Article

Evaluation of the Compatibility of Modified Encapsulated Sodium Silicate for Self-Healing of Cementitious Composites

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Abstract: Healing agent carriers play a significant role in defining the performance of the autonomous self-healing system. Particularly, the ability to survive during the mixing process and the release of the healing agent when cracks occur without affecting the mechanical properties of the cementitious composite. Up to now, these issues are still a concern since glass capsules are unable to survive the mixing process, while some types of microcapsules were reported to cause a decrement in strength as well as limited strength recovery. Therefore, this study was twofold, addressing the surface treatment of polystyrene (PS) capsules and the evaluation of the compatibility of the modified capsules for cement-based applications. Secondly, assessing the healing performance of modified PS capsules in cementitious composites. Furthermore, the study also evaluates the potential healing performance due to the synergic effect between the encapsulation method and the autogenous self-healing mechanism. The investigation was carried out by measuring the changes in the pH of pore solution, FTIR analysis, survival ratio, and bonding strength. For self-healing assessment, the compression cracks on the cement paste were created at an early age and the strength recovery was measured at the age of 28 and 56 days. To identify the chemical compounds responsible for the healing process, SEM-EDX tests were conducted. Moreover, the effect of silica fume (SF) on bonding strength and self-healing was also evaluated. Based on the results, the modified PS capsules by roughing approach showed promising performance in terms of survivability, bonding, and recovery. The modified PS capsule increased the strength recovery by about 12.5–15% for 100%OPC and 95%OPC + 5%SF, respectively. The finding observed that the combining of modified PS capsules and the inclusion of SF gave high strength recovery of about 20% compared to 100%OPC without capsules. Thus, the modified PS capsule has a good potential for self-healing of cementitious-based applications.

Keywords: self-healing; modified polystyrene capsule; sodium silicate; silica fume; autonomous; autogenous; pH; FTIR; SEM; strength recovery; surface treatment

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1. Introduction

The concept of self-healing can be classified by its mechanism and the healing system applied. Principally, the method of self-healing involves healing agents that trigger and promote self-healing in the deteriorations and cracks of cement-based composites. Figure 1 summarizes the self-healing mechanisms in cement-based applications, which are autogenous and autonomous mechanisms as agreed by most researchers. The distinction between autogenous and autonomous is that the latter approach introduces components that normally are not found in cement-based components, whilst the former depends on the ability of the concrete's mixture without any special additions. In the case of the autogenous mechanism, the processes can be associated with materials such as pozzolan and expansive additives,

which are added directly into the cement-based materials [1]. In these circumstances, the healing process involves crack blocking by hydration product of the unreacted cementitious material or sealing by the expansion of hydrated expansive materials in the crack flanks [1,2].

Figure 1. Self-healing mechanisms categorization.

Most researchers found that the autogenous healing mechanism showed good results in the healing of microcracks on the surface of the concrete. Yet, the literature also indicates that the ability of the autogenous healing mechanism is limited to the finer cracks where the crack widths are less than 0.1 mm [3,4]. Furthermore, the healing ability by pozzolan gradually becomes limited at the later stage, as the reduction of calcium oxide content due to the decrease of the total amount of cement affects the availability of calcium hydroxide ($\text{Ca}(\text{OH})_2$) for pozzolanic chemical reactivity in producing calcium silicate hydrate (CSH). For the use of expansive additive, the effect of expansive additive is significantly influenced by its exposure condition and hydrated compound production, which results in uncontrol expansion, which consequently induces cracks [1].

The most common pozzolan used in ordinary Portland cement (OPC) concrete for improving the autogenous self-healing performance are fly ash (FA), ground granulated blast furnace slag (GGBS), and silica fume (SF) [5–7]. The two former pozzolans are usually used due to its content of calcium oxide for the cementitious chemical reactivity in producing the hydration product, CSH, for enhancing autogenous healing. Furthermore, it is also common to use these pozzolans, particularly FA and GGBS, in combination with the OPC concrete system for improving autogenous healing. Nevertheless, De Rooij et al. [8] concluded that the healing performance of concrete with silica fume was less pronounced compared to concrete without silica fume. This could be associated with the reduction of $\text{Ca}(\text{OH})_2$ availability, which affects the continuous pozzolanic reactivity of silica fume particles within the cement matrix of the concrete. In addition, Granger et al. [9] suggested that the silica fume may decrease the self-healing potential of concrete if an insufficient amount of water was used, which may result in a large amount of un-hydrated cement particles.

Conversely, previous studies identify that the autonomous mechanism is a more effective method in restoring the mechanical properties of cement-based composites. Literature indicates that the chemical healing using sodium silicate had a great potential of strength recovery of cement-based composites [10–15]. Sodium silicate reacts with $\text{Ca}(\text{OH})_2$ available within cement paste and with the presence of water to produce CSH gel which is the main product responsible for strength properties. Regarding the healing agent delivery, the encapsulation method is found to be the best approach for the autonomous healing mechanism. The use of the encapsulation system in the concrete application has been discovered in the early 1990s [16]. Currently, there are various types of carriers and encapsulation

systems have been investigated by several researchers, and the findings of the works are described in Table 1.

Table 1. Studies on encapsulation method in self-healing of cementitious composites.

