Synthesis of Calcium Nitrate Self-Healing Microcapsules Using Aerosol OT-Hexane Solution for Cementitious Materials

Ala Abu Taqa
Department of Civil Engineering, Munib and Angela Masri Faculty of Engineering,
Aqaba University of Technology, Aqaba-Jordan
aabutaqa@aut.edu.jo; aa1104819@student.qu.edu.qa

Ghassan Suleiman
Department of Civil Engineering, Munib and Angela Masri Faculty of Engineering,
Aqaba University of Technology, Aqaba-Jordan
GSuleiman@aut.edu.jo

Ahmed Senouci
Department of Construction Management, University of Houston, Houston, USA
asenouci@central.uh.edu

Mohamed O. Mohsen
Department of Civil and Architectural Engineering, Qatar University;
Tajarub Research & Development, Doha, Qatar
200202128@student.qu.edu.qa, Mohamed mohsen@tajarub.org

Abstract

Calcium nitrate synthesis of in urea-formaldehyde shell has recently been used to produce self-healing microcapsules for construction applications. The original synthesis was based on water-in-oil emulsion with sulfonic acid as fundamental ingredient of the oil (continuous) phase. It has been modified herein by changing the composition of the continuous (oil) phase by mixing anionic surfactant, Aerosol OT (AOT) with hexane to prepare the solution while keeping the aqueous phase unchanged. The submicron refined calcium nitrate microcapsules. In order to characterize the microcapsules encapsulated using the aforementioned, procedure, a Scanning Electron Microscopy (SEM) was utilized. The obtained microcapsules had satisfactory diameter and shell thickness. To assess the effect of the prepared microcapsules on the compressive and flexural strengths, mortar mixes containing 75% microcapsules (by weight of cement), as an introductory dosage, were made. It has been demonstrated that incorporating the self-healing microcapsules prepared using the procedure suggested in this study did not cause significant reductions in the mortar samples' strengths. Hence, the encapsulation methodology presented here may be utilized to investigate their self-healing efficiency in cementitious materials.

Keywords: Self-healing Microcapsules; Calcium Nitrate; Aerosol; Hexane; Cementitious materials; Compressive and flexural strengths

1 Introduction

Lately, microencapsulation has been extensively adopted to generate microcapsules that have been effectively used in various specialities such as pharmaceuticals, catalysts, electronics, etc. Arefin et al., (2020), Gao et al., (2021), Patil & Bendre (2022), Vintila et al., (2020). Moreover, self-healing microcapsules have been recently utilized to repair concrete structures Al-Ansari et al., (2017), Fayyad et al., (2016), Hassan et al., (2016), Huang & Ye (2011), Kaes et al., (2014), Milla et al., (2016), Mostavi et al., (2015), Podgornik & Šumiga (2008), Schlangen & Sangadji (2013), Van-

Tittelboom et al., (2011), (Van-Tittelboom & Belie, 2013), (Yang et al., 2011). When crack tips rupture microcapsule shells, the released healing agent forms the calcium-silicate hydrate gels (C-S-H) by reacting with a catalyst to fill the cracks and prohibit their propagation.

In construction applications, different healing agents, such as polyurethane and Sodium silicate, have been prosperously selected as healing agents, Maes et al., (2014), Pelletier et al., (2022), (Van Tittelboom et al., 2011). Due to the high costs of such agents, Hassan et al., (2016) attempted to encapsulate the calcium nitrate (as a low-cost material) into urea-formaldehyde shells, which exhibited satisfactory healing efficacy. However, incorporating these microcapsules into cementitious mixes caused compressive and flexural strengths reductions (Milla et al., 2016). Consequently, Hassan et al., (2016) proposed a modification to their original encapsulation procedure to mitigate strength reduction by using a low-Hydrophilic-Lipophilic (HLB) emulsifiers (such as Span 85 and Span 60) to replace the sulfonic acid catalyst, partially (Al-Ansari et al., (2017), Milla et al., (2016). The micro capsules caused a 40% reduction in the elastic modulus for mortar samples incorporating Span 85 (Al-Ansari et al., 2017). On the other hand, the microcapsules using Span 60 had less healing efficiencyin steel-fiber concrete mixes than the micro capsules synthesized using the original procedure (Milla et al., 2016).

