Dicyclopentadiene and Sodium Silicate Microencapsulation for Self-Healing of Concrete

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Abstract: Considerable interest has been directed in recent years toward the use of self-healing materials in concrete. The concept of microcapsule healing is based on a healing agent being encapsulated and embedded in the concrete. The objective of this study was to evaluate the effects of preparation parameters, namely, temperature, agitation rate, and pH on the shell thickness and size (diameter) of the microcapsules as well as to evaluate the self-healing mechanism in concrete through experimental testing performed in laboratory. Two healing agents were evaluated in this study, i.e., dicyclopentadiene (DCPD) and sodium silicate. Based on the results of the experimental program, it was determined that, as the pH was increased from 3.0 to 3.7, the shell thickness increased for sodium silicate, while the shell thickness reached a minimum at a pH value of 3.4 for DCPD. Sodium silicate shell thickness was almost twice the shell thickness for DCPD. The most uniform and coherent microcapsules were produced at a temperature of 55°C for both sodium silicate and DCPD. For the DCPD microcapsules and up to 49°C, the solution remained an emulsion and no encapsulation took place. An increase in agitation rate resulted in a decrease in the average diameter of the microcapsules for DCPD. On the other hand, the diameter of the microcapsules remained constant for sodium silicate microencapsulation as the agitation rate was increased from 250 to 550 rpm. Testing of concrete specimens modified with the two healing agents (DCPD and sodium silicate microcapsules) was conducted. For sodium silicate, an improvement of 11% in the modulus of elasticity of the concrete was observed after healing for the microcapsules prepared at a pH value of 3.1 and at a content of 5.0%. At other pH values, the effect of the sodium silicate microcapsules on the concrete performance was negligible. For DCPD microcapsules, the healing agent was effective in increasing the modulus of elasticity of concrete after cracking by as much as 30% for the microcapsules prepared at a pH value of 3.1 and at a content of 0.25%. **DOI: 10.1061/(ASCE)MT.1943-5533.0000892.** © *2014 American Society of Civil Engineers.*

Author keywords: Self-healing concrete; Microencapsulation; Sodium silicate; Dicyclopentadiene.

Introduction

The aging civil infrastructure in the United States represents a serious challenge for maintenance and repair using only limited available resources. It is envisioned that a long-term solution of this problem can only be achieved through new and creative transformative approaches that can significantly reduce the costs associated with inspection, maintenance, and repair of infrastructure elements. One solution for this problem involves the use of a new paradigm known as *self-healing concrete*. Self-healing in concrete can be defined as the ability of concrete to autonomously heal cracks that develop throughout its structure. By incorporating self-healing properties into concrete mixes, it is expected that concrete quality design and control methods will improve, with the goal of positively impacting concrete construction processes as a whole.

Considerable interest has been given in recent years to the utilization of self-healing materials in concrete (Sharp and Clemena 2004). This has led to the introduction of a new class of smart materials that have the ability to heal after damage. Self-healing applications in concrete have led to the introduction of bacteria-based self-healing concrete and microcapsule-based self-healing concrete. Bacteria-based self-healing concrete uses mineral-producing bacteria, which were found to be able to seal surface cracks (Jonkers 2011). The concept of microcapsule healing is based on a healing agent being encapsulated and embedded in the concrete (Pelletier et al. 2011). When the crack propagates and reaches the microcapsule, the capsule breaks, and the healing agent is released into the crack to repair it. Self-healing concrete provides a proactive approach rather than a reactive countermeasure for cracks that develop within concrete structures.

In spite of these promising benefits and before self-healing microcapsules can be applied effectively to concrete infrastructure elements, specific microencapsulation preparation parameters need to be evaluated to control and to optimize microcapsule properties. Therefore, the objective of this study is twofold. First, an experimental program was designed and performed to study the effects of preparation parameters (namely temperature, agitation rate, and pH) on the shell thickness, size, and morphology

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of the microcapsules. Second, the effect of microencapsulated self-healing materials on concrete's modulus of elasticity was experimentally evaluated in the laboratory.

Background

Since their introduction in the 1950s, microencapsulation has been evaluated in numerous construction materials including mortar, lime, cement, marble, sealant, and paints (Boh and Sumiga 2008). It has also been patented and tested in the food, chemical, textile, and pharmaceutical industries. The most common mechanism to trigger microcapsule-healing is through external pressure, which ruptures the microcapsule and releases the healing agent from the core. Therefore, the microcapsule must be sufficiently stiff to remain intact during processing, concrete mixing, pouring, and setting, but it must break during damage of the concrete (Pelletier et al. 2011). In addition, the microcapsule shell provides a protective barrier between the catalyst and the healing agent to prevent polymerization during the preparation of the composite.

There are three main methods for preparation of microcapsules (Boh and Sumiga 2008): (1) the mechanical method, which mechanically applies the microcapsule around the healing agent; (2) the coacervation method, in which the microcapsule wall solidifies around a core made of the healing agent; and (3) the polymerization method where the healing agent is applied as an emulsion, which then solidifies at the interface between water and healing agent to form the microcapsule wall. The polymerization method, which was used in this study, is categorized as either in situ polymerization, in which the healing agent is added to the liquid phase of an emulsion, or as interfacial polymerization, in which the healing agent is dissolved into the liquid phase. In this study, in situ polymerization was selected for preparation of the microcapsules.

As shown in Fig. 1, the two main design parameters of interest during microcapsule preparation are shell thickness and microcapsule size (diameter). Microcapsule walls that are too thin would fail during the manufacturing process, concrete mixing, pouring, and setting (Tseng et al. 2005). In contrast, capsule shells that are too thick will not allow breaking or fracturing of the shell as the crack penetrates through the microcapsules' plane. A well-developed process of microencapsulation using the urea-formaldehyde method was developed by Brown et al. (2003). The in situ encapsulation method for water-immiscible liquids, by the reaction of urea with formaldehyde at acid pH (Dietrich et al. 1989), is the foundation of the preparation method used in this study.

Two healing agents were evaluated in this study, i.e., dicyclopentadiene (DCPD) and sodium silicate. DCPD ($C_{10}H_{12}$) is a white crystalline solid/clear liquid solution (depending on its potency) with an energy density of approximately 10,975 Wh/l. Its main use within industry and private practice is for resins/unsaturated polyester resins (Li and Hou 2005). This chemical can be used as a monomer in polymerization reactions, such as ring-opening metathesis polymerization or olefin polymerization. Sodium silicate (Na_2O_3Si), which is also known as liquid glass, is a sodium metasilicate compound. This solid or aqueous solution is used in concrete applications to reduce its porosity. When added, a chemical reaction occurs with the excess of $CaOH_2$, which is already present in concrete (Greenwood and Earnshaw 1997). When sodium silicate reacts with $CaOH_2$, the concrete permanently binds with the silicates at the surface. This results in the product being a great sealer as well as a great water repellent. Although theoretically possible, microencapsulation of sodium silicate using the urea-formaldehyde method has never been successfully accomplished before. White et al. (2001) were able to streamline the microencapsulation of DCPD by controlling its diameter as well as its morphology (Kessler et al. 2003).