Carrier Material	Shape	Dimensions	Findings	References
Glass	Cylindrical	Ø3 mm × 60 mm Ø3 mm × 400 mm	- Reduction in strength when cylindrical capsules were used. - Capsules did not survive the mixing process.	[16–18]
Glass fibers		-		
Soda glass		Ø6.15 mm × 50 mm		
Ceramics		Ø3 mm × 60 mm Ø3 mm × 400 mm	- High potential of capsule survival. - Required heating to make it flexible (due to its shape).	[19]
Polystyrene (PS) Poly(lactic acid) Poly (methyl methacrylate)		Ø1.1–Ø3.8 mm		
Hollow glass	Cylindrical	Ø1.2 mm × 75 mm Ø2 mm × 75 mm	Larger capsules caused a reduction in mechanical properties.	[20]
Concentric glass		Ø11.4 mm (outer) × 50 mm Ø6.15 mm (inner) × 50 mm	- Useful for powder healing agents. - Useful for two-component healing agents. - No capsule is included during mixing and the ability of capsule survival mixing needs to be discovered.	[21]
Urea-Formaldehyde (UF)	Spherical	Ø100–250 µm Ø200 µm Ø82–380 µm Ø200–250 µm	Very small amount of healing agent can be carried and the healing efficiency is limited.	[22–25]
Urea Formaldehyde formalin (UFF)		-	Very small amount of healing agent can be carried which affects the healing efficiency.	[26]
Silica		Ø5–180 µm Ø4.15 µm	Lead to increase in porosity.	[27,28]
Polyurethane		Ø200–250 µm Ø40–800 µm	Existence of capsule did not affect the mechanical properties.	[25,29]
Melamine		Ø2–5 µm	- Higher amounts of capsules caused significant strength reduction. - Good bond strength. - Able to survive mixing process.	[30]
Pharmaceutical-Epoxy & Glass	Cylindrical sphere & spherical	Ø5.57 mm × 15.9 mm Ø8 mm	- Required a protection layer on the capsule because the capsule dissolves with water. - Larger amounts of healing agents were carried. - Very small amount of healing agent was released.	[15]

Thao et al. [31], Joseph et al. [32], and Van Tittelboom and De Belie [33] used glass tubes as carriers for chemical adhesives in examining the crack healing of concrete beams. Joseph et al. [32] and Van Tittelboom and De Belie [33] found that the chemical healing agent (cyanoacrylate) failed to travel to the crack surface. External channels were formed in the concrete to enhance the movement of the healing agent [32]. The cyanoacrylate was introduced using syringes and resulting in successful healing of the concretes. Nevertheless, the difficulties were in assembling the glass system within the concrete as the tubes were fragile. Furthermore, Thao et al. [31] found that the crack healing process was not fully successful by the glass tube system with an external channel due to the air presence on the surface of the beams. On the other hand, work done by Huang and Ye [12] on encapsulation of sodium silicate solution in engineered cementitious composite (ECC) beams found that the sodium silicate was successfully transported into the crack. As a result, the mechanical strengths were stored and improved in comparison to control concretes.

According to Restuccia et al. [15], the selection of the suitable encapsulation method is related to various essential measurements such as (i) capsule survival (during mixing process), (ii) capsule ability to release the healing agent, and (iii) capsule compatibility with the cement mixture and healing agent to prevent any undesirable chemical reaction. Furthermore, the study also suggested that the presence of the capsule should not affect the other properties of the cementitious matrix such as workability, shrinkage, strength, and alkaline reaction. Nishiwaki [26] highlighted that the healing agent capacity and

the bond strength characteristic were the major concerns in enhancing the self-healing concrete ability using the encapsulation method. Despite so many innovative works having been done on the encapsulation methods, Lv et al. [34], Hilloulin et al. [19] and Wu et al. [35] still discovered that the bonding strength of capsule is one of the limited areas in the encapsulation techniques. Understandably, the bonding strength characteristics are strongly governed by the properties of the inter-cement matrix layer and capsule shell, which also indicate the stability of the capsule within the cement matrix. Both bonding strength and inter-cement matrix layer characteristics of the capsule affect the self-healing efficiency and mechanical properties of cement structure [34].

Nevertheless, most researchers explored the variation of capsule shell material and the capsule surface treatment to develop the survival ability of capsule during the mixing. Glass capsules had been mostly used as a healing carrier due to its brittleness characteristic, but were not able to resist stresses during mixing without any surface treatment [19,36]. One alternative was to increase the wall thickness of both glass and ceramic capsules; however, it was found that the increase of glass wall thickness from 2 mm to 3 mm enhanced the capsules' survival during mixing, but the capsules may not rupture upon crack formation [37]. One alternative was to increase the wall thickness of both glass and ceramic capsules; however, the capsules may not rupture upon crack formation [37]. Hilloulin et al. [19] heated the polymeric capsules before mixing, which transformed the capsules from a brittle to rubbery state and changed the wall thickness of the capsule. The study found an improvement in capsule survival during the mixing, but the issues were in the compatibility between the carrier's material and healing agent, where the healing agent was hardened inside the capsules. Restuccia et al. [15] investigated the pharmaceutical and glass capsules, where both capsules were coated with epoxy resin and sand for rougher surface for more resistant during mixing. Although the coating approach gave a promising results, the approach was not cost effective. Li et al. [38] used polystyrene microcapsules with epoxy resin in cement paste samples and found that the strength of the samples decreased due to the void produced by the capsules. Generally, the treatments applied on the capsule were for high resistant during mixing and a better adhesion between capsule shell and cement matrix was also expected to be improved. Thus, this suggests that there are several challenges facing the encapsulation system despite its potential application as healing agent carriers in the autonomous self-healing of cementitious composites. The past studies also discovered that the healing efficiency depended on the amount and size of the cracks and the amount of healing agent released by the breakage of capsules. Pelletier et al. [29] also investigated the effect of encapsulated sodium silicate using polyurethane microcapsules (40–800 μm) and the results indicated that the strength recovery after 7 days curing was 26% compared to only 10% for control samples (without microcapsules). Furthermore, the study discovered that the availability of capsules did not affect the mechanical properties of concrete.

