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Polymeric microcapsules with switchable mechanical properties for self-healing concrete: synthesis, characterisation and proof of concept

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Abstract

Microcapsules, with sodium silicate solution as core, were produced using complex coacervation in a double, oil-in-water-in oil, emulsion system. The shell material was a gelatin–acacia gum crosslinked coacervate and the produced microcapsules had diameters ranging from 300 to 700 μm. The shell material designed with switchable mechanical properties. When it is hydrated exhibits soft and 'rubbery' behaviour and, when dried, transitions to a stiff and 'glassy' material. The microcapsules survived drying and rehydrating cycles and preserved their structural integrity when exposed to highly alkaline solutions that mimic the pH environment of concrete. Microscopy revealed that the shell thickness of the microcapsules varies across their perimeter from 5 to 20 μm. Thermal analysis showed that the produced microcapsules were very stable up to 190 °C. Proof of concept investigation has demonstrated that the microcapsules successfully survive and function when exposed to a cement-based matrix. Observations showed that the microcapsules survive mixing with cement and rupture successfully upon crack formation releasing the encapsulated sodium silicate solution.

(Some figures may appear in colour only in the online journal)

Introduction

Microencapsulation of active compounds, either solid or liquid, has gained a lot of interest in the last two decades in a wide and diverse spectrum of industries and applications. The primary purpose of microencapsulation is to create a protective envelope for the core material to sequester it from the surrounding environment and keep it safe. For example, encapsulated living cells can be protected from the immune system [1] or probiotic bacteria can be protected in microcapsules during the production of dairy products as well as during their passage through the upper intestine system [2]. Encapsulation eases handling of materials by allowing for instance liquids to be handled as solids resulting in improved manufacturing processes as in the case of the food industry [3]. In industrial construction applications, microencapsulation has been used to protect phase change and thermal energy storage materials [4] as well as to produce hollow microspheres for air-entrained concrete with increased durability [5].

Synthesis of microcapsules can be modified accordingly to allow controlled release of active compounds, such as

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drugs, under environmental [6] or magnetic stimuli [7]. Controlled release triggered by pH changes is not only of interest in biomedical and pharmacological applications but also in reduction of coating corrosion [8]. The concept of pH sensitive microcapsules that release anticorrosive substances has expanded to construction materials. Recent studies report the production of pH sensitive microcapsules for use in concrete [9, 10]. Another release mechanism is the gradual decomposition of light sensitive microcapsules, for a variety of wavelengths, with many applications in cosmetics and agricultural industries [11].

The controlled release of the encapsulated materials is of particular interest in the field of self-healing materials. The development of microencapsulation for self-healing applications was first introduced in 2001 [12] and is one of the most studied self-healing concepts mainly within the fields of polymers and coatings. The most fundamental principle of self-healing via microencapsulation is that the microcapsules are homogeneously dispersed in the bulk volume of the host material and the release of their healing cargo is triggered by the formation of cracks that rupture their shell. Consequent chemical interactions between the encapsulated material(s) and the host matrix heal the crack restoring partially or fully the bulk material properties.

Microencapsulation production methods

The methods used for the preparation of microcapsules can be divided into physical, chemical and physicochemical techniques. Each method has advantages depending on the intended characteristics of the produced microcapsules. These include the size and shape of the microcapsules, the thickness of the shell and its mechanical properties. Selection of the most suitable production technique depends on multiple parameters. This includes the cargo material state (liquid or solid), type (organic or inorganic), miscibility as well as its chemical compatibility with the shell materials. The most common encapsulation techniques used in materials science are briefly discussed below.

Physical methods

With physical methods, the microcapsules are produced as a result of either a mechanical action (coating, drying) or a physical process (evaporation). The most reported physical methods in the literature are pan coating and spray drying.

Pan coating. Pan coating is one of the oldest techniques to encapsulate a component. It is used widely in the pharmaceutical sector mainly for the production of coated tablets. The cargo material in the form of pellets or tablets is placed in a rotating pan while the component that will form the shell is applied externally in liquid form via a high-pressure nozzle. The temperature is then raised resulting in the hardening of the shell which eventually seals the cargo material. An alternative to the high-pressure nozzle is to dry coat the cargo material. In this case the temperature elevation

will result in melting the dry shell component which will harden when the heat source is removed. Hardening of the shell material using an externally fed chemical activator is a third alternative.

Pan coating results in coated particles of high granularity, with average sizes at the best case slightly smaller than 1 mm but most often larger than that. The issue of granularity renders this method unattractive for applications where the size of encapsulated additions can affect the mechanical properties of materials and structural components. Recently two studies reported the use of pan coating to encapsulate active compounds for the production of self-healing concrete [13, 14]. Nonetheless, in both studies, issues associated with the thickness and integrity of the shell were reported.

Spray drying. Spray drying is an established encapsulation technique and widely used especially in the field of food technology. In this method, the core material is dispersed in a polymer solution to form an emulsion which then is fed to an atomisation head. This process results in the formation of droplets which are rapidly dried as the cloud of droplets passes through a controlled temperature chamber. The dehydration caused by the drying results in the formation of a hardened outer sell that sequesters the core material. Depending on the type of the initial emulsion, the type and concentration of the materials used as well as the varying manufacturing conditions the size of the produced microcapsules range from few microns up to about 4 mm. This production technique has been used to produce microcapsules for construction oriented applications, mainly for the encapsulation of phase change materials [15]. More recently, spray drying was used for the production of pH sensitive microcapsules for self-healing concrete [9].

When successful, the spray drying technique produces microcapsules with a uniform size distribution. However, undesirable agglomerated and uncoated particles have been reported as part of the process [16]. In addition, depending on the manufacturing conditions and the materials used, spray drying can lead to production of microcapsules with increased porosity [17].

Chemical methods

Chemical microencapsulation techniques are based strictly on chemical interactions between the materials used. These chemical interactions result in polymerisation or polycondensation of substances that form the wall of the formed microcapsules. The most common types of chemical techniques used are the interfacial and *in situ* polymerisation methods.

Interfacial polymerisation. In this technique microcapsule formation results from the rapid polymerisation of hydrophilic and lipophilic monomers at the interface of an oil-in-water emulsion. Typically, a multifunctional monomer is dispersed in the core material and this solution is emulsified in an aqueous phase, which contains a reactant to the monomer. Rapid polymerisation occurs at the interface of the two

distinct emulsified phases and the microcapsules are formed. Usually emulsifiers are also added into the system to ensure the proper dispersion of the formed particles. The main materials used for the formation of shells in interfacial polymerisation are polyester, polyamides and polyurethane. Although this method can be used to fabricate microcapsules with sizes in the range of $100\,\mu$m, the vast majority of commercial interfacial polymerisation processes produce microcapsules in the range from a few microns up to around $50\,\mu$m. In construction related materials, interfacial polymerisation has been used to encapsulate phase change materials [18].

In situ polymerisation. The difference between *in situ* and interfacial polymerisation is that in the former no reactants are present in the core material. Therefore, instead of the polymerisation occurring at the interface between the continuous phase and the core material, the polymerisation takes place in the continuous phase. *In situ* polymerisation is typically controlled by pH levels. Addition of a strong acid to reduce the pH triggers polycondensation. The latter yields crosslinked resins that gradually precipitate at the interface between the oil droplets and the aqueous phase. By controlling the temperature of the emulsion, the deposited crosslinked materials harden over time thus forming the microcapsules. Typical materials for *in situ* polymerisation are aminoplast resins such as urea–formaldehyde, melamine–formaldehyde, urea–melamine–formaldehyde or melamine–formaldehyde polymers modified with resorcinol. Similar to interfacial polymerisation, the production of microcapsules larger than $100\,\mu$m is possible with *in situ* polymerisation. However, the vast majority of commercial processes involving this technique as well as the majority of the studies reported in the literature used *in situ* polymerisation to produce microcapsules with average diameters from a few microns up to 100 microns. The size and morphology of the produced microcapsules depends on a wide range of factors such as the materials used, the level of the required acidic conditions, the agitation speed and the temperature used to promote hardening of the shell. Historically, this method was used in many industrial applications including carbonless paper, pesticides and cosmetics. More recently, *in situ* polymerisation became the primary method used to encapsulate healing compounds for self-healing polymers where urea-formaldehyde was used to microencapsulate adhesives [19]. Construction applications include the encapsulation of phase change materials [15] as well as the encapsulation of bacteria that promote self-healing in concrete [20].

Although chemical methods for microencapsulation are very popular and have been used widely in many industrial sectors, they have some drawbacks. Both methods require extreme pH conditions. To maintain these conditions either very strong solvents are required, like cyclohexane, or very strong acids, like hydrochloric acid. In both cases the required polymerisation catalysts, such as isocyanates, formaldehyde and resorcinol, are very toxic chemicals. Chemical scavengers can be used to reduce the amount of free unreacted harmful chemicals, but this not only requires modifications in the production process but also increases the cost of the production. Moreover, both chemical methods are known to be very successful and effective in producing microcapsules with diameters less than 100 microns. This can be a problem when the microcapsules are intended to be used in bulk materials. The smaller their size the larger the volume fraction would be necessary to deliver the desirable results. In construction, besides the cost concerns, the margin of tolerance for harmful and toxic substances is very small, raising scepticism over the use of chemical methods for producing microcapsules.

Physicochemical methods

The physicochemical methods for producing microcapsules are based on the formation of the microcapsule wall from preformed polymers either natural or synthetic.