The microcapsule self-healing method has the ability to independently resolve issues, such as internal cracking and microcracking. When a crack occurs, a path toward rapid deterioration that could lead to structural failure is possibly initiated. By filling these voids and cracks with self-healing materials, concrete structures can achieve a longer life cycle along with a reduced likelihood of damage from unwanted moisture and corrosion (Brown et al. 2003). Although DCPD is an exceptional healing agent alone, for the agent to achieve maximum effectiveness, an appropriate interaction is required to polymerize the healing agent within the damaged area. A process called ring opening metathesis polymerization (ROMP) is used to polymerize the healing agent. This process provides the following advantages for self-healing microcapsules (White et al. 2001): more durable shell life, low monomer viscosity and volatility, rapid polymerization during ambient conditions, and low shrinkage rate during polymerization.

ROMP utilizes a Grubbs catalyst (transition metal catalyst), which incorporates a high metathesis method. The use of this catalyst allows multiple chemical groups to be utilized within the chemical process (such as oxygen and water). When DCPD encounters the Grubbs catalyst, polymerization occurs (Brown et al. 2005a). Sodium silicate, however, does not require a matrix and can be used as an individual healing component. The first reaction consists of sodium silicate reacting with calcium hydroxide, which is a product of cement hydration (Nonat 2004). The second reaction occurs between sodium hydroxide and silica. In both processes, the mending agent that resides in an aqueous environment within the microcapsule itself is essential (Nonat 2004). Water enables the hydration of the damaged cement paste and allows further bonding of the mending agent. The products of both reactions fill the crack

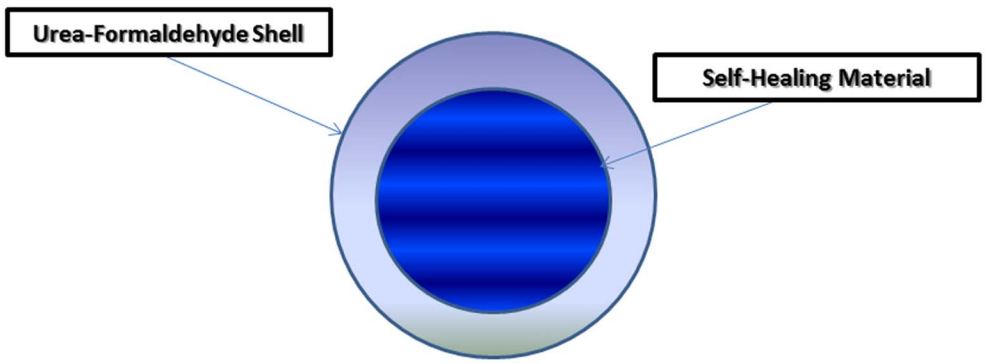

Fig. 1. Schematic of the components of a microcapsule

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Table 1. Required Chemicals for Interfacial Polymerization Synthesis

Chemical	Function	Manufacturer
Urea	Creates endothermic reaction in water	The Science Company
Ammonium chloride	Assists with curing process	The Science Company
Resorcinol (technical grade flake)	Reacts with formaldehyde and is a chemical intermediate for the synthesis process	NDSPEC Chemical Corporation
ZeMac E60 copolymer	Improves mechanical properties	Vertellus Specialties
ZeMac E400 copolymer	Improves mechanical properties	Vertellus Specialties
Octanol	Prevents surface bubbles	Oltchim
Hydrochloric acid	Lowers pH	The Science Company
Sodium silicate	Reacts with $Ca(OH)_2$	The Science Company
Sodium hydroxide	Increases pH	The Science Company
Formaldehyde	Reacts with urea during synthesis process	The Science Company
Grubbs catalyst	Reacts with DCPD and polymerizes	Materia
DETA (diethylenetriamine) mix with EPON 828	Used in synthesis of catalysts, epoxy curing agent, and corrosion inhibitors	Huntsmann
DCPD	Selected resin to heal concrete crack	Texmark–87% and 89% purity Cymetech–99% purity

and subsequently permit recovery of strength. Both processes support the presence of the aqueous mending agent, which also provides further integrity of the concrete by creating a bond and healing the crack (Brown et al. 2005b).

Experimental Program

Test Materials

The chemicals utilized in the preparation of the microcapsules based on the in situ polymerization method are presented in Table 1. The two microencapsulation laboratory procedures that were utilized in this study for preparation of DCPD and sodium silicate microcapsules are presented in Appendixes I and II, respectively.

Test Methods

An experimental program was developed to evaluate the effects of preparation parameters (namely temperature, agitation rate, and pH) on the shell thickness and size of the microcapsules using scanning electron microscopy (SEM). Microscopic analysis was conducted using a FEI Quanta 3D SEG Dual Beam SEM with focused ION beam at an acceleration voltage of 15 kV and in the backscattered electron imaging mode. The images were stored as 1,290 × 968 TIFF files. Using image analysis software (Image J), the average particle diameter and shell thickness was measured and calculated. Measured microcapsules were selected by random sampling from each developed batch. The samples were coated with a thin layer of platinum conducting film by sputtering. Each sample was sputtered for 4 min to ensure an even distribution of the coating around each shell.

Table 2 presents the experimental matrix followed in this study. Two healing agents were evaluated, i.e., DCPD and sodium silicate. During synthesis, the agitation rate, temperature, and pH were varied one at a time. The agitation rate was varied at six levels for the DCPD synthesis and at four levels for the sodium silicate synthesis, while the temperature and pH were kept constant. Similarly, to evaluate the effect of temperature, three levels were used for both DCPD and sodium silicate, while the pH and agitation rate were kept constant. Three pH levels were considered for both DCPD and sodium silicate, while the temperature and agitation rate were kept constant. The constant reference levels of temperature, pH, and agitation rate were: 55°C, 3.7, and 550 rpm, respectively, for the DCPD; and 55°C, 3.0, and 550 rpm, respectively, for the sodium silicate. This experimental matrix resulted in a total of 10 synthesis methods tested using DCPD and eight synthesis methods tested using sodium silicate.