The literature review reveals the common approaches in enhancing the encapsulation system for the self-healing ability of the cement-based composites are by (1) the modification of physical characteristics of the capsule and (2) surface treatment of capsule. For this reason, the study examined the compatibility of modified polystyrene capsules containing sodium silicate in cementitious composites for autonomous self-healing mechanism. Polystyrene capsule was selected due to its physical characteristics which are almost similar to the characteristics of glass; brittle enough to break under the force applied and chemically inert to the healing agent. One of the advantages of polystyrene is its survivability during concrete mixing compared to glass. Nevertheless, a low bonding strength between the capsule and cement matrix is expected due to the smooth surface of the capsule shell making it more exposed to the slipping effect. Thus, the aim of this research was twofold, which first to address the surface treatment of the capsule and the compatibility of the modified capsule for cement-based composite application. The investigations included the physical characteristic, survivability of the capsule, and the healing ability of the cementitious composite. Secondly, to assess the effect of the modified

capsule on the healing ability of cement-based composite. The healing performance was investigated through the mechanical test. In addition, the feasibility of the healing agent released by the modified capsule was also measured through micro analysis of cementitious composites (i.e., scanning electron microscopy, energy dispersive x-ray, and Fourier transform infrared spectroscopy). The current study also incorporates silica fume in the OPC cement system, which improves the cement matrix microstructure by improving the characteristics between the inter-cement matrix layer and capsule shell, which may also influence the bonding characteristic of the capsule. Using this approach, the study also examined the potential enhancement of autogenous healing mechanism by the encapsulation method. Commonly, the investigation on the self-healing ability of cementitious-based composite was performed on either autogenous or autonomous mechanisms. Recently, the research explores the potential of autogenous self-healing cementitious-based composite by combining the cementitious and expansive or crystalline materials. Yet, the performance of self-healing cementitious-based composite by combining pozzolan and encapsulation techniques is hardly reported and barely discussed as observed by He and Shi [1]. Thus, this investigation also gives new insight into the potential enhancement approaches for autogenous self-healing mechanism.

2. Research Significance

Based on the existing studies, the main issue of using polystyrene as capsule agent is the bonding with the paste, which, if not addressed, will reduce its effectiveness. Hence, this study proposes two different surface treatment, namely roughened and weak lines, which are expected to improve the bonding. On the other aspect, the interfacial zone between the capsule and cement matrix is one of the key factors of the bonding issue. The study also intended to improve the cement-matrix microstructure by including silica fume which is expected to enhance the bonding. Consequently, the approaches applied in this study are combining encapsulation method and blended cement, which is not a common approach in the self-healing concept. Thus, this study is also investigating the potential of this approach in improving the self-healing of cement-based composite.

3. Materials

In achieving the objective of the study, the detail of the research plan is summarized in Table 2. Detailed characterization of the materials used throughout the study is also presented in the following sections.

Table 2. Summary of the key investigation regarding the scope of research conducted.

Specimen	Evaluation	Test Method	Material Type
Investigation I: Capsule Surface Treatment and Compatibility			
1. Capsule with roughen surface 2. Capsule with weak lines surface	Capsule Survivability	pH evaluation Fourier transform infrared spectroscopy (FTIR) Physical observation	Fresh concrete
	Bonding strength of capsule	Bonding strength	Mortar
Investigation II: Effect of the Capsule on the Healing Ability			
100%OPC ¹ 95%OPC + 5%SF ¹	Strength recovery	Compressive strength test Scanning electron microscope (SEM) and energy dispersive x-ray (EDX)	Cement paste

¹ Each cement mixture was evaluated with/without capsules and with different capsule surface treatment.

3.1. Cementitious Binders and Chemical Healing Agent Materials

Ordinary Portland cement (OPC) type I Class 42.5N conforming to BS EN 197-1 [39] and silica fume (SF) were used in this study. The physical and chemical compositions of the cement binders are summarized in Table 3. The Sodium Silicate (Na_2SiO_3) solution used in this study, which is also known as water glass or liquid glass, was obtained from (Sigma-Aldrich, Malaysia) with 1.39 g/mL density and 12.5 pH, and consists of 9.4% Na_2O , 30.1% SiO_2 , and 60.5% H_2O with 12 M concentration.

Table 3. Chemical compositions and physical properties of cement and silica fume.