Ionic gelation. Ionic gelation is a very simple and fast encapsulation technique which is very popular in pharmaceutical and biomaterial based applications as well as in the food industry. The fundamental principle of this method is the fact that polyelectrolytes can undergo rapid polymerisation when they come into contact with certain multivalent ions, such as Ca^{2+}, Al^{+3} and Ba^{2+}. The polymerisation is the result of ionic exchange between the polyelectrolyte and the gelation catalyst, which is usually a solution that contains the required multivalent ions. Alginate is the most widely used material in this technique and is used mainly to encapsulate active ingredients such as cells and proteins for biomedical applications [21] or probiotic bacteria for the food industry [22]. This method has not been investigated for the production of microcapsules for construction and structural applications. However, recently some preliminary studies reported the use of alginate to encapsulate corrosion inhibitors [10] and bacteria for self-healing concrete [23–25].

Ionic gelation suffers from two main drawbacks. Firstly, is not easy to produce microcapsules with average diameter less than $500\,\mu$m. Typically, the size of the capsules produced from this method is close to 1 mm. The second issue is that the produced hydrogels are generally very porous and permeable. This can be beneficial in some applications, such as in drug or flavour delivery, but in construction related applications this can be problematic.

Complex coacervation. Coacervation is the process during which a macromolecular lump (coacervate) forms as a result of phase separation in an initially homogeneous polymer solution. In complex coacervation two oppositely charged polymers in aqueous solution interact forming a new liquid phase consisting of macromolecular coacervates. The phase separation in this case is between polymer-rich and polymer-poor phases. The formed coacervates gradually migrate to the interface of the droplets thus forming the microcapsule shell. Complex coacervation can produce both mononuclear or
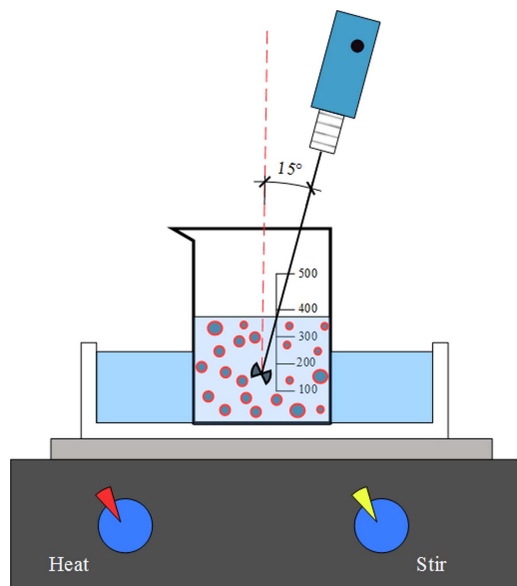
Figure 1. Schematic showing the equipment configuration for the production of the microcapsules.

polynuclear microcapsules [26]. The probability of this phenomenon to occur depends on a range of factors including the size of the formed droplets, the core/shell ratio and the type of emulsifiers used. The most widely used combination of complementary polymers in complex coacervation is gelatin and gum arabic. This technique is known to produce microcapsules ranging from 10 to 1000 μm and has been used widely in pharmaceutical/cosmetic applications, the food industry and the textile sector. Recent studies used complex coacervation to encapsulate phase change materials in a gelatin–gum arabic polymeric shell [15]. The greatest advantage of complex coacervation is that it utilises environmentally friendly materials, usually of food grade, in contrast to toxic and dangerous chemicals used in other techniques (e.g. melamine, formaldehyde, isocyanates). In addition, due to its versatility complex coacervation allows process adjustments to be made during the encapsulation procedure. If for example during the wall formation step, the pH conditions are not correct, the batch can be reheated, which will re-dissolve the coacervate. The pH can then be adjusted accordingly allowing for batches to be corrected, resulting in less wastage. This *in-process intervention* cannot be done with the other techniques discussed above.

In this study, complex coacervation is used for the production of polymeric microcapsules that contain liquid sodium silicate. So far this microencapsulation technique has not been used to produce microcapsules for self-healing applications. Sodium silicate was selected as the healing compound due to its compatibility with cement based materials. When in contact with the calcium hydroxide present in concrete, sodium silicate interacts chemically to produce crystalline and amorphous products that can promote healing. Recent results showed that liquid sodium silicate considerably improved the self-healing efficiency in cracked mortar specimens [27]. Recent attempts to produce microcapsules for cement-based materials include the use of

polymeric microcapsules for encapsulating sodium silicate [28, 29]. However, the available data on the physical characteristics, the mechanical properties, the functionality and the survivability of the produced microcapsules is very limited. In addition, these studies [28, 29], used *in situ* polymerisation for the production of microcapsules. The strong acidic conditions associated with *in situ* polymerisation resulted in the polycondensation of the sodium silicate. Thus, the latter is encapsulated in a solid state.

The synthesised microcapsules presented here were found to be very stable at dormant conditions and had excellent resistivity in highly alkaline environments. The microcapsules proved to be strong enough to sustain cycles of drying and rehydration without any damage to the shell or core material.

## Materials and experimental methods

Materials

All chemicals were used as received unless otherwise specified. Pig gelatine (280 Bloom) was purchased by Weishardt Group, gum acacia (Instant gum AA) was purchased by Nexira Inc. and mineral oil (SipMed 68) was purchased by Brenntag NV. Reagent grade sodium silicate powder, sodium hydroxide solution (30%), acetic acid solution (20%) and grade-I glutaraldehyde (50% in H_2O) solution were purchased by Sigma Aldrich chemicals. For the proof of concept experiments cement CEM-I 52.5 was used.

Chemical structure and thermal stability

The chemical structure of the produced microcapsules was characterised by mid-infrared Fourier transform infrared spectroscopy (FTIR) whereas their thermal stability was assessed with thermogravimetric analysis (TGA). FTIR measurements were taken at ambient temperature (21 °C) using Perkin Elmer Spectrum 100 performing 16 scans per band point. TGA experiments were performed with a Perkin Elmer STA 6000 analyser heating the samples up to 260 °C at a rate of 5 °C min^{-1}.

Particle size distribution, morphology and shell thickness

Microscopy techniques were used to study particle size distribution, shape, morphology and shell thickness of the microcapsules. For this purpose, a Leica DM2700 upright optical microscope with an attached fluorescent cube and a 5 kV accelerating voltage high resolution scanning electron microscope (SEM) were used. The microcapsule morphology was examined in both hydrated and dried states using the optical microscope. Depending on the test type, all the microcapsules were mounted on either glass slides or aluminium stubs. For the shell thickness measurements, the microcapsules were placed on an aluminium stub and left to dry in vacuum for 24 h. Then they were carefully sliced using a surgical knife.
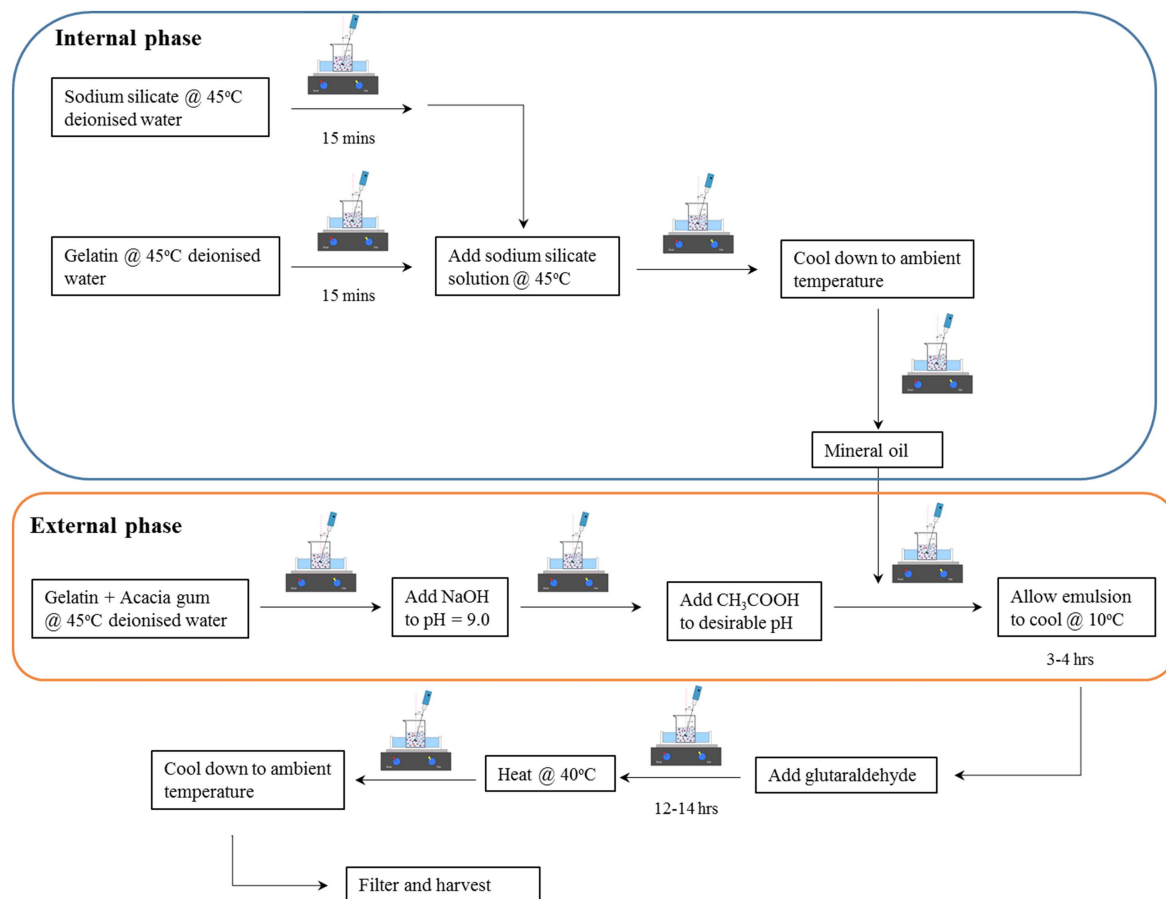
Figure 2. Flow chart of the processes involved in the production of the gelatin/gum shell microcapsules enveloping sodium silicate solution.