Table 2. Experimental Test Matrix

Variables	DCPD	Sodium silicate
Agitation rate (rpm)	250, 350, 450, 550, 800, and 1,000	250, 350, 450, and 550
Temperature (°C)	49, 52, and 55	51, 53, and 55
pH value	3.1, 3.4, and 3.7	3.0, 3.1, and 3.2

Concrete Testing

The incorporation of the prepared microcapsules in concrete's response to loading was evaluated in the laboratory. Thirty-three concrete cylinder specimens with height equal to 20.32 cm (8 in.) and

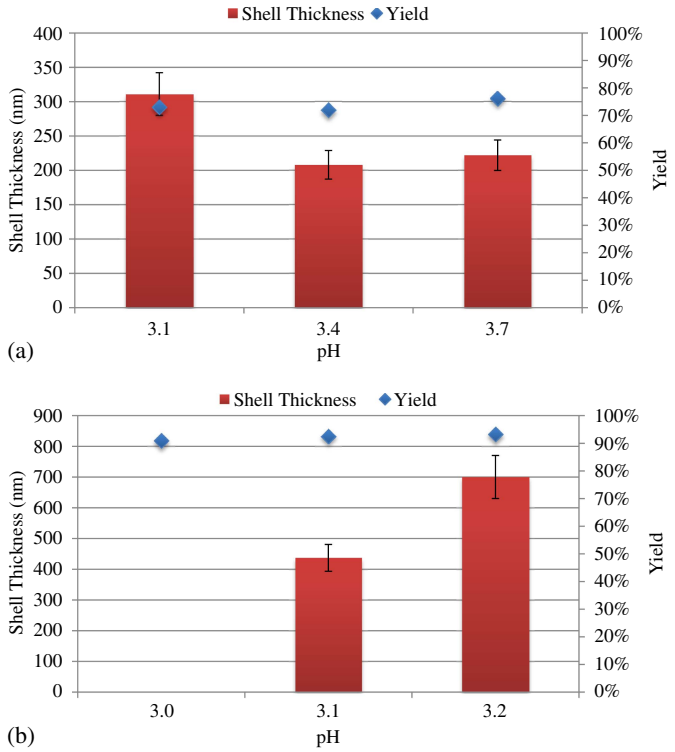

Fig. 2. Effect of pH values on the shell thickness for (a) DCPD microcapsules; (b) sodium silicate microcapsules

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diameter equal to 10.16 cm (4 in.) were prepared using a standard ready-mix concrete with a water/cement ratio of 0.5, a cement content of 285 kg/m^3 (825 lbs/yd^3) and a nominal compressive strength of 28 MPa (4,000 psi). Sodium silicate microcapsules, prepared at a pH value of 3.1, were added to the mixing water at a content of 0.5, 1.0, 2.5, and 5.0% by weight of cement. Sodium silicate microcapsules were also prepared at three pH values (3.0, 3.1, and 3.2) to vary the shell thickness and were added to the mixing water at a content of 5.0% by weight of cement. DCPD was used at a content of 0.25% by weight of cement for microcapsules prepared at a pH of 3.1, 3.4, and 3.7 to vary the shell thickness. The cylinders were steam-cured in a temperature-controlled and humidity-controlled chamber. The heat and moisture penetrated the specimens quickly, fully hydrated the concrete material, and strengthened the concrete cylinders so they could be used directly after accelerated curing. Cylindrical concrete specimens were demolded after 24 h and were cured by applying steam curing at 20–25°C for six days.

Specimens were tested based on a modified version of ASTM C 469, standard test method for static modulus of elasticity and Poisson's ratio of concrete in compression, by applying 70% of the peak concrete strength. The maximum load was increased to 70% of the peak strength instead of 40% as required in ASTM C 469 to induce damage in the concrete specimens and to observe the effect of the microcapsules on the healing process. Specimens were loaded and unloaded for three cycles and were then left in the curing room for 48 h to heal. After the healing period, specimens were then retested using the same test protocol. The initial tangent modulus, which is defined as the slope of the tangent to the stress-strain curve at the origin, was calculated before and after healing. Three replicates were prepared for each testing condition with an average coefficient of variation of 10% in the modulus of elasticity.

Results and Analysis

Microcapsule Parametric Analysis

Numerous factors can affect the morphology, diameter, and shell thickness of the prepared microcapsules. Morphology, diameter, and shell thickness calculations were conducted based on image analysis of SEM images. Yield was calculated according to the following equation:

$$\%\text{Yield} = \frac{\text{Weight of microcapsules}}{\text{theoretical weight of ingredients}} \times 100 \qquad (1)$$

The highest yield for DCPD was 79.0% at an agitation rate of 350 rpm, temperature of 55°C, and a pH of 3.7. The highest yield for sodium silicate was 94.9% at an agitation rate of 350 rpm, a temperature of 55°C, and a pH of 3.2. Figs. 2, 3, and 4 report the percent yield for DCPD and sodium silicate microcapsules as a function of pH, temperature, and agitation rate, respectively.

Effects of pH on Morphology and Shell Thickness

Fig. 2 presents the effects of pH on the shell thickness for DCPD [Fig. 2(a)] and sodium silicate microcapsules [Fig. 2(b)], respectively, in terms of mean (represented by the filled bar) and standard deviation (represented by the line bar as a ± one standard deviation) of the measured shell thicknesses. The target value for the shell wall thickness is between 140–200 nm. Results shown in Fig. 2(a) indicate that the increase in pH values resulted in an overall decrease in the shell thickness for DCPD, with a minimum mean shell thickness at a pH value of 3.4. As shown in Fig. 2(b), the increase in pH values resulted in an increase in the shell thickness for sodium silicate. At a pH value of 3.0, the shell wall of the

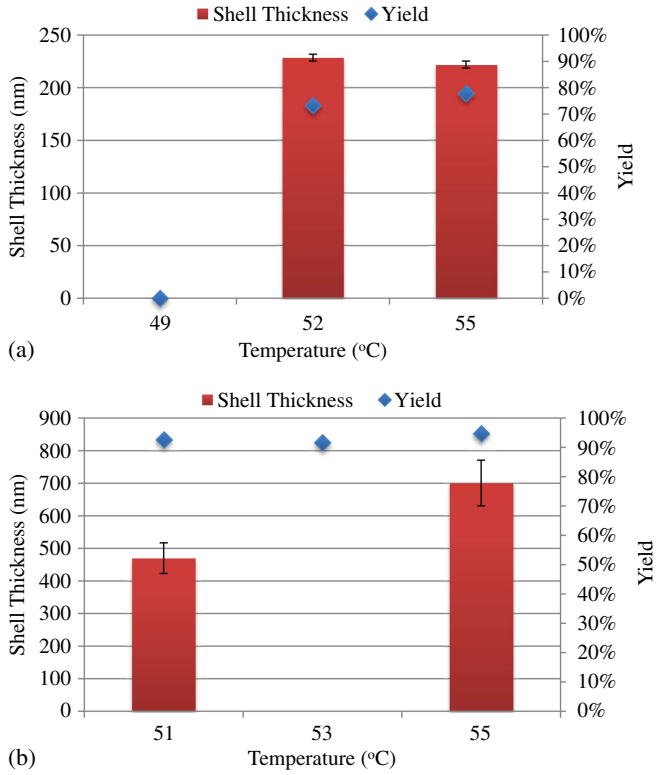

Fig. 3. Effect of temperature on the shell thickness for (a) DCPD microcapsules; (b) sodium silicate microcapsules