Extensively in literature, various oil and water emulsions have been prepared using the anionic surfactant, Dioctyl Sodium Sulfosuccinate (Aerosol-OT, AOT) Aveyard et al., (1986), Hensel

et al., (2017), (Kalyanram et al., 2017), (La Mesa et al., 1992). The dominant advantage of AOT is that it does not need any other co-surfactant to effectively form aggregates in non-polar solvents. This makes AOT more appropriate for the preparation of water-in-oil emulsions than other surfactants (Kizling & Kronberg, 2001), (Leong & Candau, 1982). Accordingly, researchers had successfully used AOT in hexane solutions to synthesize different nano particles (Eastoe et al., (1991), Gupta & Gupta (2004), (Kizling & Kronberg, 2001), (Srivastava et al., 2011).

The paper presents a new modification to the encapsulation procedure of calcium nitrate as a self-healing agent that were proposed by Al-Ansari et al., (2017) and Hassan et al., (2016) to produce refined and smaller size microcapsules with no significant undesirable effects on the cementation's materials' mechanical properties. Such modification utilized the AOT to stabilize the continuous phase (hexane solution) while the aqueous phase components were kept unaltered. After that, the Scanning Electron Microscopy (SEM) was used to recognize the microcapsule's characteristics (shell thickness and diameter). Moreover, the effect of incorporating such microcapsules on the 7 day mortar compressive and flexural strengths was also assessed.

Based on the results, it has been recommended to direct future tests towards investigating the strengths of large concrete samples at different ages with incorporating different dosages of the prepared self-healing microcapsules.

2 Methodology and Design of Experiment

2.1 Preparing the Microcapsules

2.1.1 Synthesis

The procedure suggested by Hassan et al., (2016) for preparing the self-healing microcapsules forms the basis of this study. Calcium nitrate was utilized as the healing agent, encapsulated in a shell consists of urea and formaldehyde and polymerized in a water-in-oil emulsion. As per the original encapsulation procedure, the aqueous phase has been prepared by dissolving 10 grams of the calcium

nitrate, 0.5 grams of the resorcinol, 0.5 grams of the ammonium chloride, 12.67 grams of the formaldehyde and 5 grams of urea in filtered water. However, the components of the continuous phase were changed by mixing 5.8 grams of AOT with 180 grams of Hexane as an organic solvent.

2.1.2 Emulsification and Polymerization

40°C and 1500 RPM elevated temperature and shear rate, respectively, were used to stir the constituents of the continuous phase as suggested by (Hassan et al., 2016) and (Milla et al., 2016). Drops of the aqueous phase have been added to the continuous over 10 minutes. The emulsion was kept to react for 1.5 hours and then, it has been left to settle for few minutes. After settling, the hexane was poured and the produced microcapsules were spread on a wide pan for air drying.

2.2 Characterization by the Scanning Electron Microscopy

The characteristics of the microcapsules (i.e. diameter, shell thickness, shape…etc.), have been assessed by the scanning electron microscope (SEM) imaging technique. A tape with double sides tape was attached to a stubbed mount and the microcapsules were dispersed on top of such tape. Platinum was then used to cover the microcapsules for four minutes. Finally, a secondary electron mode of a 3 kV accelerating voltage was used to capture the images.

2.3 Testing of Mortar Samples

Three mortar mixes were made in this study. The first mix was considered as the control mix (normal mortar without microcapsules). The second and the third mixes incorporated a dosage of 0.75% (of cement weight) as the microcapsule's dosage, with the former being produced using the encapsulation procedure without AOT and the latter being produced using the proposed procedure in this study (with AOT). 740 grams of Portland cement CEM I Class 42.5 R were mixed with 2035 grams of natural sand and 359 grams of water. No microcapsules have been added to the control mix while 5.55 grams of microcapsules prepared using the original procedure have been incorporated to the second mix and same amount of the microcapsules prepared using the procedure proposed in this study have been added to the third mix.