Physical Properties		
	OPC	Silica Fume
Color	Grey	Dark Grey
Specific gravity	3.15	2.22
Specific surface area, (m^2/g)	1.65	20.55
Form	Powder	Ultra-Fine Powder
Chemical Compositions (% by Mass)		
	OPC	Silica Fume
SiO_2	19.5	95.3
Al_2O_3	5.3	0.7
Fe_2O_3	2.3	0.3
Na_2O	0.2	0.2
K_2O	1.0	0.8
CaO	61.8	0.3
MgO	2.3	0.4
SO_3	3.8	3.2

3.2. Characterization and Preparation of Capsules

Polystyrene (PS) capsules with 24 mm length, 10 mm diameter, and 0.7 mm wall thickness were used as healing agent carrier in this study. The capsule has a smooth texture and consists of two parts that were glued together to prevent any separation or leakage that may happen afterward. Modifications on the texture of the capsules were made to enhance their bonding characteristics within the cement matrix and the capability of self-healing agent release. Two surface modifications were applied, (1) by roughening the surface of the capsule, which was done using P400 grit sandpaper, and (2) by engraving inclined lines on the roughened surface of the capsule using Dehaki electric mini drill. The surface texture modifications are shown in Figure 2. Additionally, a hole was made at one end of the capsule and the sodium silicate solution was filled in the capsule through the hole. The hole was then sealed with silicone glue to prevent any leakage.

Figure 2. Photo of surface texture of capsule (a) without modification (smooth), (b) roughened, and (c) weak lines.

The strength of PS capsules was measured using an Instron compression machine with a maximum capacity of 1 kN and the loading rate applied was 0.125 mm/min, as shown in Figure 3. The strength of capsules was measured in vertical and horizontal positions of

the capsule placement due to the various orientations of the capsules within the cement composite materials. The strength of PS capsules is tabulated in Table 4.

Figure 3. Compressive strength testing of polystyrene capsule.

Table 4. Strength characteristic of the capsule at various capsule positions.

Capsule Surface Texture	Compressive Strength of Capsule (N/mm ²)	
	Vertical Position	Horizontal Position
Smooth	4.1	2.4
Roughen	3.5	2.2
Weak lines	2.3	1.1

Note: Surface texture for capsule without modification is known as smooth.

3.3. Sample Preparation

The preparation of the sample required was based on the research plan as described in Table 2 (see Section 3). To ensure the compatibility of the modified capsule within the cement-based material, mortar and concrete samples were used with the incorporation of different types of capsule surface textures.

For the evaluation of capsule survival capability, the investigation was conducted on 100%OPC concrete mixture. The concrete mix design was based on 0.50 water to cement ratio (w/c) and cement content of 390 kg/m³. The concrete mixtures were incorporated with three (3) different types of capsule surface texture and 10 capsules were embedded in each of the concrete mixtures. A total of nine (9) groups of concrete mixtures were mixed at three (3) different mixing speed levels (low, medium, and high). The fresh concrete sample was immediately taken after an hour of the mixing process and pH and FTIR tests were performed to examine the survivability of the capsule. Physical capsule inspection was also carried out on the fresh concrete mixture. In investigating the bonding of the capsule, the test was conducted on mortar specimens. The mortar samples were prepared with the inclusion of different types of capsule surfaces. The mix design for mortar was in accordance with ASTM C190 [40], where the mortar was produced by fixed w/c of 0.50, and the cement to sand ratio was 1:2.75.

In examining the efficiency of autonomous self-healing, cement paste with a constant w/c of 0.50 was prepared. Two cement mixtures were used throughout this study, control

and silica fume blended cements, where the former consisted of 100%OPC, while the latter included 5% of SF (by weight of total binder). The samples were prepared with and without capsules, where the capsules were added by about 2% of the total volume. A previous study by Pelletier et al. [29] indicated that the volume fraction of 2% capsule did not adversely affect the strength of concrete. Cement paste cubes were casted in $50 \times 50 \times 50 \text{ mm}^3$ steel molds and the capsules were added manually and placed in the center of each cubic sample. The specimens were demolded after 24 h of casting and then cured by immersing in a water tank at ambient temperature.

4. Experimental Procedures

4.1. Capsules Survival Capability

This study is focused on the survival capability of the capsules during the mixing process due to the importance of the brittleness characteristic of the healing agent carrier. According to literature, most glass capsules carrier could not satisfy this requirement [36]. To assess the capsule survival capability, capsules were added directly during the mixing process and the assessments were conducted on the capsule rupture resistance during mixing using pH evaluation on the fresh concrete pore solution. Fourier transform infrared spectroscopy (FTIR) test was also conducted on 24 h old hardened concrete. The most common method in the evaluation of pH of fresh concrete is using a pH electrode [41], where a ruptured capsule may disperse the sodium silicate solution and resulted in an increment of the pH level of fresh concrete. The fresh concrete samples were collected at 1 h after mixing at three different mixing speed levels (low, medium, and high). The samples were then placed under a vacuum pump for pore solution extraction and the pH of the resulted solutions was tested using BP3001 Benchtop pH meter. For FTIR investigation, small samples were taken randomly from the fresh concrete mixes and left for 24 h to harden. Then, the samples were grounded using mortar and pestle. Then, the grounded powder sample was tested using Perkin Elmer Spectrum 100 FTIR spectrometer with ATR mode at a range of $650\text{--}4000 \text{ cm}^{-1}$ and a spectral resolution of 1 cm^{-1} . Visual inspection was also performed on the capsules embedded in the concrete mixture, which indicated the ability of the capsules to withstand mixing stresses. After the mixing process, the capsules were collected manually and cleaned from the cement paste as shown in Figure 4. Then, the capsules were examined for any defect and the survival ratio was determined, adopting a similar approach by Gruyaert et al. [42].