Survivability in alkaline environment

Since the microcapsules are intended for use in cement based composites which are known for their highly alkaline environment (pH ⩾ 11), it was very important to verify that the produced microcapsules were stable in such environments. Microcapsule survivability was investigated in a simulated concrete environment. For this purpose, an alkaline sodium hydroxide solution in deionised water was used. The pH was adjusted by gradual addition of 10 M sodium hydroxide.

Micromechanical analysis

Micromechanical analysis was performed on the shell material using a Dynamic Mechanical Analyser (Perkin Elmer DMA-8000). Experiments were performed using thin strips (2.5 × 7 × 11 mm) of crosslinked shell material. The shell material produced by crosslinking gelatin and gum acacia producing a thick slab of polymerised gel. The strips were cut from the fully saturated gel using a surgical knife and were loaded in tension at a frequency of 2 Hz. The temperature spectrum of the tests was between 22 °C and 80 °C at a rate of 2 °C min^{-1}.

Elemental analysis (EDX)

All the EDX discussed here was performed using a Nova nanoSEM 450 equipped with a Bruker Quantax Xflash 6/100 EDX detector. All SEM–EDX samples were coated with platinum and examined under a 10 kV accelerating voltage.

Production of microcapsules

Figure 1 shows the experimental set up used to produce microcapsules. A 600 ml beaker, immersed in a water bath, was used to produce the emulsion. The beaker-water bath system was placed on a hot plate. A mechanical stirrer carrying a four blade Rushton turbine was used to stir the emulsion. The stirrer operated at an angle of 15° to the vertical axis.

The microcapsules were produced by mixing together two separately prepared phases. The external phase, that formed the shell of the microcapsules, and the internal phase, which represents the cargo material. To prepare the external phase, gelatine and gum acacia were dissolved in deionised water at 45 °C, under stirring, taking care to avoid lumps of undissolved material. Sodium hydroxide was then added with a pipette to adjust the external phase to pH 9 to ensure the
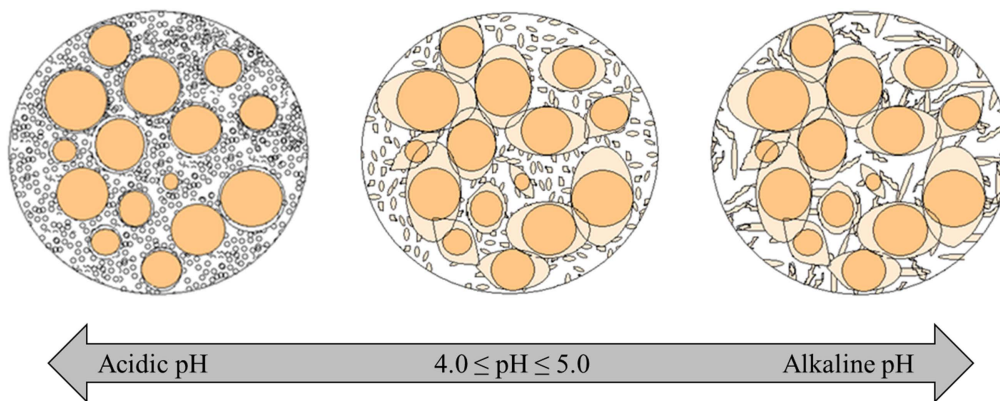
Figure 3. The effect of the external phase pH on the morphology of the formed microcapsules.
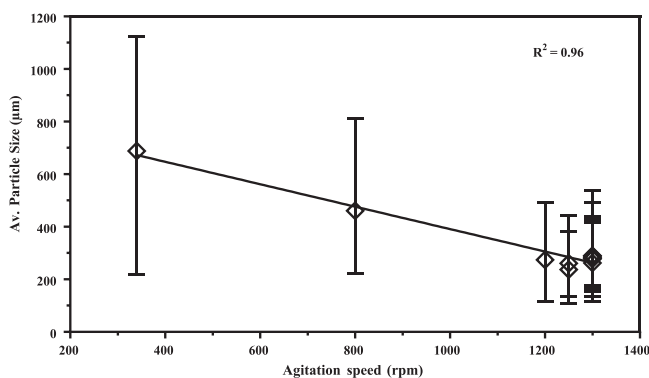

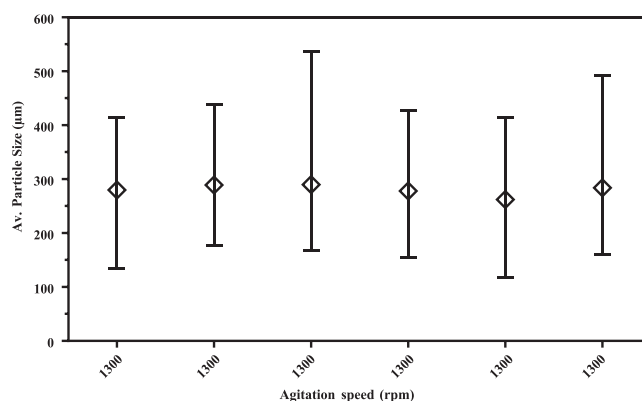**Figure 4.** Microcapsules' size variation with increasing agitation speed during manufacture.

Figure 5. Repeatability of the proposed method at an agitation speed of 1300 rpm.

Figure 6. Microcapsule average size variation with agitation time at a speed of 1300 rpm.

charge on the gelatine is above its isoelectric point and to aid the dissolution process. The external phase was left until all material had dissolved and there was no trace of particulate matter. Then, acetic acid was added slowly to the target pH each time. Different pH values influence the size and morphology of the microcapsules. The addition of acid resulted in localised changes to solution opacity as the charge on the gelatine polymer shifts to cationic. At this point, the coacervate phase started to form due to the electrostatic interaction between the anionic gum acacia and the cationic gelatine. When the target pH was achieved, droplets of coacervate were formed and dispersed within the water phase. At this stage, the bulk aqueous phase was cloudy in appearance.

For the production of the internal phase, initially gelatine was added to de-ionised water at 45 °C, under stirring, with the gelatine powder poured into the vortex to prevent lumps forming. Here gelatine was used as an emulsifier since the utilisation of other chemical emulsifiers (e.g. spans/tweens) would affect the proper deposition of the coacervate. Gelatine was left to dissolve for 15 min, until the solution was clear and free of particulate matter. Temperature was kept constant to prevent cooling that would lead the gelatine forming a gel. At a different beaker sodium silicate was added to deionised water at 45 °C, under stirring, with the sodium silicate powder
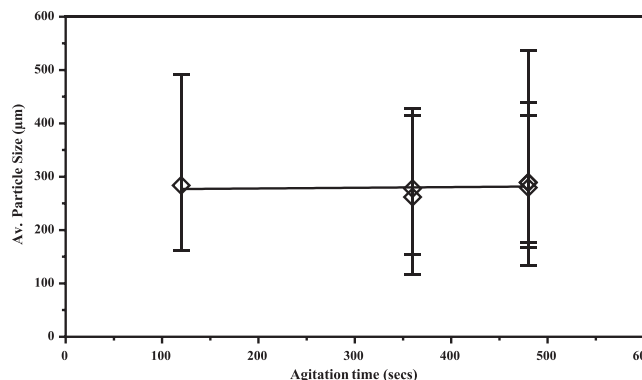
poured into the vortex to prevent lumps forming. The solution was left to dissolve for 15 min, until the solution was clear and free of particulate matter. With the temperature of the gelatine solution kept at 45 °C, the sodium silicate solution was added to it slowly under stirring. Then, the new solution was allowed to cool down to ambient temperature under stirring.

To prepare the capsule internal phase it is critical to form a water in oil emulsion (w/o). For this purpose, the combined
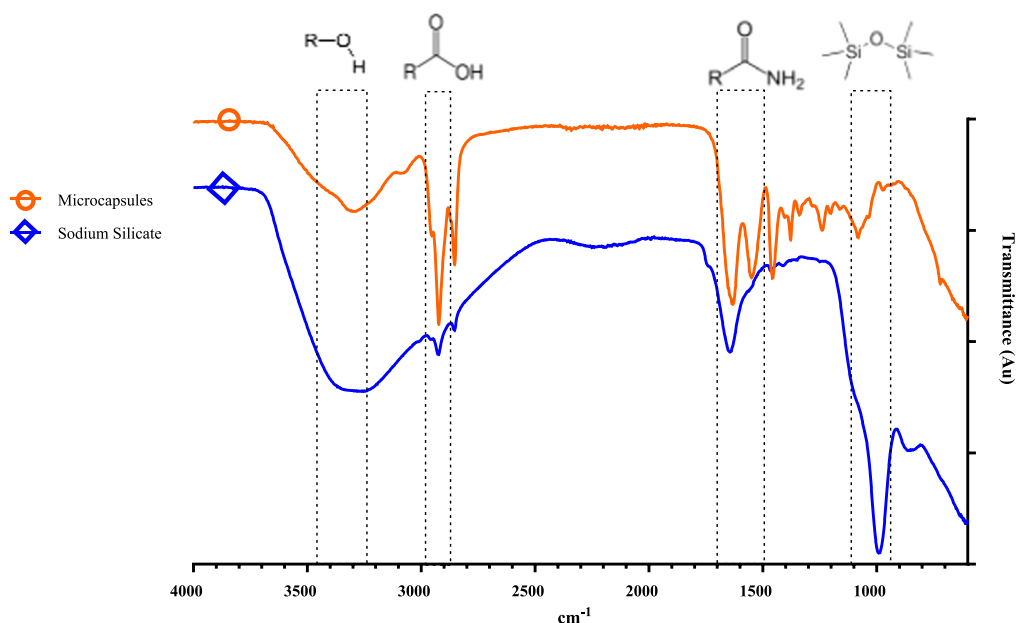
Figure 7. FTIR spectra for the microcapsules with sodium silicate and for pure sodium silicate solution.

gelatine-sodium silicate solution was added slowly to chilled mineral oil under high speed stirring. The quality and stability of this emulsion is absolutely critical. This can be easily checked by taking a small sample of the emulsion in a pipette and dropping it into a small clean beaker containing deionised water. If the droplet remains cohesive, then it is confirmation that a w/o emulsion has been achieved. If the droplet immediately disperses into the aqueous phase, the emulsion has inverted and is an oil in water (o/w) emulsion. The addition of an o/w emulsion to the external phase will result in a failed encapsulation.