From each mix, three standard mortar cubes (50mm x50 mm x50 mm) and three standard prisms (40 mm x 40 mm x 160 mm) were casted. The testing matrix is summarized in Table 1. After 24 hours, the casted samples were demolded and tested at 7 days for compressive and flexural strengths as per ASTM C109 and ASTM C348, respectively.

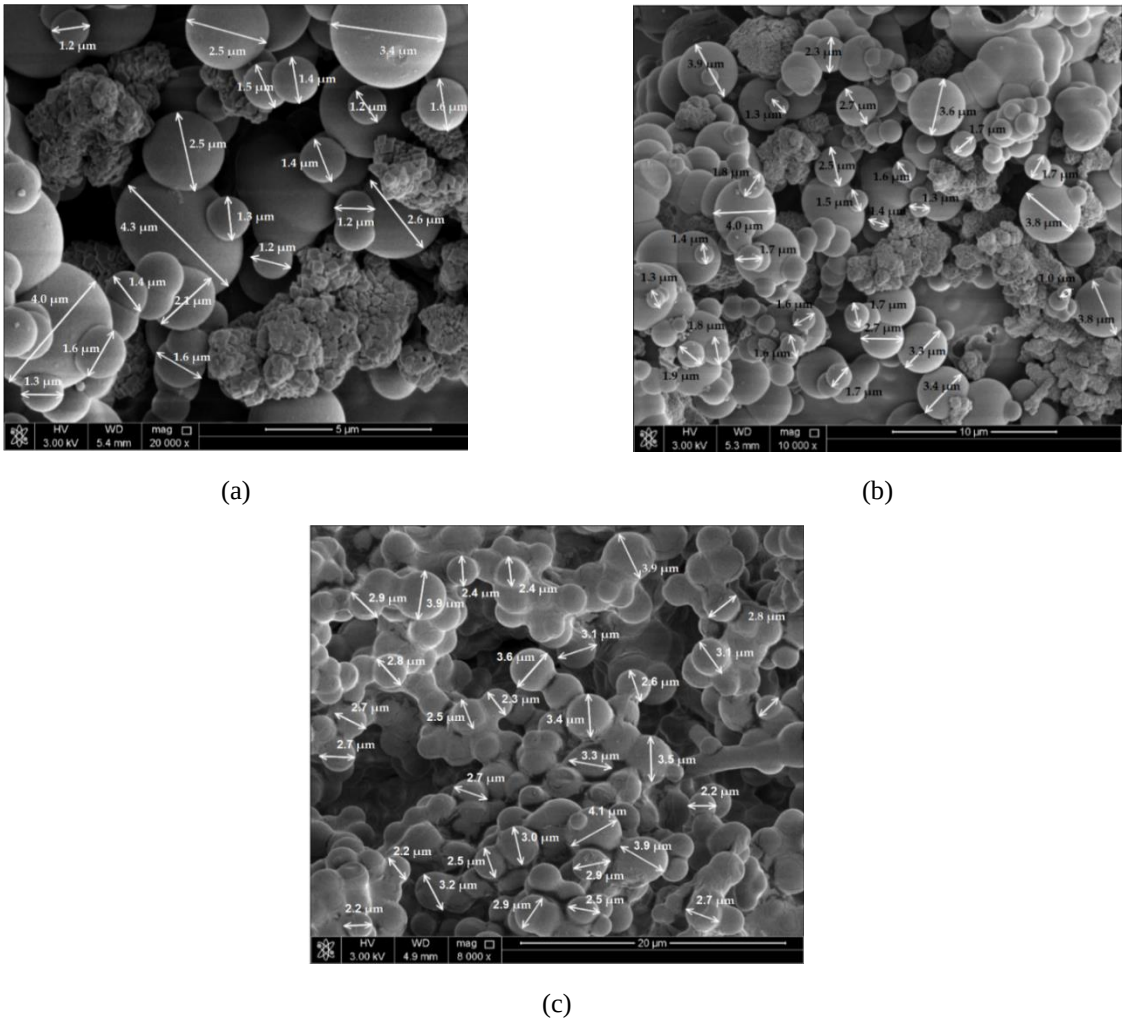
Table 1: Testing matrix of mortar samples