Figure 4. (a) Removing cement paste from aggregates and capsule, (b) capsule surrounded within fresh concrete mixture, and (c) sample of physical inspection on capsule defects.

4.2. Bonding Strength of Capsule

The bonding strength of capsules plays a significant role in defining the performance of self-healing cement-based composites, where higher bonding strength prevents the capsule from slipping inside the cement matrix and forces the capsule to rupture and release the healing agent. In this study, the bonding strength investigation was conducted following the method described by Hilloulin et al. [19]. The polystyrene (PS) capsule was inserted partially in a mortar cube of $50 \times 50 \times 50 \text{ mm}^3$. Half of the capsule is exposed,

and the other half is placed inside the mortar cube as shown in Figure 5. The samples were then left for 24 h to harden and then demolded. After 7 days of water curing, the sample was dried for 3 h. A screw nut was then glued at the top of the exposed part of the capsule and left to harden. Then, a screw was attached to the nut, and the sample was placed in an Instron 3365 tensile testing machine at a fixed displacement rate of 2 mm/min. The bonding strength was calculated using Equation (1).

$$\beta = \frac{F}{\pi \times d \times L} \quad (1)$$

where β is the bonding strength, F is the maximum force at failure, d is the diameter of the capsule, and L is the length of the capsule inserted in the mortar cube.

Figure 5. Bonding strength set-up and the schematic diagram of the sample.

4.3. Crack Formation

A similar pre-cracking method by Saleh et al. [43] was adopted in this study, by introducing compression cracks on the cement paste samples. The crack was created at the age of 7 days, which was at the early paste age. At this age, the concrete structure is not allowed to resist any load, but the microcracks formed under early age shrinkage may propagate and raises durability and compressive strength issues in the concrete.

The load was applied at 80% of the ultimate compressive strength, with a loading rate of 0.5 kN/s, which created hairline cracks on the cement paste samples. Thereafter, the pre-cracked samples were kept in a water tank and was reloaded until failure at 28 and 56 days. The strength regained was based on the hydration products of cementitious compounds that were deposited on the open cracks.

4.4. Compressive Strength Recovery

The compressive strength was measured in accordance with BS EN 12390-3 [44] and the evaluation was done on the average of three samples at 7, 28, and 56 days. The test was conducted in two sets of specimens, where the test was performed until failure for the ultimate compressive strength of non-pre-cracked specimens. A similar test procedure was performed on the pre-cracked specimens. For the healing efficiency, there is no standardized test method and recovery analysis for the self-healing concrete. Different researchers formulated different healing index assessment methods. Nevertheless, most of

the healing analysis index is based on the properties' performance restored after healing in comparison to properties' performance of sample without damage aspect. With regard to this, the author adopted the same concepts of healing analysis, in which the strength recovery was evaluated with respect to the strength of 7-days. The strength recovery (%) was calculated using Equation (2).

$$SR(\%) = \frac{\sigma_{p,n} - \sigma_{p,7}}{\sigma_{u,n} - \sigma_{p,7}} \times 100 \quad (2)$$

where $\sigma_{p,n}$ is the stress of pre-cracked samples at the age of n days, $\sigma_{p,7}$ is the stress of pre-cracked samples at the age of 7 days and $\sigma_{u,n}$ is the stress of un-cracked samples at the age of n days.

4.5. Microstructure Study

Scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDX) tests were conducted to determine the healing compounds developed on the crack surface at the microstructural level. SEM-EDX samples were prepared by extracting small chips from the crack planes of the cement paste sample. The chunks of cement paste samples were immersed in acetone for 24 h to stop further hydration and then left to dry for 48 h in a desiccator. The sample was then gold-coated using a K550X Emitech sputter coater and tested for SEM-EDX using Hitachi S-3400N scanning electron microscope with 0.2–0.30 kV accelerating voltage. SEM was used to capture images at 7 and 28-days while EDX was used to analyze the healing compound developed at 28-days.

5. Results and Discussion

5.1. Capsules Survival Capability

Figure 6 shows the pH values of the concretes where the pH level of all concrete mixes containing capsules were higher than pH 11.7, which was obtained for the control concrete, 100%OPC without capsule regardless of the mixing speed level. The result also indicates that a slight increment in pH level with the increase of mixing speed levels. Nevertheless, the pH level of all concrete mixtures was below the pH limit of fresh cement, 12.5 [45], regardless of the mixing speeds. The variation in pH level obtained by all concrete mixes could be associated with less flocculation between cement particles, which is due to the impact during the mixing between all solid components. The dispersion of cement particles allows more surface area of the cement particles to be covered with water to initiate the chemical reactivity. Another consequence is the rapid chemical reactivity leads to more hydration products precipitated on the surface of cement particles. Thus, the calcium hydroxide and the release of calcium ions in the hydration product increased the pH level of the concrete pore solution. The finding also observed a noticeable increase in the pH level for the concrete containing capsules with weak lines surface regardless of the mixing speed levels. It can be seen that the modification of the capsule surface decreased the wall thickness of the capsule, which increased its brittleness [19]. The surface modification, which combines the roughened surface with the engraved line creates points of weakness on the capsule. Thus, this could be associated with a high tendency to rupture due to the impact of aggregate upon the concrete mixing particularly at high mixing speed. Nonetheless, Behnood et al. [41] reported that the pH of fresh normal OPC concrete is commonly around 13 and the author also suggested that the fluctuation in the alkalinity of fresh concrete for the first hour was governed by the fast dissolution of the alkali sulphates of cement and the presence of calcium sulphate phases. Given this, the finding suggests that both modified capsule surfaces were well-mixed through the medium mixing speed.