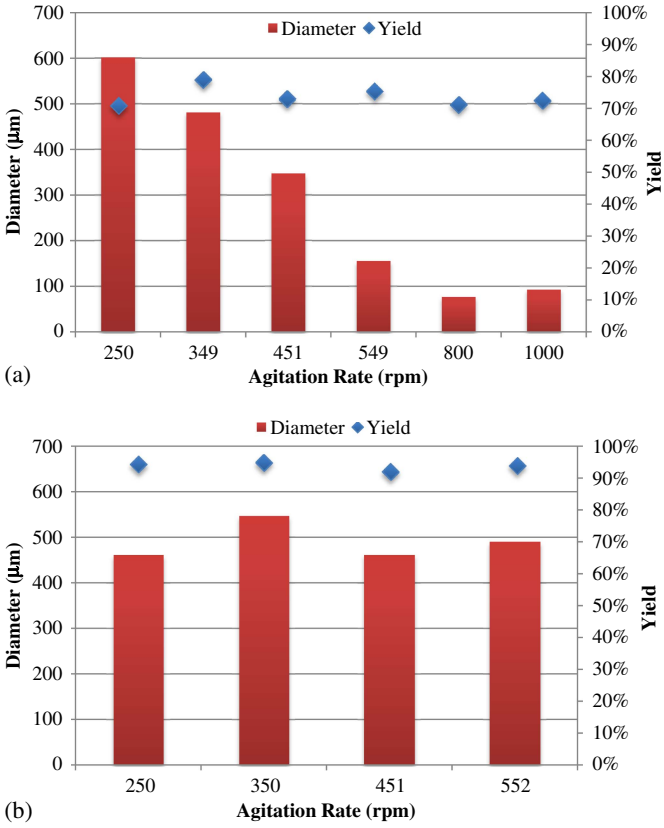

Fig. 4. Effect of agitation rate on the diameter for (a) DCPD microcapsules; (b) sodium silicate microcapsules

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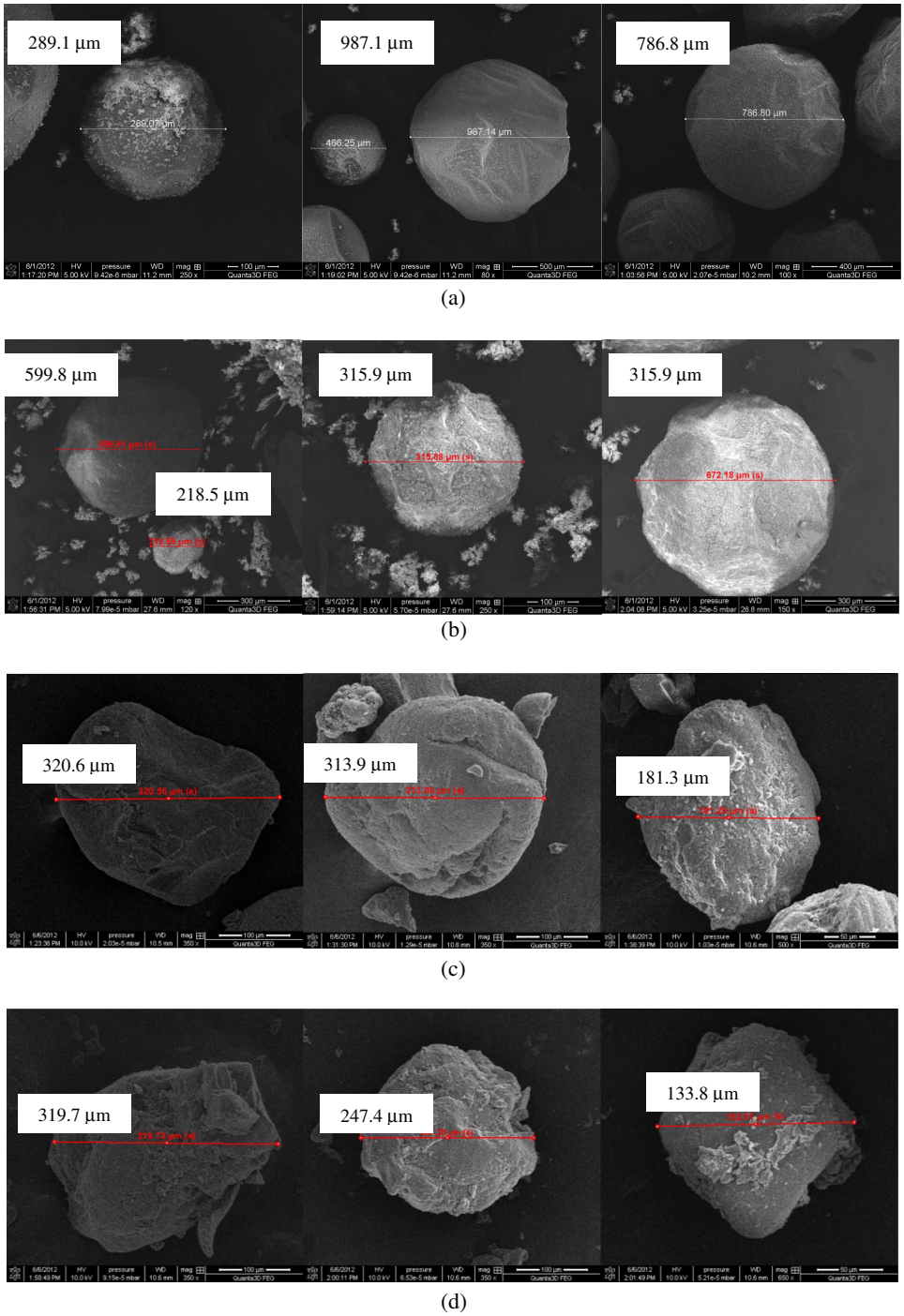
sodium silicate microcapsules became extremely thin, and the microcapsules tended to collapse during the measurements of their shell thickness. As a consequence, the measurement of the microcapsules' shell thickness was not possible. The maximum shell thickness of sodium silicate microcapsules was almost twice the maximum shell thickness of DCPD microcapsules. This phenomenon was due to sodium silicate being transformed into a gel-like solution prior to microencapsulation. This gel solution made the compound much easier to encapsulate and produced a much stronger shell wall.

Fig. 5 presents SEM images of the microcapsules prepared with DCPD and sodium silicate at different pH values. It is observed that the microcapsules prepared with DCPD were closer to a spherical shape and more uniform than the microcapsules prepared with sodium silicate. In addition, the size of the microcapsules was reduced as the pH value was increased. The outer surface of the microcapsules had a rough permeable layer, whereas the inside was smooth and free of cavities.

Effects of Temperature

Fig. 3 presents the effects of temperature on the shell thickness for DCPD [Fig. 3(a)] and sodium silicate microcapsules [Fig. 3(b)], respectively, in terms of mean (represented by the filled bar) and standard deviation (represented by the line bar as a ± one standard



(a)

(b)

(c)

(d)

Fig. 5. Effect of pH values on the morphology of microcapsules for (a) DCPD at pH = 3.1; (b) DCPD at pH = 3.7; (c) sodium silicate at pH = 3.0; (d) sodium silicate at pH = 3.2

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deviation) of the measured shell thicknesses. For the DCPD microcapsules at 49°C, the solution remained an emulsion and no encapsulation took place. For sodium silicate, there were no microcapsules formed at 53°C. Fig. 6 presents SEM images of the microcapsules for DCPD [Figs. 6(a and b)] and sodium silicate [Figs. 6(c and d)] prepared at different temperatures. Also in this case, the microcapsules prepared with DCPD had a shape closer to spherical and more uniform than the microcapsules prepared with sodium silicate. In addition, the size of the microcapsules was reduced as the temperature was increased.