Mix No.	Batch ID.	MC dosage (% of the cement weight)	Samples for the compression testing	Samples for the flexural testing
Without MC (Control)	1	0.00	3	3
	2		3	3
With 0.75 MC (non-modified procedure, without AOT)	1	0.75	3	3
	2		3	3
With 0.75 MC (with AOT)	1	0.75	3	3
	2		3	3

3 Discussion Of The Results

3.1 Microcapsules' SEM Imaging

Figure 1 shows the prepared microcapsules' diameters at different imaging scales. A round more than 150 microcapsules were selected randomly from the images and the average diameter value of all of them was calculated. It has been found that the produced microcapsules had diameters in the range of 1µm to 5 µm and an approximated average diameter of 2.5 µm. Such values are smaller than the same of the microcapsules prepared using the procedures developed by (Al-Ansari et al., 2017) (70 µm) and (Hassan et al., 2016) (51 µm). A perfectly spherical and uniform shape of the produced microcapsules could be also noted in Figures1 (a-c).

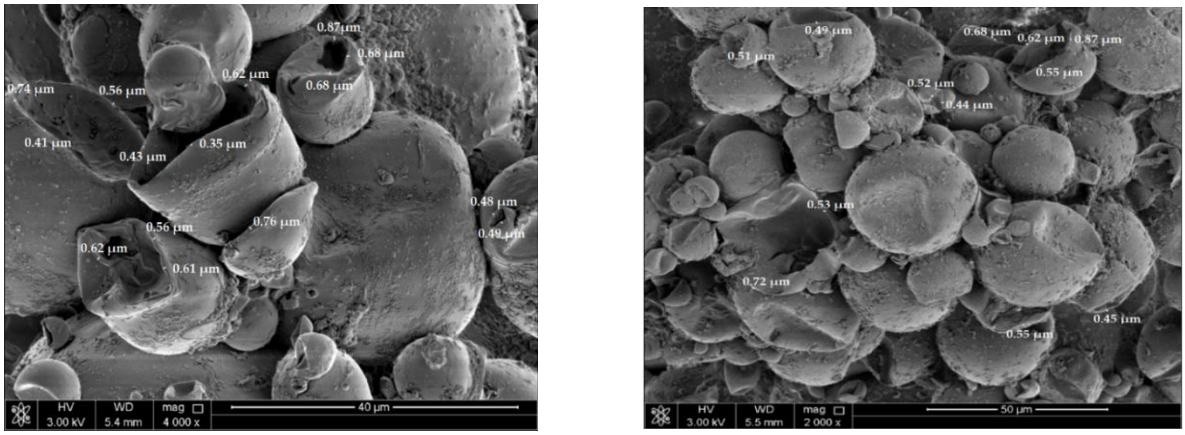


(a) (b)

(c)

Fig. 1: SEM images of the prepared microcapsules showing their diameters at different imaging scales (a) 5 µm (b) 10 µm (c) 20 µm

From Figure 2, the shell thicknesses of the prepared microcapsules could be approximated. As shown in Figures 2 (a) and (b), the shell thicknesses of randomly selected microcapsules were between 0.35 µm to 0.70 µm with an approximated average shell thickness of 0.60 µm. Such values are also smaller than the same which have been recorded by Al-Ansari et al., (2017) (0.80 µm) and (Hassan et al., 2016) (0.90 µm). This observation may support a conclusion that the efficiency of the self-healing of the AOT microcapsules be enhanced because the thinner shell thickness is easier to be ruptured by the crack tip when the cracks are initiated in cementitious elements.