Figure 6. pH of 100%OPC concrete containing capsule after 1 h mixing.

In assessing the capsule survivability, the FTIR spectrum analysis on the main chemical products, Si-O bond was measured on the concrete of 1-day age. The reason for this is that the leaking of sodium silicate may react with either calcium hydroxide or pozzolan in cementitious composites to form calcium silicate hydrate (CSH) gel to heal the concrete crack. Thus, the leakage of sodium silicate may produce a rich amount of CSH. As shown in Figure 7, the FTIR spectra of concrete with capsule for all levels of mixing speeds are almost similar. A sharp bending at 993 cm^{-1} was observed for all concretes with all capsule surface modifications regardless of the mixing speeds. The Si-O band at 950 cm^{-1} confirms the existence of hydration product, CSH in the concretes [46]. Nonetheless, there is a slight shift in peak and shape change to wavenumber about 1000 cm^{-1} for concrete with weak line capsule at high mixing speed. It is noted that the bands at $900\text{--}1110\text{ cm}^{-1}$ are associated with the formation of more CSH gels [14,47–49]. Thus, the FTIR spectrum analysis findings agreed with the findings obtained by pH evaluation of concretes containing capsules. The FTIR observations provide indirect confirmation on the existence of hydration product, CSH, by the stretching bands, which corresponds to the availability of the alkalinity in concrete. Furthermore, the findings also suggest that all types of capsule surface modifications were compatible with medium concrete mixing speed. Observation on the capsules after the mixing process was conducted in the study to confirm the defect caused by the stresses during the mixing process on the capsules. The survival ratio of the capsules is reported in Figure 8, and it shows that the survival ratio decreased pronouncedly for the concretes mixed with high mixing speed regardless of the capsule surface modification. As can be seen in Figure 9, the capsules remain intact, but several capsules were partly broken after the mixing. Most of the defects occurred at the rounded end of the capsule. A similar finding by Hilloulin et al. [19] is observed, where the capsule had a greater survival ratio than 80%, except for the weak line capsules with high mixing speed. The weak lines capsules had a detrimental effect due to the decrease of the capsule wall thickness, which supposedly increased the pH level observed in the concrete.

Figure 7. FTIR spectrum of 100%OPC mixes containing capsules with different types of surface texture at various rates of mixing speed.

Figure 8. Survival ratio of capsules with various surface types at different level of mixing speed.

Figure 9. Capsules after mixing with high mixing speed level (a) rough capsules and (b) weak line capsules.

5.2. Capsule's Bonding Strength

One of the most significant aspects related to capsule compatibility is the bonding strength of the capsule within the cement matrix [42,50]. This characteristic is paramount due to the importance of the breakage of the embedded capsules for the release of the healing agent solution within the concrete to heal the cracks. This breakage of the capsule could only occur without the slipping of the capsule from the cement matrix. In relation to this, the study examined the effect of surface modification of the capsule with mortar matrix on the bonding characteristics. As can be seen in Figure 10, the modifications of the capsule surface helped to enhance the bonding strength regardless of mortar mixes. The results found that the bonding strength for 100%OPC mortar with rough capsules increased to 5.7 MPa, with an increment of 78.1% compared to smooth capsules. The bonding strength of modified PS capsule increased about 60–125% than those of non-surface treated PS capsule observed by Hilloulin et al. [19]. The result also indicated that combining the surface treatment with blended cement matrix improved the bonding strength of PS capsule, which the bonding strength increased about twice than bonding strength of 100%OPC mortar, regardless of surface modification type. Figure 10 also shows that, regardless of surface modification, the polystyrene (PS) capsules had higher bonding strength compared to both glass and ceramic capsules obtained by previous studies [19]. This could be associated with the brittle nature of the capsule shell material, where both glass and ceramic can rupture more easily compared to PS. As expected, the weak lines capsules had the higher bonding strength regardless of mortar mixes. It was noted that the bond strength of weak lines capsule with 100%OPC mortar increased about 39% compared to those of the 100%OPC mortar with rough capsules. This increment in bonding strength is related to the increase in the interface area between the capsule surface and mortar matrix due to the surface modification effect. Furthermore, the formation of engraved lines on the capsule walls enhanced the interlocking effect between the capsule's interface area and the mortar matrix, which made the capsule intact within the mortar matrix. This finding agreed with work done by Kessler et al. [51], Brown et al. [52] and Feng et al. [53], which discovered that the deposition of polymerization resulted in a rough texture microcapsule that improved the capsule's bonding within the cementitious matrix.