Once the appropriate w/o emulsion was achieved, it was then added to the bulk aqueous external phase solution. The w/o emulsion should remain as water immiscible droplets. The shear forces from the propeller can break down some of the droplets. This could lead to small quantities of the sodium silicate to escape from the emulsified internal phase which in turn will result to a slight rise in pH. It is apparent that a significant rise in pH would point to the release of a significant quantity of the active compound. This would signal that the vast majority of the formed droplets were destroyed during agitation.

The positioning and the angle of the stirrer are very important parameters. The goal is to create a high shearing area between the walls of the vessel and the stirrer. This area will control the particle sizing. As most internal phases are lower in density than water, the tendency to float to the surface must be prevented. There must be sufficient turbulent flow to prevent this, and radial flow to achieve the breakdown of the internal phase into the desired target particle size range.

The target particle size was achieved by adjustment of the stirrer speed. A careful balance between radial shear and turbulent flow was required. Any areas suffering from reduced agitation can lead to the escape of the active material from the emulsion and hence to an unsuccessful procedure.
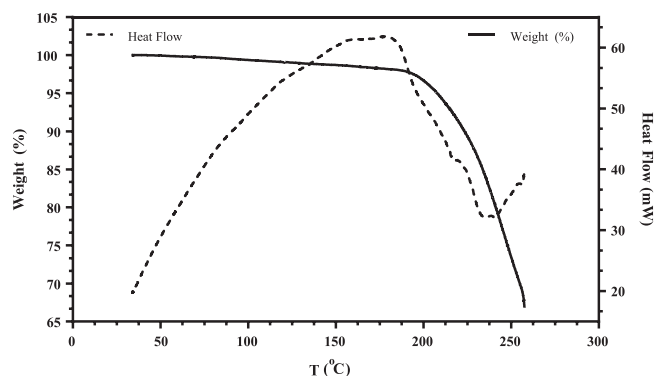

Figure 8. Weight loss and heat flow curves for microcapsules under thermogravimetric analysis.

Frequent sampling and microscopic evaluation was performed to ascertain whether the appropriate particle size had been achieved. Once this confirmed, the vessel was then allowed to cool slowly to 10 °C over the course of 3 to 4 h. As the batch cooled, the solubility of the coacervate phase decreased and the viscosity of the external phase solution increased. The coacervate complex begun to deposit at the interface of the oil droplets and the bulk aqueous phase, until a continuous wall or shell was formed.

The critical temperature for the wall formation is approximately 26 °C with porcine sourced gelatine. When the temperature of 10 °C was reached a quantity of glutaraldehyde was added, crosslinking the primary amine groups in the lysine groups on the gelatine polymer. The emulsion was left stirring overnight. The following day, the batch was heated to 40 °C, speeding any unreacted crosslinking and driving some of the water out of the capsule walls, resulting in a denser coacervate membrane around the internal phase droplets. Once cooled to ambient, the capsules were filtered, washed with deionised water and re-filtered, before being

(a)   (b)
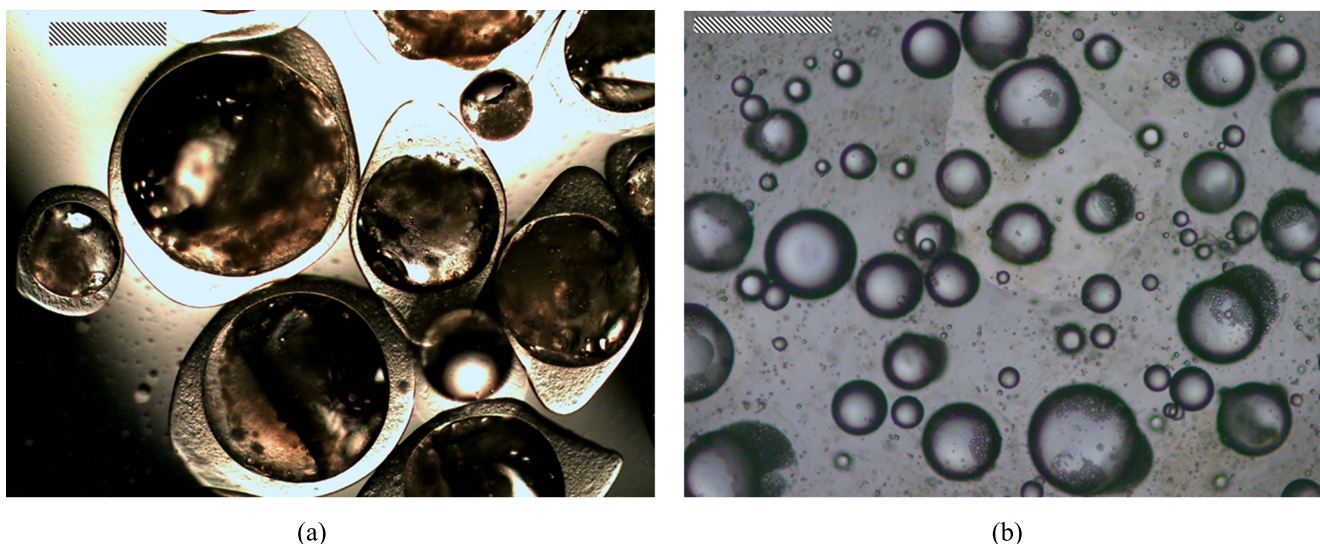
Figure 9. Optical microscope image of the produced microcapsules: (a) larger microcapsules with the characteristic 'rugby-ball' shape and (b) smaller more spherical microcapsules (Scale bars correspond to 500 μm).

dispersed in the preservative solution (grade-I glutaraldehyde) to keep the capsule suspension homogenous. Figure 2 illustrates in a flow chart the processes involved in the production of the microcapsules carrying sodium silicate.

The cooling stage, which controls the deposition of the coacervate that forms the wall, requires careful control. Cooling too fast causes the coacervate phase to wrap around the emulsion droplets in an uncontrolled manner, leading to uneven wall formation and possibly permeable capsules. Cooling too slowly may allow the active material to leach into the bulk aqueous phase, disrupt the pH and prevent coacervation and wall formation.

Similarly, the pH of the external phase plays an important role on the morphology of the formed coacervate. As the coacervation process relies on naturally derived raw materials, some batch to batch variation is inevitable. The morphology of the coacervate is also influenced by concentration/dilution and the surface area of the internal phase oil droplets. If the pH is too alkaline, long narrow 'plank-like' strands of coacervate can form, this displays poor deposition and final wall quality. If the pH is too acidic, tiny spherical droplets of coacervate form, which can lead to limited deposition of coacervate and yields final capsules with very thin walls. Intermediate pH yields an elongated oval coacervate morphology. Figure 3 illustrates the differences on the produced microcapsules with varying pH.

Results and discussion

Particle size distribution and repeatability

Particle size distribution was calculated using image analysis on microscopic images obtained from samples taken from 11 different batches. To investigate the effect of the agitation speed on the size of the produced microcapsules, different
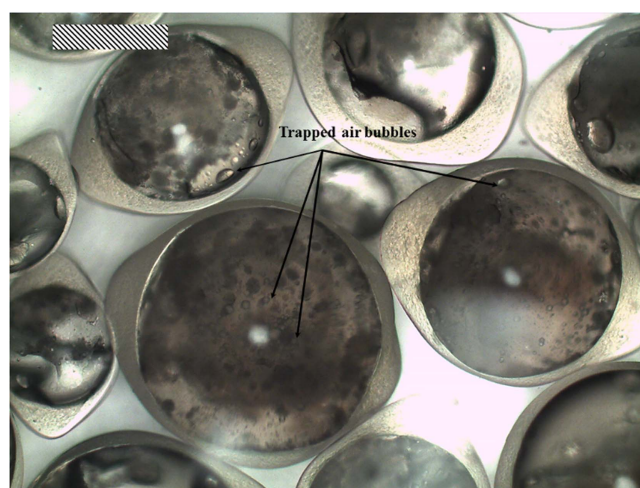

Figure 10. Typical brightfield optical microscope image showing the air bubbles trapped in the nucleus of the microcapsules. (Scale bar corresponds to 500 μm).

levels of stirring speeds were investigated. Figure 4 shows the particle size variation with increasing agitation speed.