(a) (b)

Fig. 2: SEM images of the prepared microcapsules of the prepared microcapsules showing their shell thicknesses at different imaging scales (a) 40 µm (b) 50 µm

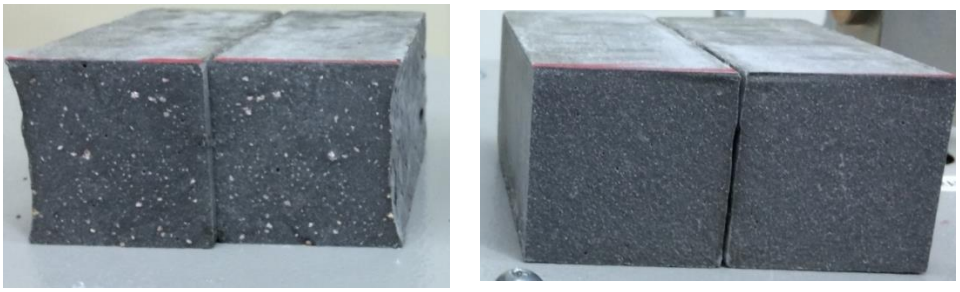
3.2 Testing the Compression & Flexural Strengths

As aforementioned, 6 mortar samples were tested for compression from each mix and same for the flexural strength. ASTM E178 standard was used to check the outlier observations and exclude them before computing the average values.

For the second and third mixes (containing microcapsules) and regardless the microcapsules preparation procedure, it has been found that the reductions in the compressive strength values (compared to the control mix that does not contain microcapsules) were very small and could be neglected (0.34% for the second mix and 0.27% for the third mix)

However, for the flexural strength, it could be found that the average reduction in the flexural strength values for the second mix (which contains microcapsules prepared with the non-modified procedure, without AOT) was about 15.3% which may be considered significant. On the contrary, the average reduction in the flexural strength's values was only 0.31% for the third mix (which contains microcapsules prepared with the modified procedure suggested in this study (with AOT)). Such results suggested that utilizing AOT for the polymerization of the self-healing microcapsules will decrease the undesirable effects on the cementitious mixes' strengths and mechanical properties.

After carrying out the flexural test on the mortar prisms, pictures of the fracture surfaces have been captured as shown in Figure 3. From the visual observation of such pictures, one may conclude that the distribution of the modified microcapsules (with AOT, Figure 3 (b)) was more uniform and the microcapsules sizes were smaller compared to the pictures of the samples containing microcapsules prepared with the non-modified procedure (without AOT, Figure 3 (a)). Such observation strengthens the results demonstrated previously in this study that using AOT for the synthesis of microcapsules results in refined microcapsules which may enhance the physical, chemical and mechanical properties of the cementitious mix.



(a) (b)

Fig. 4: Images of the Prisms' Fracture Surfaces after Flexural Strength Testing (a) Sample Incorporating microcapsules Prepared using the Non-Modified Procedure (without AOT) and (b) Sample Incorporating microcapsules prepared using the Modified Microcapsules (With AOT)

4 Conclusions

From this study, the following points could be concluded:

- The modified microcapsules prepared in this study (with AOT) had diameters in the range of 1.0 µm to 5.0 µm and an approximated average diameter of 2.5 µm. Such values are smaller than the same of the microcapsules prepared using the previous encapsulation procedures. Perfectly spherical and uniform shape microcapsules were obtained.
- The shell thicknesses of randomly selected microcapsules prepared using the procedure presented in this study (with AOT) were found to be in the range of 0.35 µm to 0.90 µm with an approximated average shell thickness of 0.60 µm. Such values are also smaller than the same of the microcapsules prepared using the previous encapsulation procedures. This observation may support a conclusion that the efficiency of the modified self-healing microcapsules (with AOT) may be enhanced because the thinner shell thickness is easier to be ruptured by the crack tip when the cracks are initiated in cementitious elements
- For the mix containing the modified self-healing microcapsules (with AOT), the average reductions in the compressive and flexural strengths of mortar mixes at 7 days were only 0.27% and 0.31%, respectively (which could be neglected). This observation demonstrates that using AOT for the synthesis of self-healing microcapsules can decrease the potential unfavourable effects on the cementitious mixes' mechanical properties in general and the flexural strength in particular.
- Using AOT for the synthesis of microcapsules results in refined microcapsules which may enhance the physical, chemical and mechanical properties of the cementitious mix.

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