (SEM, Phenon, Pro G2). To assess the thermal stability, the microcapsules were dried under vacuum for 2 days before the thermogravimetric analysis (TGA) using PerkinElmer STA6000 between 40 and 700 °C at a rate of 5 °C/min, under air atmosphere. Cement paste prisms are produce to explore the behavior of microcapsules after casting, using Ordinary Portland Cement (CEMI 52.5N), a water-to-cement ratio of 0.45 and 10 wt% of microcapsules.

3. RESULTS AND DISCUSSION

a. The formation of the double emulsion

The double emulsion typically formed on the microfluidic device is show on Figure 2, where the water-in-oil-in-water droplets are stabilized by the presence of PVA acting as a surfactant. The microfluidic device allows the production of monodisperse droplets in a more robust way then the other techniques used for the same purpose (e.g., emulsification polymerization). Moreover, by varying the flow rates is possible to tune the size and the shell thickness of the double emulsion, as shown in Figure 2.

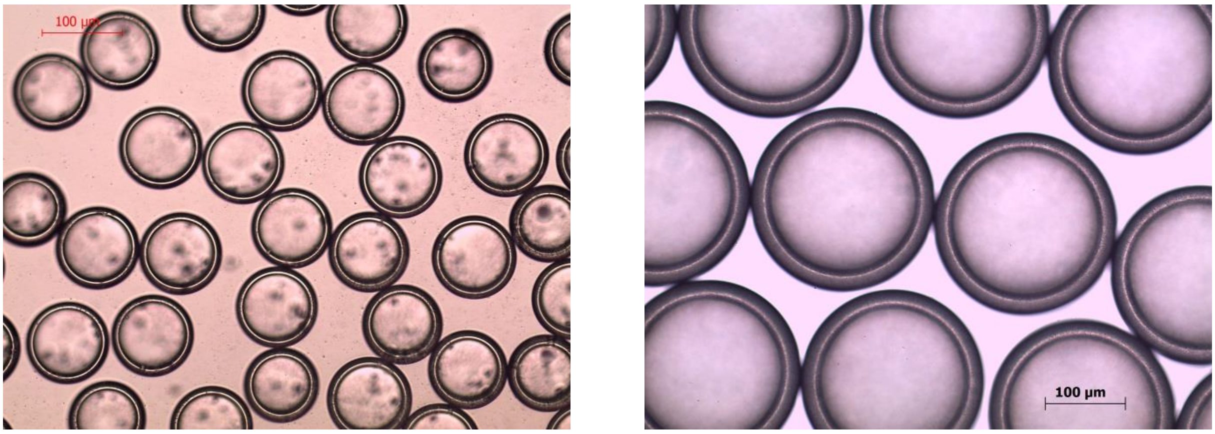

Figure 2 – OM images of double emulsion produced at the flow rate of 0.7-0.35-80 µL/min (left) and 5-6.7-67 µL/min (right), for the inner, middle and outer fluid, respectively.

b. Production and characterization of the capsules

During the formation of the capsules, the double emulsion is used as a template and the radical polymerization of the oily phase results in the formation of the polyacrylate shell. However, due to the heterogenous exposition of the capsules under the UV-light, the shell is currently forming dimples which, in some cases, lead to the formation of holes (Fig. 3). SEM images of the surfaces of cement paste containing microcapsules shows the survival of the capsules; moreover, it is possible to see debonded and ruptured microcapsules (Fig.3).

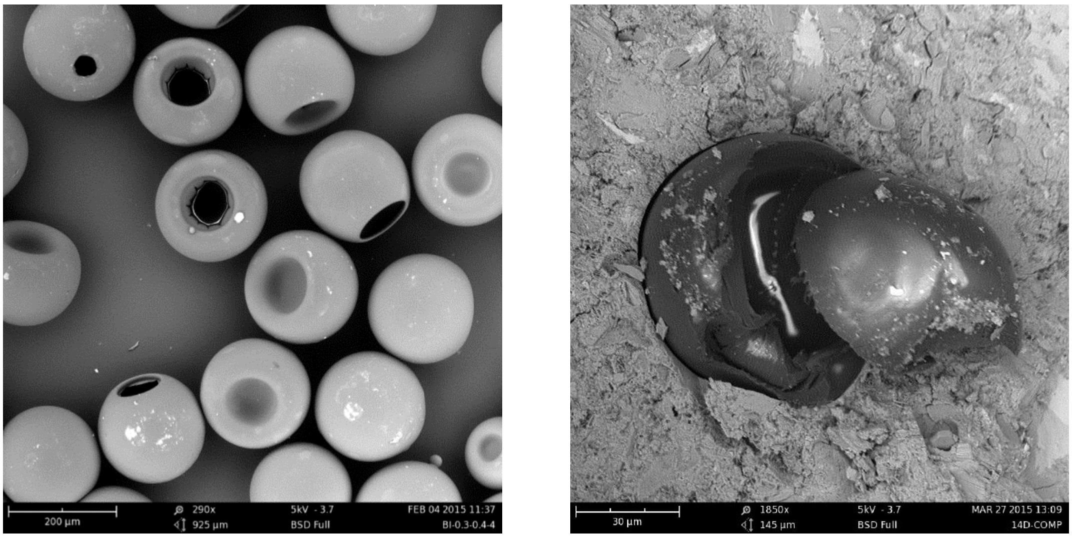

Figure 3 – SEM images of the microcapsules (*left*) and the casted broken capsule (*right*).

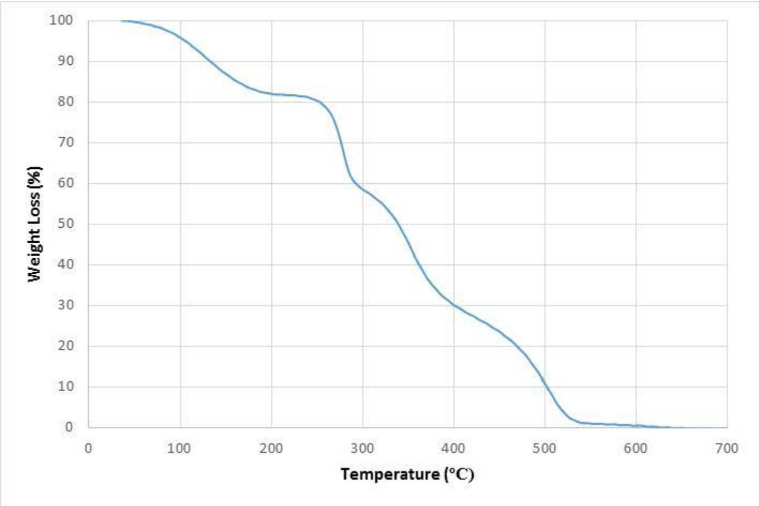

Figure 4 - TGA analysis of the microcapsules.

Thermogravimetric analysis of the microcapsules shows the mass loss between 70 and 200 ºC, corresponded to the evaporation of the water present inside of the capsules. The mass loss between 250 and 550 ºC corresponds to the decomposition of the acrylate shell. The mass loss around 18% is agreeing with the images of the SEM, where several capsules are with holes and therefore are not capable of retain water inside.

4. CONCLUSION

Microfluidics stands as a promising new technology for the production of microcapsules for self-healing concrete, where the size and the shell thickness of the capsules can be tuned. Initial results indicate the formation non-uniform capsules and thus, currently the system is being optimized.

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