Following the trends observed in other microencapsulation techniques, variation of the agitation speed of the emulsion has a profound effect on the size of the formed microcapsules. High agitation speeds resulted into breaking down the oil phase into much smaller droplets and eventually into smaller microcapsules. Interestingly, at low speeds not only the average size of the microcapsules is large, but also the particle size distribution is rather wide. The size distribution becomes narrower with increasing speed. In terms of repeatability, the method proved very robust as illustrated in figure 5. No significant differences were observed at either the average size or the range of the produced microcapsules.

Similarly, agitation time did not seem to have an effect on the produced microcapsules. In this study three different
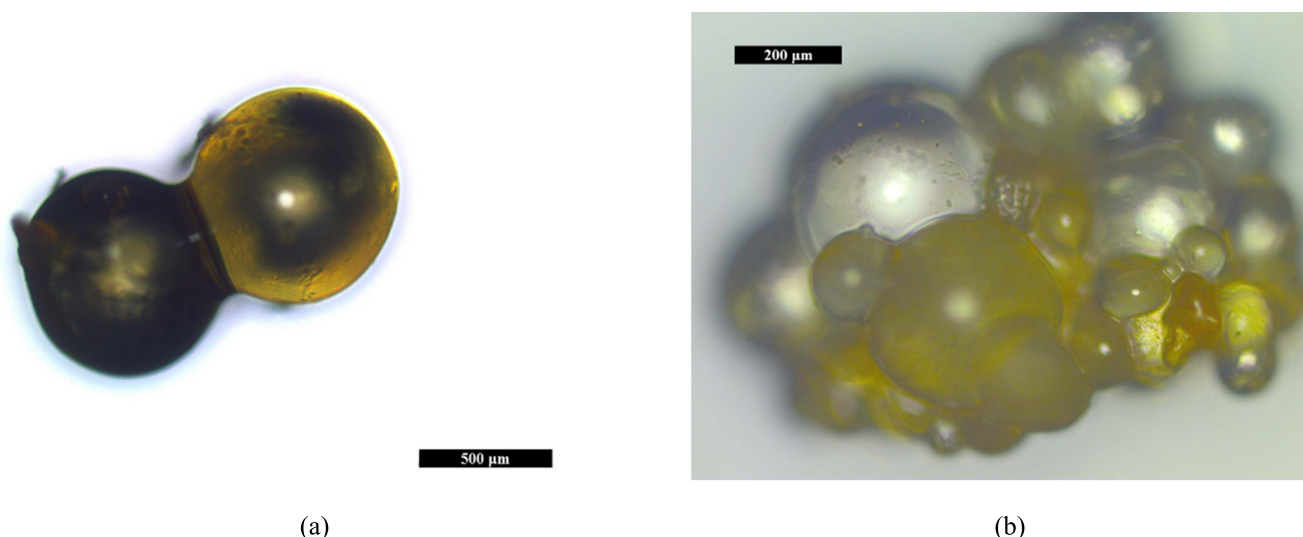
Figure 11. (a) A pair of dried microcapsules and (b) agglomerated dried microcapsules.
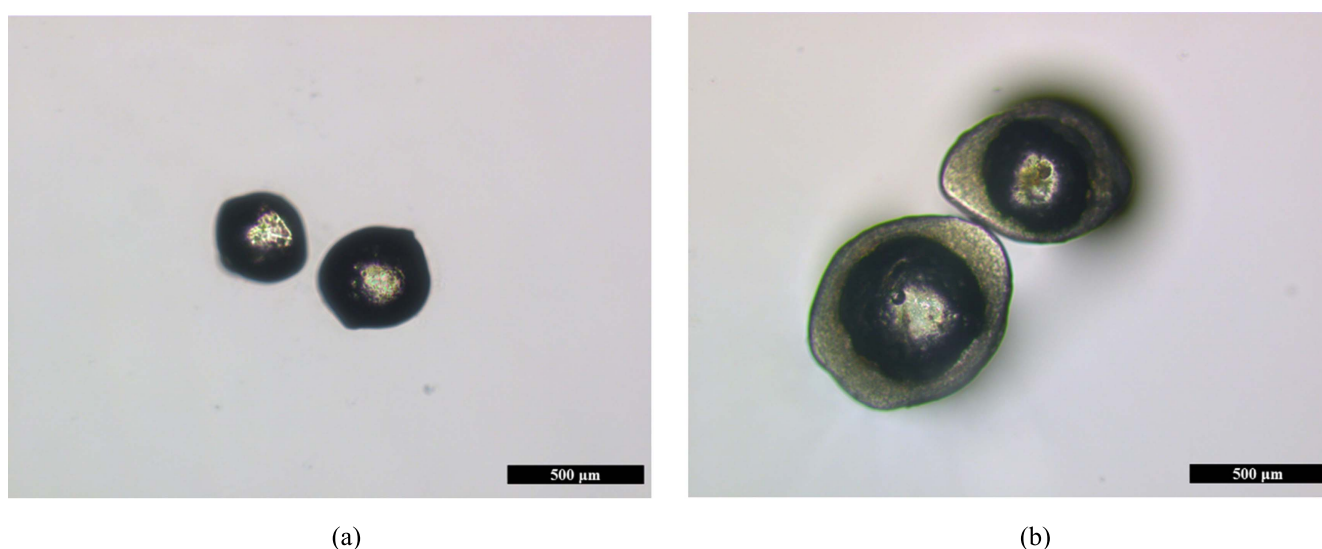
Figure 12. Microcapsules at: (a) dry state and (b) saturated state.

agitation times were investigated: 120, 360 and 480 s. As figure 6 shows, the average size of the formed microcapsules is a function of the agitation speed rather than the mixing time.

Chemical structure and thermal stability

Figure 7 shows the FTIR spectra of pure sodium silicate and encapsulated sodium silicate.

The spectrum of sodium silicate consists of a broad band at around $3400 \, \text{cm}^{-1}$ and a peak at around $1650 \, \text{cm}^{-1}$ that corresponds to an O–H absorption band. The asymmetric stretching vibration of Si–O–Si bonds is verified by the observed peaks between 980 and $1100 \, \text{cm}^{-1}$. On the other hand, acacia gum as a polysaccharide with free carboxyl groups gives a negative charge on the molecule. In the spectra obtained for the microencapsulated sodium silicate, the large

peak formed at about $2900 \, \text{cm}^{-1}$ is ascribed to the occurrence of carboxyl (COOH) groups from the acacia gum. This is an indication that not all the COOH groups were involved in the complex coacervation process. However, in the region of about $1500–1700 \, \text{cm}^{-1}$ characteristic amide peaks were observed. This verifies the formation of the polymeric coacervate, since during the complex coacervation process, the COOH groups of the polysaccharide (acacia gum) interact with the amine groups of proteins existing in the gelatin to form a crosslinked complex that contains amides. Microcapsules also demonstrate the characteristic peak attributed to Si–O–Si bonds in the region of $1000–1100 \, \text{cm}^{-1}$. Figure 8 shows the thermogravimetric test results on a sample of dried microcapsules.

The results show that the microcapsules are very stable at temperatures below $100 \, °\text{C}$ with almost negligible change in their weight. Rapid thermal degradation of the microcapsules

(a)

(b)
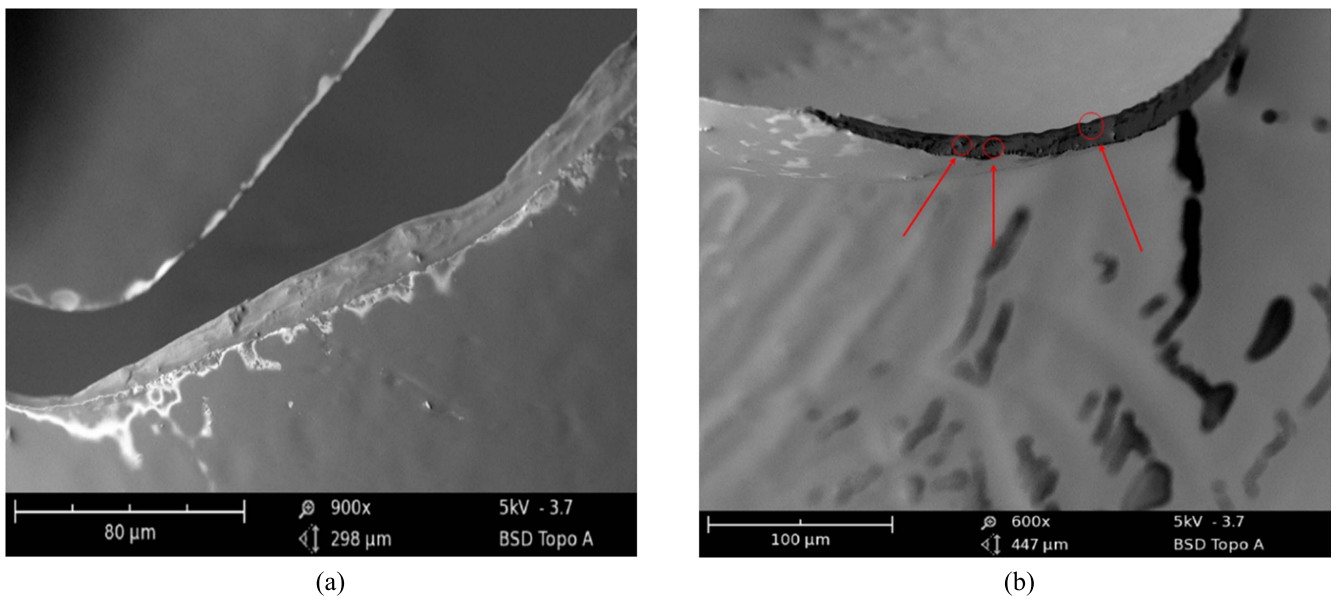
Figure 13. Characteristic SEM images of microcapsules' shell sections: (a) dense homogeneous section of the microcapsules shell and (b) microcapsule shell section with red circles and arrows indicating the location of the pores.