Effects of Agitation Rate

Fig. 4 shows the effect of agitation rate on the diameter of the microcapsules for DCPD[Fig. 4(a)] and sodium silicate microcapsules [Fig. 4(b)], respectively, in terms of mean (represented by the filled bar) and standard deviation (represented by the line bar as a $\pm$ one standard deviation) of the measured microcapsules' diameter. The increase in agitation rate resulted in a decrease of the average diameter of the microcapsules for DCPD. This is due to the large microcapsules being broken up into smaller ones when high shear (due to the centrifugal forces) is applied. The optimum size of the

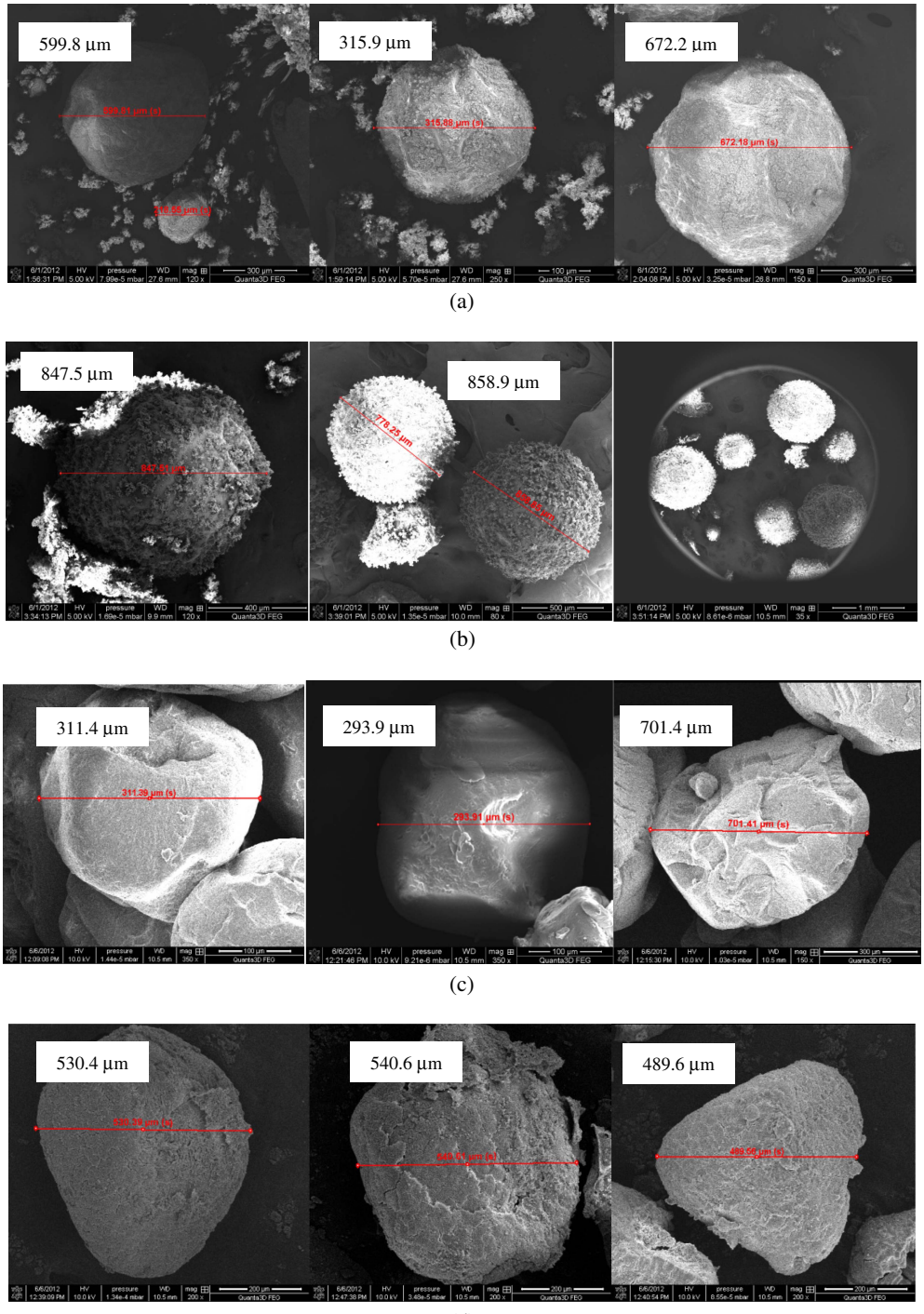

Fig. 6. Effects of temperature on the morphology of microcapsules for (a) DCPD at $T = 55$°C; (b) DCPD at $T = 52$°C; (c) sodium silicate at $T = 55$°C; (d) sodium silicate at $T = 51$°C

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microcapsules is dependent on the crack size that is expected to be filled during the healing mechanism. On the other hand, the diameter of the microcapsules remained constant for sodium silicate microencapsulation as the agitation rate increased, as shown in Fig. 6(b). This phenomenon may be attributed to the attempt to stabilize the alkalinity of the sodium silicate solution for the microencapsulation procedure using urea-formaldehyde. The SEM images presented in Fig. 7 also show a reduction in diameter with the increase in agitation rate for DCPD. The same trend is observed in Fig. 8, which provides SEM pictures of DCPD microcapsules produced at different agitation rates with a lower magnification rate compared with Fig. 7, to show several DCPD microcapsules in a single picture and to provide a better idea of the size distribution observed for DCPD microcapsules.

Laboratory Evaluation of Self-Healing Concrete

A set of laboratory tests was performed to measure the modulus of elasticity of plain concrete with and without self-healing microcapsules before and after a one-week healing period. The