Nevertheless, it is also noted that the PS capsule with smooth surface texture, which had no surface treatment, had lower bonding strength compared to those found by Hilloulin et al. [19] except to the mortar blended with silica fume. Furthermore, the findings also discovered that the existence of silica fume gave the highest bond strength regardless of capsule surface modification. It is noted that the presence of pozzolan increased the formation of CSH gel [54,55], which densifies the cement microstructure and consequently improved the interfacial zone between capsule's shell and mortar–cement matrix. The adhesion between capsule and cement matrix needs to be strong to allow the breakage of the capsule during concrete cracking [42]. According to Lv et al. [34], the improvement of cement matrix microstructure and capsule's shell influenced the stability of the capsule within

the cement matrix and enhanced the potential self-healing efficiency and the mechanical strength of the cementitious matrix.

Figure 10. Bonding strength characteristic of capsules with variations of mortar mix combinations (Ψ Hilloulin et al. (2015)).

5.3. Compressive Strength Recovery

Figure 11 shows that the compressive strength recovery performance of cement paste with the inclusion of capsules containing sodium silicate solution. Only the mix with the rough and weak line surface treatment capsules were tested, as the smooth surface generally had poor bonding strength. A noticeable compressive strength recovery of about 12.5% was observed on 100%OPC with the capsule surface treatment compared to those of 100%OPC without capsule at 28-days. No significant difference was observed on the compressive strength recovery performance of 100%OPC with regard to different capsule surface modifications. The increment of compressive strength recovery is due to the strength regain within the cement matrix as the sodium silicate reacts with the cementitious matrix and, consequently, forms a product to seal and heal the crack. Sodium silicate reactivity is controlled by the availability of calcium hydroxide produced by the cement reactivity, where the residual sodium silicate may transform to crystallize [56]. This could be associated with no significant effect on the strength recovery of 100%OPC cement paste with the capsule surface modification. On the other aspect, the high bonding strength of PS modified surface capsule ensured the capsule rupture, which was observed on the dispersion of healing agent solution. The strength regain obtained was due to the enhancement of hydration reactivity at early age, which was obtained by the chemical reactivity of the cementitious compounds with sodium silicate solution.

The study also found that the modified PS capsule with sodium silicate increased the compressive strength recovery of 95%OPC + 5%SF cement paste by about 15% and 20% compared to those of the same blended mixture without capsules and 100%OPC (without capsule), respectively. As discussed earlier, the strength gain was due to the healing process associated with a combination of effects between continuous hydration of unreacted cementitious particles and the reactivity of sodium silicate with $\text{Ca}(\text{OH})_2$ due to initial chemical reactivity between cementitious particles. This suggested that the presence of sodium silicate enhanced the strength development of cementitious composite at an early age. Additionally, the pozzolan physical characteristics enhanced the microstructure densification, where the finer particles filling the pores within the cement matrix. Thus, this result indicates that the modified PS capsule with sodium silicate method enhanced the autogenous self-healing of silica fume blended cementitious composite. Nevertheless, the compressive strength recovery increased with age regardless of capsule surface treatment or cement mixture.

Figure 11. Strength recovery performance of cementitious combinations with various capsules' surface modification.

5.4. Microstructural Investigation

SEM images presented in Figure 12 show the morphology of the cement matrix on the crack plane of the pre-cracked samples that were loaded at 7-days. Figure 12b shows the morphology of the cement matrix for 100%OPC that is similar to the dry soil pattern, which indicates that the sodium silicate solution was dispersed and covered the flank surface area of the crack. The formation of ettringite filling the pores within the cement matrix of 100%OPC cement paste was also noted in Figure 12a. A similar cement matrix morphology nature of 100%OPC was observed at the crack surface of 95% + 5%SF sample, as can be seen in Figure 12d. This confirmed the leakage of sodium silicate on the cement matrix surface. The dispersion of sodium silicate started to crystallize instantly due to the moisture availability within the cement matrix [18,56]. This crystallization is caused by the reaction of silica with the oxygen available in water, and the formation of silica oxide crystals. The deposition of silica oxide crystals as the result of sodium silicate reaction on the cementitious matrix can be seen in Figure 12d [18]. Moreover, SEM images had also shown the availability of common chemical products such as calcite (CaCO_3), portlandite (Ca(OH)_2), ettringite, and CSH gel. Furthermore, Figure 12c showed the availability of un-hydrated silica fume particles on the crack plane of 95%OPC + 5%SF sample at the age of 7 days. The availability of such un-hydrated silica fume particles is the main reason for the autogenous healing ability at a later age.

SEM images of the pre-cracked samples that have undergone the healing period of 28-days are presented in Figure 13. The microstructure observed the availability of portlandite (Ca(OH)_2), CSH gel, and calcite as the hydration product of the cementitious composite for both samples, 100%OPC and 95%OPC + 5%SF. Denser layers of CSH were observed in 100%OPC samples especially for the sample containing sodium silicate capsules, as shown in Figure 13a,b. The finding suggests that the sodium silicate enhanced the chemical reactivity of the cementitious compound that promoting the healing process and this resulted in the increment of strength recovery. The EDX elemental analysis of 100%OPC without and with sodium silicate capsules reveals the presence of silica (Si) of 8.72% and 11.44%, respectively. The increment of silicon atomic ratio led to a reduction of Ca/Si ratio from 1.54 to 1.35, which is an indication of a high amount of healing products that contribute to strength recovery. The lower the Ca/Si ratio results in the higher strength of cementitious composite (Kunther et al., 2017).

