Construction and Building Materials 184 (2018) 713–722

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Microfluidic fabrication of microcapsules tailored for self-healing in cementitious materials

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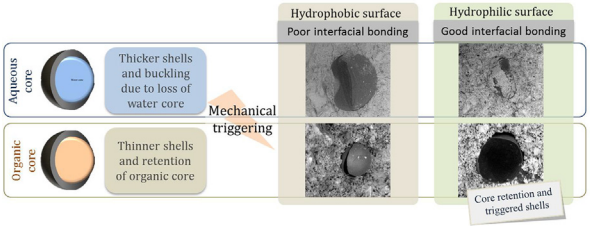
HIGHLIGHTS

- Aqueous and organic core were encapsulated using microfluidics.
- Retention of colloidal silica and organic phase was demonstrated.
- Microcapsules were functionalised to increase shell-matrix interfacial bonding.
- Core retention and hydrophilic surface facilitated physical triggering.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 February 2018
Received in revised form 20 June 2018
Accepted 2 July 2018

Keywords:
Cementitious materials
Self-healing
Mechanical triggering
Microcapsules
Microfluidics

ABSTRACT

Autonomic self-healing in cement-based infrastructure materials has recently emerged as a promising strategy for extending the service life of concrete infrastructure. Amongst the various self-healing systems being developed, the use of microcapsules has received significant attention partly because of its ease implementation. Up to date, microcapsules for self-healing applications have been mainly manufactured using bulk emulsifications polymerisation techniques. However this methodology raises concerns regarding shell dimensions and interfacial bonding. This study proposes for the first time the fabrication of microcapsules with tailored characteristics for mechanically triggered self-healing action in cement-based composites. For this, a microfluidic device was used to produce a double emulsion template for the formation of microcapsules, containing both aqueous and organic liquid core. In addition, a novel method has been proposed to functionalize the microcapsules' surface with hydrophilic groups in order to increase the interfacial bond with the cementitious host matrix. The core retention was studied using EDX and TGA, and their mechanical triggering was investigated via SEM of the microcapsules embedded in the cement paste. The results demonstrated the capability of microfluidics to produce microcapsules with liquid organic core, thin shell, hydrophilic surface and appropriate fracture strength for use in mechanically triggered self-healing of cementitious materials.

1. Introduction

Under service conditions, concrete structural elements develop microcracks which, with continuous environmental and mechanical loading, have the tendency to coalesce and form larger cracks. The latter create a preferential pathway for aggressive species (e.g. oxygen, CO_2, chloride ions, sulphates) to penetrate the concrete, reducing its alkalinity and generating fertile conditions for steel corrosion to initiate. The construction codes of practice generally treat material and structural degradation as inevitable events. The long-term material behaviour is largely overlooked and structural weathering is treated using expensive maintenance regimes. In the UK alone, repair and maintenance actions resulted in a cost of ~£50 billion/year [1]. In the United States, the cost for repair, rehabilitation, strengthening and protection of the concrete structures was estimated between $18 and $21 billion/year [2]. In addition, the associated costs for maintenance due to steel corrosion

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https://doi.org/10.1016/j.conbuildmat.2018.07.005
0950-0618/

reach $23 billion/year in the U.S. only [3,4]. Furthermore, indirect costs due to traffic jams and loss of productivity calculated through life cycle analyses can be more than 10 times the direct cost of maintenance and repair [5,6].

To overcome the limitations associated with crack propagation and maintenance actions, the concept of self-healing has emerged [7,8]. For self-healing, the formation of cracks is not problematic as long as it is counteracted by an autonomous process of healing the damage [9]. In other words, it relies on a self-initiated response of the system to detect and recover autonomically, without external interaction. A promising approach to achieve self-healing is the addition, during the mixing process, of microcapsules containing healing agent. Upon triggering, the shell releases the healing agent and the crack is then repaired, as shown schematically in Fig. 1. Capsule-based self-healing have been reported to successfully heal cracks up to 1 mm [10].

For this mechanically triggered self-healing, several microencapsulation techniques have been explored to produce aqueous or organic core materials, such as coacervation [11,12], in-situ polymerization [10,13–15] and sol-gel [16]. These liquid cores include organic precursor for polymeric healing [15–17], bacterial spores suspended in organic substract [10] and mineral healing agents [11–13,18,19]. However, the interfacial bonding between the shell and the cementitious materials is a concern, since it may lead to debonding of the capsules instead of rupture [20]. In general, a good interfacial bonding between a polymeric material and the cementitious matrix is ensured by the presence of hydrophilic groups, which are compatible with the water-based cementitious matrix [21–24]. In contrast, the formation of poly(urea-formaldehyde) (PUF) shell, for example, relies on the deposition of water-insoluble prepolymer in the oil/water interface which ultimately becomes highly cross-linked forming and encapsulating the core material [25]. Despite the presence of the hydroxyl, amino and carboxyl polar groups in the PUF shell, the interfacial bonding with the cementitious matrix may not be efficient and debonding has been observed [15]. Likewise, shell prepared with non-polar phenol-formaldehyde groups results in poor interfacial bonding and may debond upon crack formation [17]. Alternatively, coacervation and sol-gel reactions offer alternative routes to the production of microcapsules with compatible shell to promote the interfacial bonding via chemical reactions. This was confirmed by elemental analysis of the interface between the gelatine microcapsules, showing the presence of ettringite and calcium silicate hydrates (C-S-H) [18]. Similarly, EDX analysis suggested a chemical reaction between the silica capsules' shell with the matrix, resulting in a tight interface [26]. However, conventional bulky emulsification methodologies typically produce microcapsules with a wide range of sizes and shell thicknesses. Since the physical triggering is based on the dimensions of the shell, the variety of size and shell thickness results in poor control of the release of the healing agent.