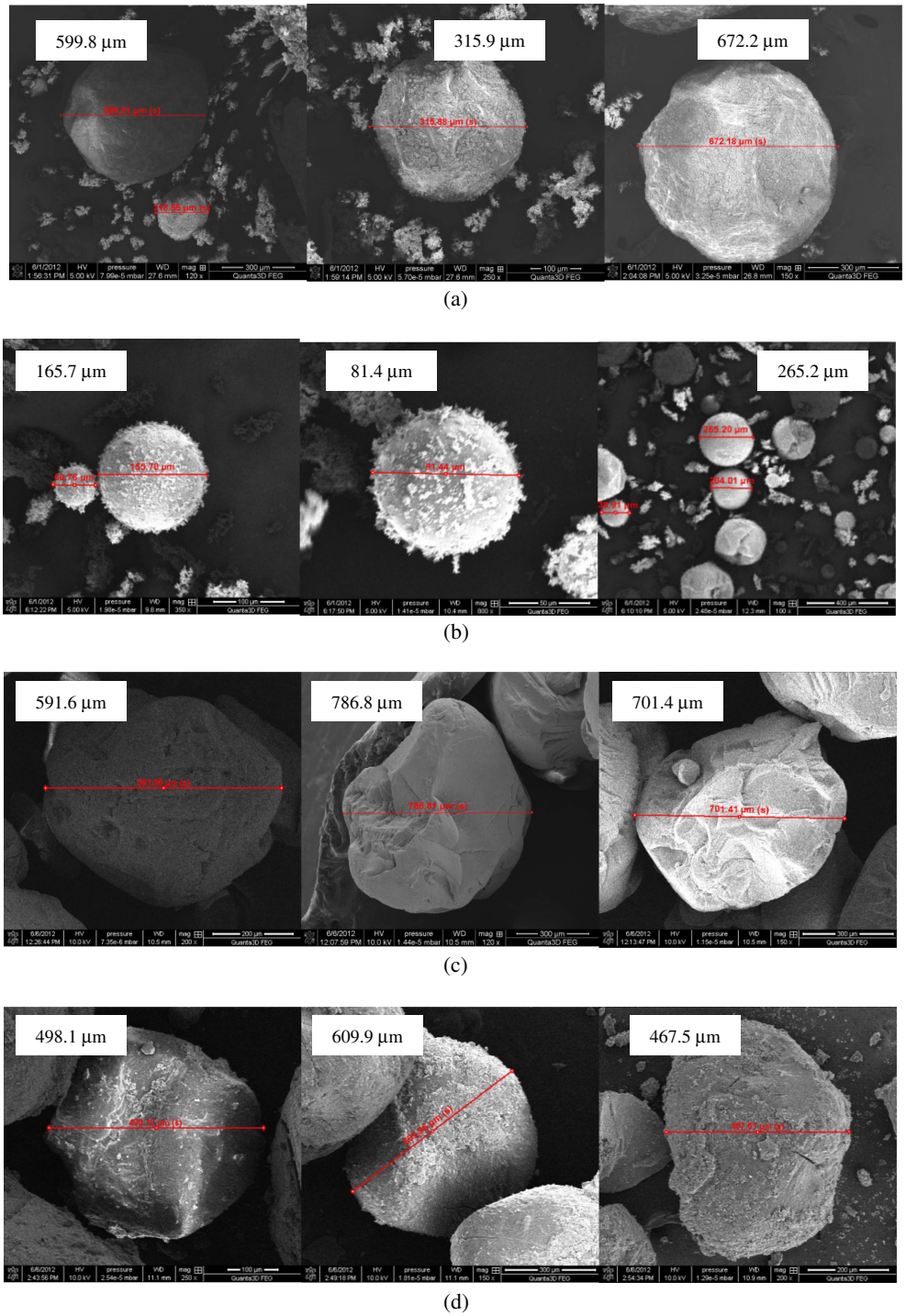

Fig. 7. Effects of agitation rate on the morphology of microcapsules for (a) DCPD at 250 rpm; (b) DCPD at 549 rpm; (c) sodium silicate at 257 rpm; (d) sodium silicate at 551 rpm

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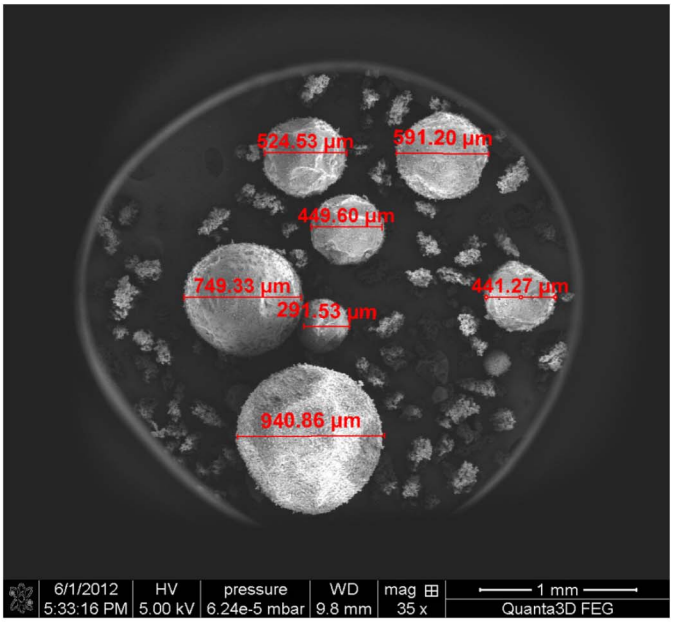
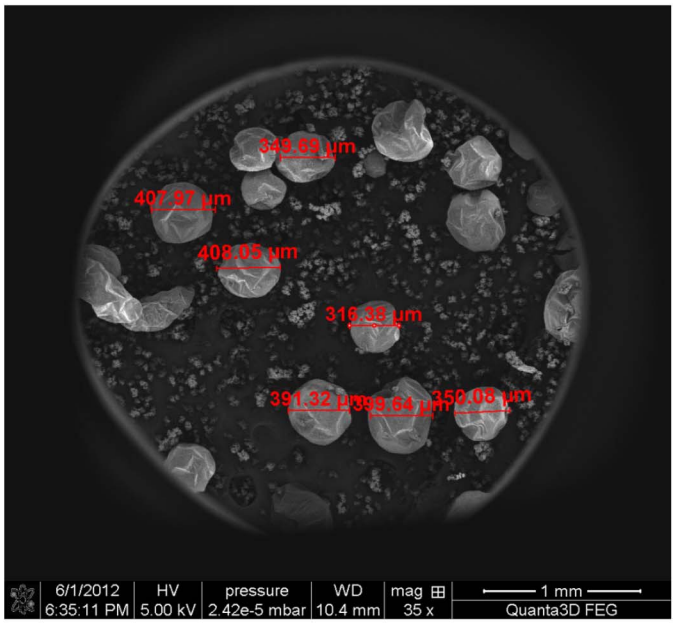


(a)



(b)

Fig. 8. Qualitative size distribution for dcpd microcapsules as a function of agitation rate: (a) 350 rpm; (b) 450 rpm

objective of this experimental investigation was to obtain preliminary information on the relation between production parameters of the microcapsules of self-healing agents (which affect the morphology and shell thickness of the microcapsules) and the effectiveness of the microcapsules in enhancing the concrete self-healing properties.

Fig. 9 presents the effects on the concrete modulus of elasticity before and after healing of DCPD (with a content of 0.25% of the cement weight) and sodium silicate (with a content of 5% of the cement weight) microcapsules prepared at different pH values. Error bars showing the average variability (coefficient of variation of ±10%) that was observed in the measurements are also provided. The following observations are made based on the results presented in Fig. 9:

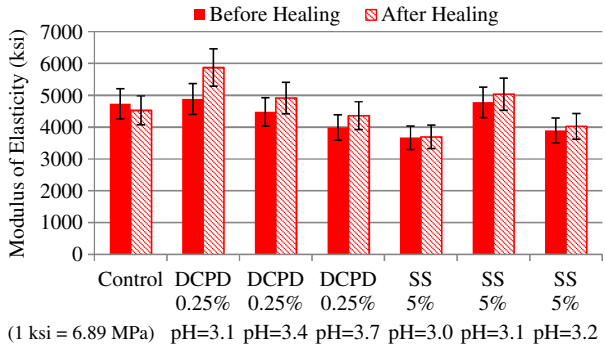


Fig. 9. Effect of preparation pH of microcapsules on concrete modulus of elasticity before and after healing