Figure 12. Development of healing compounds at 7 days for both 100%OPC (up) and 95%OPC + 5%SF (down). 100%OPC cement paste at the age of 7 days (a) without capsule, and (b) with capsules 95%OPC + 5%SF cement paste at the age of 7 days (c) without capsule, and (d) with capsules.

Nevertheless, a denser cementitious microstructure was observed on 95%OPC + 5%SF, as shown in Figure 13c,d. This indicates the existence of the additional formation of calcium silicate hydrate (CSH) as the result of pozzolanic reactivity and sodium silicate solution reacted with the available un-hydrated calcium particles and $\text{Ca}(\text{OH})_2$ on the crack planes. As understood, this chemical reactivity produces CSH gel and $\text{Ca}(\text{OH})_2$ that healed the cracks. Similarly, the increment in Si atomic ratio due to the presence of silica fume and sodium silicate solution had reflected on the Ca/Si ratio of cementitious composites for the samples without and with capsules. A further reduction of Ca/Si ratio was observed from 1.47 to 1.18 for 95%OPC + 5%SF samples without and with capsules, respectively. This confirmed the high hydration reactivity obtained due to the combination of silica fume and healing agent, sodium silicate solution.

The availability of calcium (Ca) element in the composition of healing product is also an indication of the chemical reaction between the present Ca ions due to the presence cementitious compounds and the presence of sodium silicate, which these formed additional amounts of CSH, as observed in Figure 13c,d. These findings conform to the findings obtained by Huang and Ye [57], where sodium silicate is responsible for most of the healing process. Thus, these hydration products play a significant role in strength recovery, which explains the strength regain due to the self-healing process. Figure 14 shows the EDX analysis for healing compounds at the age of 28 days.

Figure 13. Development of healing compounds at 28 days for both 100%OPC (up) and 95%OPC + 5%SF (down). 100%OPC cement paste at the age of 28 days (a) without capsule, and (b) with capsules. 95%OPC + 5%SF cement paste at the age of 28 days (c) without capsule, and (d) with capsules.

Figure 14. Cont.

Figure 14. EDX analysis for healing compounds at 28 days for 100%OPC (up) and 95%OPC + 5%SF (down) (a) 100%OPC without capsules, (b) 100%OPC with capsules, (c) 95%OPC + 5%SF without capsule, (d) 95%OPC + 5%SF with capsule.

6. Conclusions

An important aspect of the encapsulation method for self-healing application in a cement-based application is the compatibility of the capsule within the cement matrix and also the self-healing effects. From the observed results and discussions, the modified capsule is proposed based on the following conclusions below.

6.1. The Compatibility between Capsule and Cement-Matrix

All PS surface treatments showed a potential for the application in cement-based composites. The modified surface capsules exhibited good performance during the mixing process and had a high bonding strength. However, the dual effect of surface treatment and the inclusion of silica fume significantly improved the bonding strength of the PS capsule.

6.2. The Effect on the Self-Healing Performance

The strength recovery results showed that the modified PS capsule enhanced the strength recovery of the paste compared to the mixtures without capsule (at 12.5% and 15% for 100%OPC and 95%OPC + 5%SF, respectively). However, the result found that the variation in PS capsule surface treatment did not significantly influence the strength recovery performance. Thus, the roughened surface treatment is the best approach for the PS capsule application in cement-based composites. The microstructural studies, SEM and EDX, revealed the dispersion of sodium silicate solution on the crack area and the healing agent promoted the healing process by the formation of new CSH gel. The elemental compositions of Ca/Si ratio for 100%OPC and 95%OPC + 5%SF were at 1.35 and 1.18, respectively. The lower value of the ratio indicated the high amount of healing products that are responsible for strength recovery. Furthermore, the study also found a promising strength recovery obtained by 95%OPC + 5%SF with a modified capsule, where the strength recovery was increased about 20% compared to those of 100%OPC (without capsule). Thus, the finding confirmed that the autogenous self-healing could be enhanced by the synergic effect between the encapsulation technique and blended cement. However, these results need to be validated with other pozzolan blended cementitious composites.

PS capsules are known due to its brittleness characteristic, good chemical resistance, and cheap material. Although the PS capsule brittleness characteristic is better than the glass capsule, the bonding strength between the capsule and cement matrix is a major concern. This study shows the PS capsule can be used successfully by treating its outer surface texture. In conclusion, the findings suggest that the most practical surface treatment of the PS capsule is by roughening the capsule surface. Although the PS capsules may

not survive during mixing, the PS capsules can be placed in the molds during casting. Furthermore, the capsules' placement can be focused on the area that is expected to defect. The use of silica fume with capsule surface treatment demonstrated a better improvement in the bonding strength of PS capsules. Furthermore, a promising healing performance was also observed on the silica fume blended cement with the incorporation of encapsulated sodium silicate. Thus, the use of pozzolan in the OPC system with encapsulated sodium silicate improves the autogenous self-healing ability of cementitious composites.

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