Figure 14. Microcapsules exposed to different pH levels.

began at 190 °C. These findings indicate that the microcapsules will be able to survive the temperatures that develop during the setting of concrete due to cement hydration. These temperatures can vary from ∼40 °C to ∼80 °C depending on the application and the type of concrete.

Microcapsules' morphology

As discussed earlier, when harvested from the reaction vessel, the microcapsules are filtered and stored in glass beakers in solution. At this stage their shell is swollen and the microcapsules have a characteristic 'rugby-ball' shape (figure 9(a)).

This shape is a result of the turbulent flow conditions of stirring during the wall formation stage. The 'leading edge' and 'trailing edge' have slightly more wall material than across the diameter at a 90° angle. However, this characteristic shape of microcapsules was mainly evident in larger microcapsules. As the agitation speed during production increased alongside with a reduction in the pH of the emulsion, the resultant microcapsules became more spherical (figure 9(b)).

Due to the complex coacervation process, it has been reported that coacervate deposition during shell formation can bring together more than one oil droplets [26]. Formation of multinuclear microcapsules was not observed in this study. However, the turbulence during stirring created several air bubbles in the solution which in many cases agglomerated with the oil droplets and together were encapsulated (figure 10). Entrapment of air pockets was evident in both large and small microcapsules.

When left to dry, the microcapsules lose water from their outer shell. The shell shrinks gradually and the 'rugby-ball' shape becomes more spherical. When dried, the microcapsules tend to coalesce and stick together (figure 11). Their separation at this point without damaging them is almost impossible.

The stability after the drying process was tested both at ambient conditions (figure 11(b)) and at 50 °C (figure 11(a)). The latter was selected as a temperature close to the one that develops during the hydration and setting of cement. In both drying procedures, the microcapsules were stable and no disintegration, damage or collapse was noticed. Moreover, upon rehydration the microcapsules undergo swelling and switch back to their original hydrated shape (figure 12). From dried state to swollen/saturated state the microcapsules remain intact. This indicated that their shells are hard enough to sustain this process.

Shell thickness and survivability

Images obtained from the SEM showed that the shell of the microcapsules is very dense and homogeneous (figure 13). A few pores were observed scattered across the thickness of the wall. The homogeneity and porosity of the shell thickness was not found to be affected by the size of the microcapsules. The microscopic images of the hydrated microcapsules (figure 10) reveal that the shell thickness of the particles varies and is not uniform around their perimeter due to the 'rugby-ball' effect. This was also observed in dried microcapsules. The thickness of the shell varies between 5 and 20 μm around the periphery of the microcapsules. It is plausible that the thicker parts of the dried shell correspond to the locations of the leading and trailing edges of the hydrated particles.

The survivability of the microcapsules in high pH solutions mimicking concrete environment was found to be very good. Three different stock solutions were prepared with pH values of 11.5, 12.5 and 13.5 and both dry and hydrated microcapsules were exposed to these solutions. The stock solutions were prepared by adding NaOH dropwise in deionised water under continuous agitation. Figure 14 shows
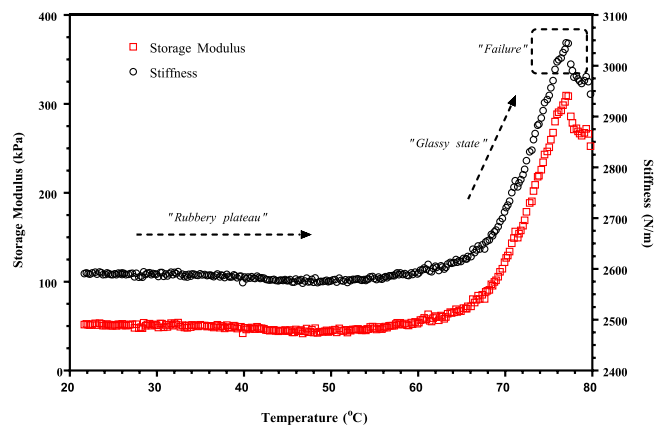
Figure 15. Stiffness and storage modulus evolution with time for the microcapsules' shell material.

dried microcapsules before exposure to increasing pH levels and after 60 days of conditioning in the highly alkaline environment.

Both types of microcapsules (dried and hydrated) swelled when exposed to the high pH solutions but they kept their consistency and morphology. No damage was observed even after being exposed to high pH environment for two months. The observed swelling took place within the first five minutes of exposure.

Micromechanical analysis

In dynamic mechanical analysis (DMA) an oscillatory force is applied to a sample and the material's response to that force is monitored. By analysing the material's load—deformation response, DMA gives the stiffness of the sample alongside with the storage modulus (E'). The storage modulus is related to elastic modulus of the material as it corresponds to the in-phase elastic response of the sample. Figure 15 shows the evolution of storage modulus and stiffness with temperature.

Over time and with increasing temperature the measured deformations increased until the point of failure. In the swollen hydrated state the crosslinked coacervate had increased volume and thus the polymeric chain segments increased mobility slightly. This increased mobility translates to a greater degree of compliance and hence in lower stiffness and storage modulus values. Increasing temperature resulted in gradual evaporation of the water from the polymeric chains. The free volume of the material was reduced; the polymeric chain segments came closer with decreasing space for movement. This phenomenon, which is very common to viscoelastic polymers [30], resulted in a very rapid transition of the sample from a soft 'rubbery' state to a more stiff 'glassy' state. This rapid transition was observed at approximately 60 °C.

These observations show that upon drying, the shell material shifts its behaviour and becomes hard and brittle rather than soft and rubbery as it is in the hydrated state. This transition is very important since it suggests that the shell material during the mixing process, which is a wet procedure,
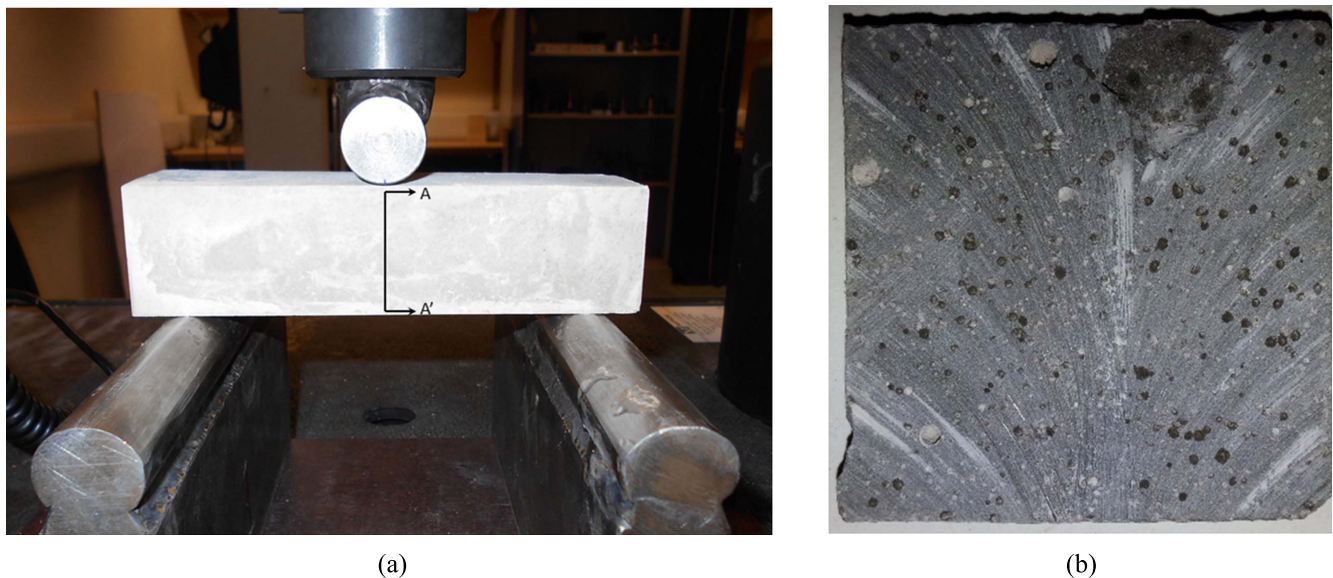
Figure 16. (a) Three-point bending test set-up and (b) digital image across the section AA$'$ showing the ruptured microcapsules appearing as 'wet' spots on the split face.

will remain rubbery and thus the microcapsules have increased chances of surviving the process. More importantly, when microcapsules dry, along with the host matrix, the shell will shift to a brittle material ready to rupture upon crack formation.

Proof of concept

To prove the concept, microcapsules were mixed in a cement paste mix at a concentration of 5% with respect to cement weight. The cement paste was manufactured in a 10 lt planetary type mixer using CEM-I 52.5 type cement with water to cement ratio of 0.3. The microcapsules were dispersed in water to ensure that: (i) they remained hydrated and hence 'rubbery' and (ii) that no clusters were formed. The water-microcapsules solution was added slowly to the mixer and mixed with cement until a smooth cohesive paste was produced. In this proof of concept investigation, both large ($\geqslant 500\,\mu$m) and small ($\leqslant 300\,\mu$m) microcapsules were used. The paste was then moulded in six standard prisms ($40 \times 40 \times 160$ mm), three with large and three with small microcapsules. All prisms were compacted using a vibrating table.