1. As expected, no self-healing process was detected for the control specimens (i.e., without self-healing), for which a small decrease of the modulus of elasticity (smaller than the variability of the measurements) was recorded. This result suggests that the control specimens were subjected to a small but not negligible damage, with likely formation of microcracks within the specimens.
2. The concrete modulus of elasticity after healing of specimens with DCPD was significantly higher than that before healing. The healing agent was effective in increasing the modulus of elasticity of concrete after cracking by as much as 30% for the microcapsules prepared at a pH value of 3.1 and at a content of 0.25%. This phenomenon indicates that the self-healing process was activated and that the self-healing material produced a higher stiffness and, as a consequence, a higher strength (which, for concrete, is positively correlated with the stiffness) than those of the original undamaged concrete. This after-healing stiffness increase was more pronounced for lower values of the pH, which correspond to higher thicknesses of the microcapsules' walls. The best performance of the after-healing concrete was obtained for pH = 3.1.
3. The modulus of elasticity of the concrete with DCPD before healing decreased significantly for increasing pH (i.e., for lower values of the microcapsules' shell thickness). At a pH value of 3.1, the average modulus of elasticity of the specimens with DCPD was almost the same (slightly higher) than that of the specimens of plain concrete, while at a pH value of 3.7 the modulus of elasticity was about 15% lower than that of the plain concrete specimens. While further testing is needed to identify the exact reason for this trend, it is possible that the use of microcapsules may be analogous to air entrainment, which is known to reduce the mechanical properties of concrete.
4. Sodium silicate caused a significant decrease in the modulus of elasticity before healing when compared to the control concrete mix for pH values of 3.0 and 3.2, while it did not affect the modulus of elasticity of the specimens for a pH value of 3.1. The data available at this point are insufficient to identify the reason for this trend. The lower stiffness (and strength) of the concrete with sodium silicate before healing should not be a concern as long as the design accounts for the proper values.
5. The modulus of elasticity of the concrete with sodium silicate was higher after healing than before healing for pH = 3.1. At other pH values, the effect of the sodium silicate microcapsules on the concrete modulus of elasticity was negligible. The increase in the modulus of elasticity for pH = 3.1 was 11% after healing.

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6. The shell thickness of the microcapsules significantly affected both the before and after healing modulus of elasticity of the concrete with sodium silicate self-healing agent. In particular, it appears that too-low or too-large pH values (i.e., too-small or too-large shell thicknesses) are detrimental to the performance of both before and after healing concrete. This phenomenon can be explained by noticing that, for too-small shell thicknesses, the microcapsules collapsed during mixing of the concrete, while for too-large shell thicknesses, the microcapsules were not broken by the concrete microcracks and, thus, the self-healing agent was not activated. Among the pH values considered in this study, pH = 3.1 provides the best performance for the concrete with sodium silicate.

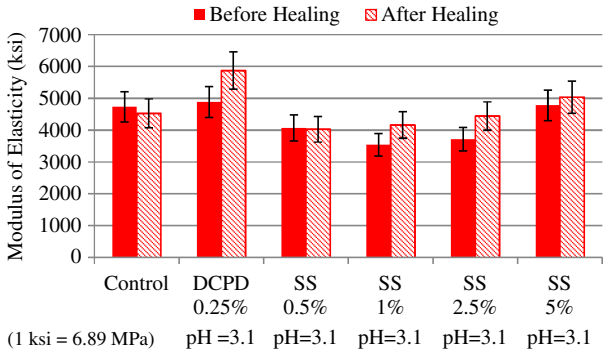

Fig. 10. Effect of amount of microcapsules (% of cement weight) on concrete modulus of elasticity before and after healing

Fig. 10 shows the effects on the concrete modulus of elasticity before and after healing of DCPD (with a content of 0.25% of the cement weight) and different contents of sodium silicate (i.e., 0.5%, 1%, 2.5%, and 5% of the cement weight) microcapsules. Error bars showing the average variability (coefficient of variation of ±10%) that was observed in the measurements are also provided. It was observed that the concrete modulus of elasticity after healing increased for all specimens with self-healing agents, with the exception of specimens with sodium silicate content equal to 0.5%. This result suggests that such low content of sodium silicate was insufficient to provide adequate healing that can enhance the capacity of the prepared concrete. The DCPD self-healing action was very effective even at the very low content considered in this research, i.e., 0.25%. In addition, DCPD did not affect negatively the modulus of elasticity of the concrete before healing. The presence of sodium silicate microcapsules reduced the modulus of elasticity of the concrete before healing, with the exception of the specimens with sodium silicate content equal to 5%, for which the modulus of elasticity was practically the same as for the plain concrete. From the results presented in Figs. 9 and 10, for sodium silicate microcapsules, the best performance of the concrete before and after healing was found for a pH of 3.1 and a content of 5%.

Specimens that cracked during testing were used for visual observation of crack healing. Fig. 11 presents a visual inspection of a cracked specimen before and after one-week healing for the concrete prepared with 0.25% DCPD (pH = 3.4) and 5.0% sodium silicate (pH = 3.1). These pictures were taken under the same environmental conditions. This figure shows that a portion of the surface crack healed due to the presence of the self-healing agent, which was released into the crack after the microcapsules