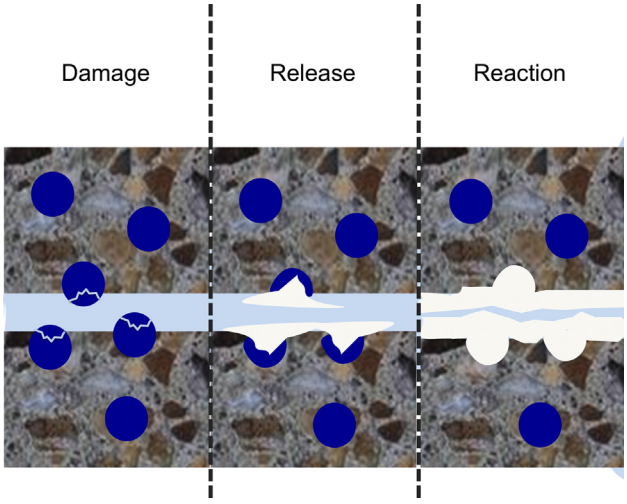

Fig. 1. Schematic of mechanically triggered capsule-based self-healing in cementitious matrix (Credit: Dr. Chrysoula Litina).

Although still unexplored for self-healing of cementitious materials, microfluidic encapsulation is a resourceful tool to produce monodisperse capsules with precise control over the core/shell ratio and high encapsulation efficiency [27,28]. Using the double emulsion template, a wide variety of shell materials can be explored, and the properties can be modulated to fine-tune payload, permeability and shell properties of the microcapsules [29,30]. The technique has also been reported to encapsulate materials with potential to be used as healing agent, such as such as amines for polymeric healing [27], biological cargo [31] and mineral agents [32]. Thus, this effective platform to produce core-shell structures can be used to investigate the importance of core retention and the interfacial bonding for physical triggering.

This work explores the microfluidic approach for production of microcapsules with polymeric shells encapsulating compounds for self-healing action in cementitious materials. Aqueous and non-aqueous compounds were encapsulated by an acrylate shell producing monodisperse microcapsules. The retention of colloidal silica, a mineral healing agent, and mineral oil within the resultant microcapsule is demonstrated using energy dispersive X-ray analysis (EDX) and thermogravimetric analysis. To enhance the interfacial bonding between the microcapsules and the cementitious matrix, the acrylate shell was functionalised with carboxylic groups which increase the hydrophilic nature of the shell. In addition, glass transition temperature, Young's modulus and tensile strength of the acrylate shell used of the production of the microcapsules, were investigated with respect to their compliance with the host matrix. The research focuses on the potential of this controlled emulsification process as a technique to generate microcapsules for the systematic investigation of capsule-based self-healing cement-based materials.

2. Materials and methods

2.1. Production of microcapsules

A complete set up of the microfluidics system is shown in Fig. 2a [33]. To produce the double emulsion template, a flow-focusing microfluidic device (Dolomite Microfluidics, UK) was used, as shown in Fig. 2c, d. In this emulsion, the compound to be encapsulated formed the inner phase whereas the polymeric shell, which was a photocurable oil, formed the outer phase. The former was injected through the capillary tube, while the photocurable oil (dispersed phase) was pumped through the central channel and the continuous phase flowed in the two side channels (Fig. 2d). The fluids met at the cross-junction, forming jets of the dispersed phase containing the inner phase as the fluids streamed into the main outlet channel. The fluids were injected using pressure pumps (Dolomite Microfluidics, UK) at typical flow rates of 2–6 μL/min, 2–7 μL/min and 50–80 μL/min for the inner, middle and outer fluids, respectively. For the aqueous core microcapsules, the double emulsion of water-in-oil-in-water (w/o/w) was formed with an inner aqueous solution that contained 5 wt% poly(vinyl alcohol) (PVA, MW 31000–50000, 98–98.8% hydrolyzed, Acros Organics) and 50 wt% colloidal silica (LUDOX HS-40, 40 wt% colloidal silica suspension in water, Sigma Aldrich). For the organic core microcapsules, the double emulsion of oil-in-oil-in-water (o/o/w) was formed with an inner fluid containing a mineral oil phase (light mineral oil, Sigma Aldrich). For the middle phase, two solutions were produced, BH and BI. The former, comprised of 50 wt% 1,6-hexanediol diacrylate (HDDA, Sigma Aldrich) and 50 wt% bisphenol A glycerolate dimethacrylate (BisGMA, Sigma Aldrich) whereas BI solution consisted of 50 wt% isobornyl acrylate (IBOA, Sigma Aldrich) and 50 wt% BisGMA. The solutions were mixed using a magnetic stirrer until a homogenous solution was achieved and followed by the addition of 1 wt% of photoinitiator hydroxy-2-methylpropiophenone (Sigma Aldrich). As outer fluid, 2 wt% aqueous solutions of PVA was used. To functionalise the surface of the microcapsules, an aqueous solution consisting of 5 wt% PVA and 1 wt% of acrylic acid (Sigma Aldrich) was used as outer fluid. The polymerisation of the shell took place using a UV-lamp (Sylvania, BL350) exposed over the collection tube shortly (Fig. 2b) after the formation of the double emulsion droplets