The specimens were demoulded after 24 h and immersed in water to cure for seven days. On the seventh day, the samples were removed from the curing bath and were cracked under three-point bending using a 30 kN static frame. The loading rate used was 0.10 mm min^{-1}. Due to the brittle nature of cement paste the prisms were completely split after fracture occurred. The fractured surfaces as well as samples extracted from them were investigated to verify the survivability, distribution and rupture of the microcapsules.

Proof of concept results

The cement paste prisms were loaded under three-point bend as shown in figure 16(a). Once they were split a digital image along the section AA$'$ was taken (figure 16(b)).

Macroscopic observation of the split section showed a substantial number of 'wet' spots. This was an indication that the microcapsules remained dormant in the host matrix and upon crack formation they ruptured releasing their contents. These spots were more evident macroscopically for larger microcapsules (figure 16(b)). To prove further that the microcapsules survived mixing and ruptured successfully, chips were extracted from the split faces and viewed with the optical microscope (figure 17). From brightfield observations of the fractured surfaces was not very clear which cavities corresponded to microcapsules (figure 17(a)). Switching to the UV light the microcapsules could be easily spotted (figure 17(b)) as they fluoresce under UV exposure.

Magnified image of the microcapsules (figure 17(c)) revealed the fractured microcapsules which remained embedded in the host matrix forming a dome like shape. The inside of the fractured microcapsules seemed very well shaped and the absence of any debris was obvious. The microcapsules evidently ruptured during the formation of the crack and not during mixing and casting. If that was the case, the observed microcapsules would not have retained their spherical shape as rupture during mixing would have led to total collapse. More importantly, the observed dome like cavities would have filled with hydration products.

In addition to optical microscopy the extracted chips were viewed with SEM as well. The scanning electron images also verified the rupture of the microcapsules (figures 18 and 19).

Using image analysis, the shell thicknesses were measured. The measured thicknesses in this case confirmed the
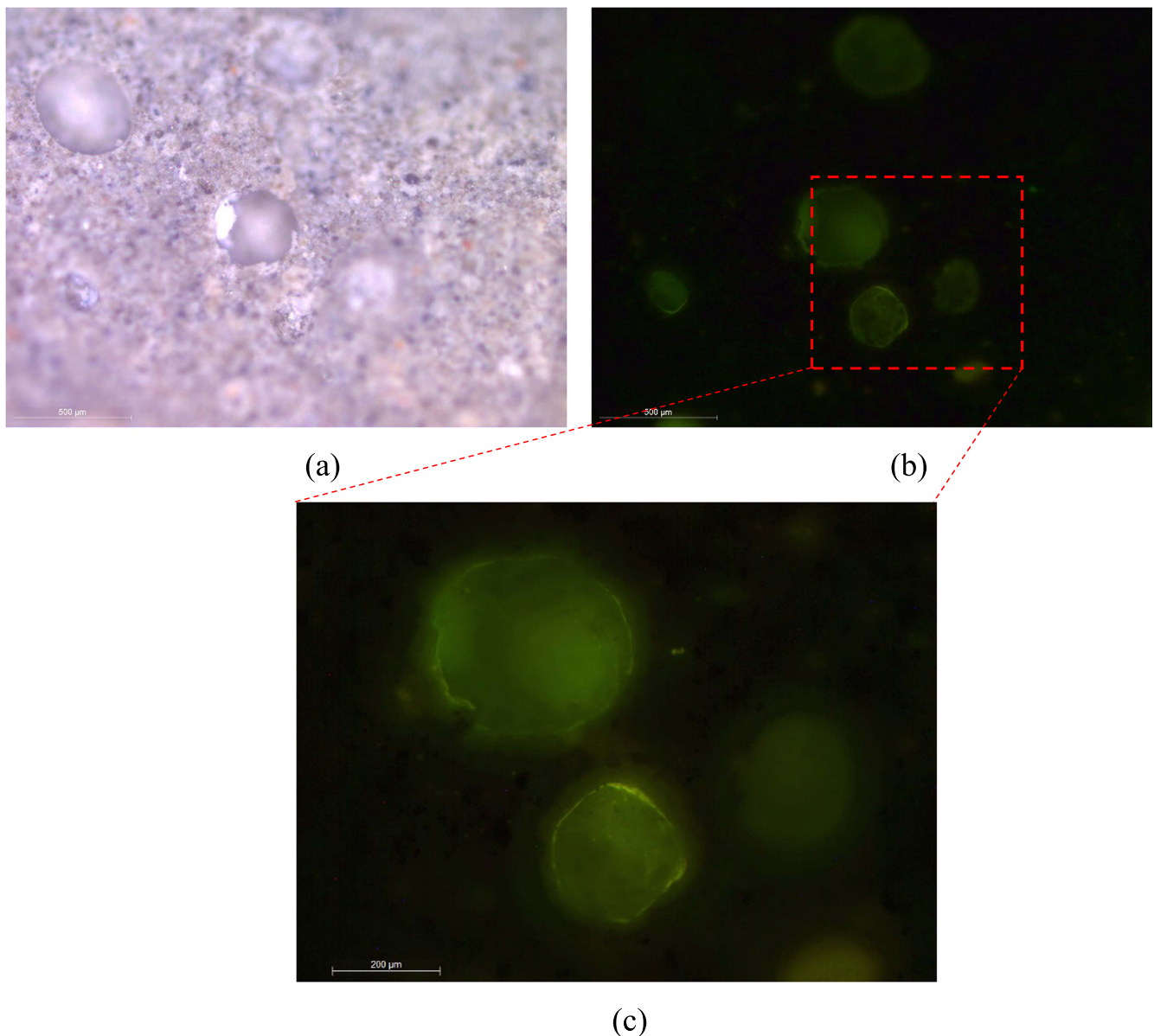
Figure 17. Microscopic images from crack plane: (a) brightfield image of the crack plane; (b) microcapsules fluorescing under UV light and (c) magnified image of the ruptured microcapsules.

values obtained on single, not embedded, microcapsules (figure 13). Moreover, the variation on the shell thickness is once more evident. In most of the cases the microcapsules were very well bonded to the cement paste. However, in few occasions shells debonded from the matrix were observed (figure 18). Further investigation showed that the debonded shell was characteristic of the larger microcapsules ($\geqslant 500\,\mu$m). Microcapsules with average size of $\sim$300 μm showed better cohesion and bonding with the surrounding matrix. A possible explanation of this phenomenon is the fact that larger microcapsules, with their 'rugby-ball' shape, have a surplus amount of shell material deposited in their outer perimeter. When embedded into the paste and during setting of the material, the microcapsules start gradually to dry and release the water from their shells. However, the larger

microcapsules require substantially more time to dry and their change in size and shape is more intense. Therefore, cavities are being formed between their shell walls and the surrounding matrix. SEM–EDX analysis was performed to preliminarily validate the nature of the elements in the close vicinity of ruptured microcapsules. Figure 19 shows a representative example from the EDX.

These hydration products have the elemental composition of calcite, calcium silicate hydrates and calcium hydroxide. More importantly, the analysis showed traces of sodium, which was a strong indication that the microcapsules successfully ruptured during fracture releasing their cargo material. These findings confirmed the initial macroscopic observations that indeed the microcapsules survived mixing and ruptured successfully.
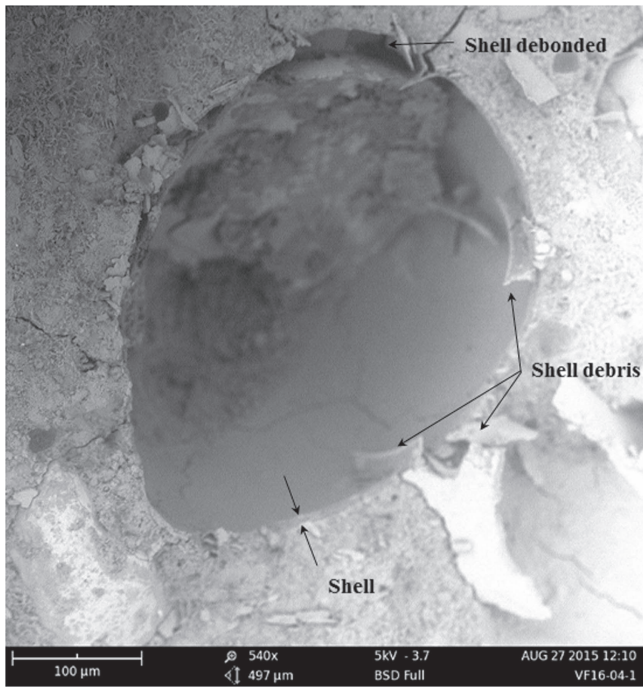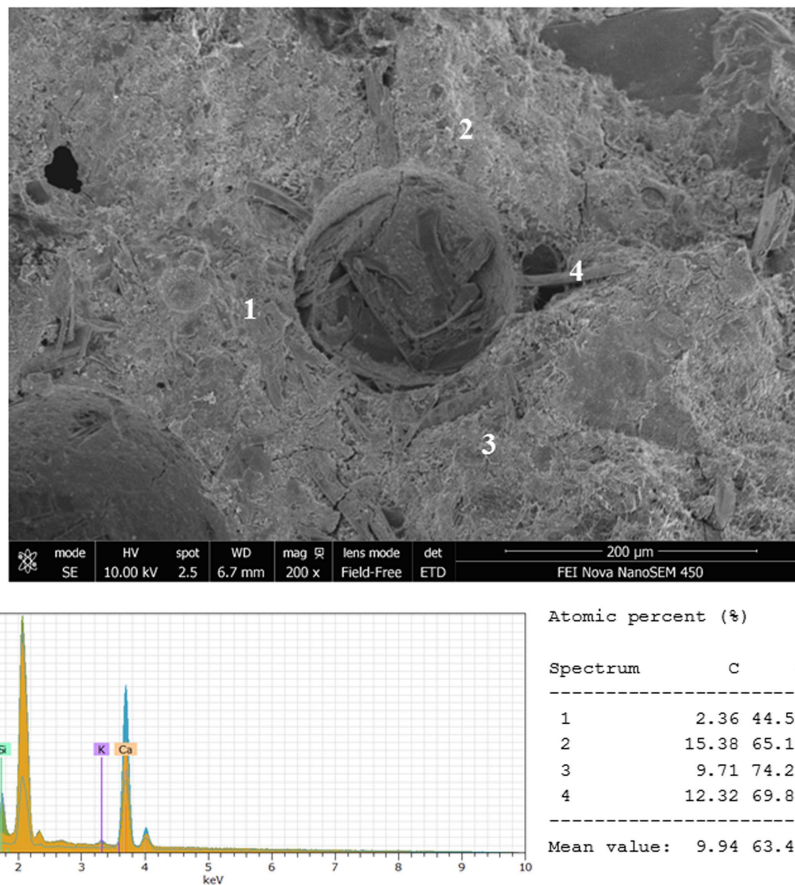
Figure 18. Typical SEM image of fractured microcapsule embedded in the cement paste matrix.