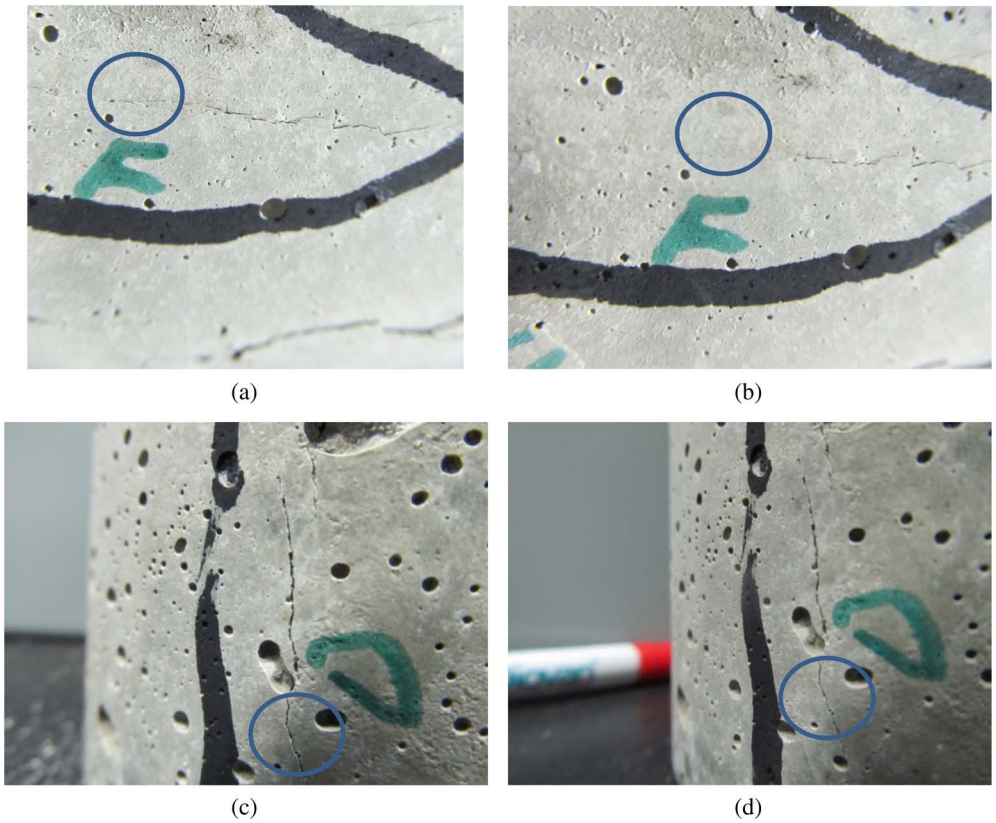

Fig. 11. Crack healing after one-week recovery: (a) DCPD before healing; (b) DCPD after one-week healing; (c) sodium silicate (1%) before healing; (d) sodium silicate (1%) after one-week healing

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were broken due to the stresses produced by the concrete cracks. From these results, it appears that DCPD-based microcapsules were effective in healing the cracks in the concrete specimens. It is noted that microcapsules are designed to heal small cracks (microcracks), and this approach appears to not be effective to heal large cracks.

Conclusions and Recommendations

The objective of this study was to evaluate the effects of preparation parameters (namely, temperature, agitation rate, and pH) on the shell thickness and size (diameter) of microcapsules of healing agents for use in self-healing concrete. Two healing agents were evaluated in this study, i.e., DCPD and sodium silicate. Based on the results of the experimental program, the following conclusions were made:

- As the pH was reduced, the shell thickness of the DCPD microcapsules increased. Unlike DCPD, the shell thickness of sodium silicate microcapsules increased for increasing pH. The shell thickness of sodium silicate microcapsules was almost twice the shell thickness of DCPD microcapsules.
- The more uniform and coherent microcapsules were produced at a temperature of 55°C for both DCPD and sodium silicate healing agents. For the DCPD microcapsules, the solution remained an emulsion and no encapsulation took place at 49°C. For sodium silicate, no microcapsules were formed at 53°C.
- The increase in agitation rate resulted in a decrease in the average diameter of the microcapsules for DCPD. By contrast, the diameter of the microcapsules remained almost constant for sodium silicate microencapsulation as the agitation rate increased.
- DCPD-based microcapsules were effective in increasing the modulus of elasticity of concrete after healing even at a content as low as 0.25% of cement weight. For DCPD microcapsules, the healing agent was effective in increasing the modulus of elasticity of concrete after cracking by as much as 30% for the microcapsules prepared at a pH value of 3.1 and at a content of 0.25%.
- For sodium silicate, an optimum pH value and content needs to be identified to produce microcapsules that enhance the modulus of elasticity of concrete before and after healing. An improvement of 11% in the modulus of elasticity of the concrete was observed after healing for the microcapsules prepared at a pH value of 3.1 and at a content of 5.0%.

This study represents a first step toward evaluating the use of microcapsules for self-healing of concrete. Based on the results presented in this study, further research is needed to better identify the effects of microencapsulated healing agents on the performance of self-healing concrete before and after healing. For example, the research results presented in this study open an interesting question on the overall detrimental effects of sodium silicate on the concrete modulus of elasticity before healing, which is observed but cannot yet be explained based on mechanical principles using only the data collected in this research. Different testing procedures (e.g., estimation of the dynamic modulus of the concrete before and after healing) should also be used to further confirm the results presented in this paper and to better understand the self-healing mechanism. Research is also needed to quantify the long-term effectiveness of the self-healing mechanism.

Appendix I. DCPD Microencapsulation Procedure

The adopted procedure was performed by using in situ polymerization in an oil-in-water emulsion. The main steps of this procedure can be summarized as follows:

1. Place 200 ml of deionized (DI) water in a 1,000 ml beaker;
2. Dissolve 50 ml of 2.5 wt.% EMA copolymer using a magnetic stirrer and ultrasound water bath to develop an aqueous solution;
3. Agitate using an IKA RW 20 digital mixer, with a driving 55-mm low-shear three-bladed mixing propeller placed just above the bottom of the beaker;
4. Under agitation, add 5.00 g urea, 0.50 g resorcinol, and 0.50 g ammonium chloride in the solution;
5. Set the pH by using sodium hydroxide (NaOH) and hydrochloric acid (HCl) dropwise with a disposable pipet;
6. Add two to three drops of 1-octanol to reduce surface bubbles;
7. Allow the solution to stabilize for approximately 6–8 min at the appropriate pH and rpm agitation rate before 100 ml of DCPD is added at a slow stream rate;
8. Allow the solution to stabilize for 13–15 min before adding 12.7 g of 37% of weight aqueous solution of formaldehyde to the emulsion;
9. Wrap and cover the solution with aluminum foil and slowly heat to the set temperature;
10. Turn off the hot plate after 4 h of continuous agitation;
11. Once cooled to ambient temperature, separate the suspension of microcapsules under vacuum filtration; and
12. Rinse microcapsules with DI water three times with 500 ml of DI water then allow to air dry for 48–72 h.

Appendix II. Sodium Silicate Microencapsulation Procedure

This procedure was accomplished by using in situ polymerization in an oil-in-water emulsion. The main steps of this procedure can be summarized as follows:

1. Place 200 ml of DI water in a 1,000 ml beaker;
2. Dissolve 50 ml of 2.5 wt.% EMA copolymer using a magnetic stirrer and ultrasound water bath to develop an aqueous solution;
3. Agitate using an IKA RW 20 digital mixer, with a driving 55-mm low-shear three-bladed mixing propeller placed just above the bottom of the beaker;
4. Under agitation, add 5.00 g urea, 0.50 g resorcinol, and 0.50 g ammonium chloride;
5. Set the pH by using sodium hydroxide (NaOH) and hydrochloric acid (HCl) dropwise with a disposable pipet;
6. Add two to three drops of 1-octanol to reduce surface bubbles;
7. Allow the solution to stabilize for approximately 6–8 min at the appropriate pH and rpm agitation rate;
8. Mix 170 ml of DI water with 60 ml of an aqueous sodium silicate and add to the solution;
9. Agitate the solution for approximately 5 min. While under agitation, slowly add HCL to the solution to form a gel/aqueous solution;
10. Add 100 ml of the gel/aqueous solution to the emulsion while maintaining a pH of 3.0–3.5;
11. Allow the solution to stabilize for 13–15 min before adding 12.7 g of 37% of weight aqueous solution of formaldehyde to the emulsion;
12. Wrap and cover the solution with aluminum foil and slowly heat to the set temperature;
13. Turn off the hot plate after 4 h of continuous agitation; and
14. Once cooled to ambient temperature, separate the suspension of microcapsules under vacuum filtration; and
15. Rinse microcapsules with DI water three times with 500 ml of DI water and allow to air dry for 48–72 h.

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