Conclusions

This study reports on the results of synthesising gelatin/acacia gum microcapsules to envelope liquid sodium silicate for use in the production of self-healing concrete. Complex coacervation was selected as the production technique and the resulted microcapsules had average diameters ranging from ~300 to ~700 microns and shell walls with thicknesses from 5 to 20 microns. The microcapsules were found to change their geometry between wet and dry conditions, switching from an ellipsoid shape (saturated state) to a perfect spherical (dried state). The dehydration/rehydration cycles did not affect the structural integrity of the shell. Microcapsules were found to be very stable when exposed to strong alkaline solutions that imitate exposure to concrete's alkaline environment. In the proof of concept investigation their survivability in alkaline environments was validated in a cement paste matrix. Thermogravimetric tests showed that the produced microcapsules were very stable up to 190 °C.

A unique feature of the developed system is that it can transition its mechanical behaviour between hydrated and dried conditions, converting from a rubbery soft state to a glassy stiff state. This transition in properties helped the

Atomic percent (%)						
Spectrum	C	O	Na	Si	K	Ca
1	2.36	44.51	–	–	–	53.13
2	15.38	65.10	0.40	2.58	–	16.55
3	9.71	74.22	0.07	2.47	0.00	13.53
4	12.32	69.82	–	–	–	17.86
Mean value:	9.94	63.41	0.23	2.52	0.00	25.27

Figure 19. Typical SEM/EDX image of a small fractured microcapsule ($\leqslant 300$ μm); elemental analysis showed the existence of different hydration products as well as traces of sodium.

microcapsules to survive the wet mixing process with cement and when the composite dried to rupture successfully upon crack formation. Their survivability and rupture was verified both macroscopically and microscopically. EDX in the vicinity of the ruptured microcapsules revealed traces of sodium verifying the macroscopic observations that the microcapsules survived mixing and successfully released their cargo upon fracture.

Acknowledgments

References

[1] Murua A, Portero A, Orive G, Hernández R M, de Castro M and Pedraz J L 2008 Cell microencapsulation technology: towards clinical application *J. Control. Release* **132** 76–83

[2] Krasaekoopt W, Bhandari B and Deeth H 2003 Evaluation of encapsulation techniques of probiotics for yoghurt *Int. Dairy J.* **13** 3–13

[3] Gouin S 2004 Microencapsulation: industrial appraisal of existing technology and trends *Trends Food Sci. Technol.* **15** 330–47

[4] Tyagi V V, Kaushik S C, Tyagi S K and Akiyama T 2011 Development of phase change materials based microencapsulated technology for buildings: a review *Renew. Sustain. Energy Rev.* **15** 1373–91

[5] Bury M A, Ong F, Attiogbe E, Nmai C and Smith J 2014 Microsphere-based admixture for durable concrete *Concr. Int.* **36** 59–63

[6] Qiu Y and Park K 2012 Environment-sensitive hydrogels for drug delivery *Adv. Drug. Deliv. Rev.* **64** 49–60

[7] Hu S H, Tsai C H, Liao C F, Liu D M and Chen S Y 2008 Controlled rupture of magnetic polyelectrolyte microcapsules for drug delivery *Langmuir* **24** 11811–8

[8] Grigoriev D O, Köhler K, Skorb E, Shchukin D G and Möhwald H 2009 Polyelectrolyte complexes as a 'smart' depot for self-healing anticorrosion coatings *Soft Matter* **5** 1426

[9] Dong B, Wang Y, Fang G, Han N, Xing F and Lu Y 2015 Smart releasing behavior of a chemical self-healing microcapsule in the stimulated concrete pore solution *Cem. Concr. Compos.* **56** 46–50

[10] Xiong W, Tang J, Zhu G, Han N, Schlangen E, Dong B, Wang X and Xing F 2015 A novel capsule-based self-recovery system with a chloride ion trigger *Sci. Rep.* **5** 10866

[11] Bédard M F, De Geest B G, Skirtach A G, Möhwald H and Sukhorukov G B 2010 Polymeric microcapsules with light responsive properties for encapsulation and release *Adv. Colloid Interface Sci.* **158** 2–14

[12] White S R, Sottos N R, Geubelle P H, Moore J S, Kessler M R, Sriram S R, Brown E N and Viswanathan S 2001

Autonomic healing of polymer composites *Nature* **409** 794–7

[13] Lee Y-S and Ryou J-S 2014 Self healing behavior for crack closing of expansive agent via granulation/film coating method *Constr. Build. Mater.* **71** 188–93

[14] de Koster S A L, Mors R M, Nugteren H W, Jonkers H M, Meesters G M H and van Ommen J R 2015 Geopolymer coating of bacteria-containing granules for use in self-healing concrete *Procedia Eng.* **102** 475–84

[15] Jamekhorshid A, Sadrameli S M and Farid M 2014 A review of microencapsulation methods of phase change materials (PCMs) as a thermal energy storage (TES) medium *Renew. Sustain. Energy Rev.* **31** 531–42

[16] Ghosh S K 2006 Functional coatings and microencapsulation: a general perspective *Funct. Coatings Polym. Microencapsul.* 1–28

[17] Fang X, Shima M and Adachi S 2005 Effects of drying conditions on the oxidation of linoleic acid encapsulated with gum arabic by spray drying *Food Sci. Technol. Res.* **11** 380–4

[18] Cho J S, Kwon A and Cho C G 2002 Microencapsulation of octadecane as a phase-change material by interfacial polymerization in an emulsion system *Colloid Polym. Sci.* **280** 260–6

[19] Brown E, Sottos N R and White S R 2002 Fracture testing of a self-healing polymer composite *Exp. Mech.* **42** 372–9

[20] Wang J Y, Soens H, Verstraete W and De Belie N 2014 Self-healing concrete by use of microencapsulated bacterial spores *Cem. Concr. Res.* **56** 139–52

[21] Dandoy P, Meunier C F, Michiels C and Su B-L 2011 Hybrid shell engineering of animal cells for immune protections and regulation of drug delivery: towards the design of 'artificial organs' *PLoS One* **6** e20983

[22] Sultana K, Godward G, Reynolds N, Arumugaswamy R, Peiris P and Kailasapathy K 2000 Encapsulation of probiotic bacteria with alginate-starch and evaluation of survival in simulated gastrointestinal conditions and in yoghurt *Int. J. Food Microbiol.* **62** 47–55

[23] Palin D, Wiktor V and Jonkers H M 2015 Bacteria-based agent for self-healing marine concrete *Proc. 5th Int. Conf. on Self-Healing Materials (Durham, USA)* pp 2–6

[24] Wang J, Mignon A, Snoeck D, Wiktor V, Van Vliergerghe S, Boon N and De Belie N 2015 Application of modified-alginate encapsulated carbonate producing bacteria in concrete: a promising strategy for crack self-healing *Front. Microbiol.* **6**

[25] Palin D, Wiktor V and Jonkers H M 2016 A bacteria-based bead for possible self-healing marine concrete applications *Smart Mater. Struct.* **25** 1–6

[26] Ach D, Briançon S, Broze G, Puel F, Rivoire A, Galvan J-M and Chevalier Y 2015 Formation of microcapsules by complex coacervation *Can. J. Chem. Eng.* **93** 183–91

[27] Kanellopoulos A, Qureshi T S and Al-Tabbaa A 2015 Glass encapsulated minerals for self-healing in cement based composites *Constr. Build. Mater.* **98** 780–91

[28] Pelletier M, Brown R, Shukla A and Bose A 2011 *Self-Healing Concrete with a Microencapsulated Healing Agent* (USA: Kingston)

[29] Gilford J III, Hassan M M, Rupnow T, Barbato M, Okeil A and Asadi S 2014 Dicyclopentadiene and sodium silicate microencapsulation for self-healing of concrete *J. Mater. Civ. Eng.* **26** 886–96

[30] Menard K 2008 *Dynamic Mechanical Analysis: A Practical Introduction* (Boca Raton, FL: CRC Press)