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RESEARCH ARTICLE

THE NANOCAPSULE WITH POLYMER CORE AND SILICA COATING AS CEMENT ADDITIVE FOR CONCRETE WITH SELF HEALING PROPERTY

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ABSTRACT

Nano silica, a new pozzolanic material, due to having a high specific surface, constitutes a strong adhesion agent in concrete and like pozzolan, fills the micro fractures and capillary pores, and thus increases the density, reduces the permeability, and enhances the strength and durability. But in the event of fracturing of the already treated concrete, the nano silica treatment appears to perform poorly.Thus, in the current work, a new nano silica type material with polymer core and silica shell – the nanocapsule – was introduced together with the synthesizing procedure. In order to investigate the improvements that nanocapsulecould do to the concrete properties, such as self-healing, specimens with 10 percent cement, with and without thenanocapsule treatment, were put to tests. Fractures were introduced by subjecting the specimens to 150 cycles of freezing and thawing before being evaluated for durability and strength using the ultrasonic pulse velocity and the compressive strength tests. FESEM imaging was carried out on a healed fracture and on nanocapsule while TEM imaging was carried out on nanaocapsule in order to appraise the formations at microstructure level. The ultrasonic pulse velocity and compressive strength were both found enhanced in the case of treated specimens. With increasing time, the ultrasonic pulse velocity for fractured, treated specimens was found approaching that of the intact, treated specimens which is evidence of the self healing progress brought by the treatment. The microstructure images also proved the materialization of the nanocapsule.

INTRODUCTION

Pozzolans have gained a foothold among other additives in the effort of enhancing the properties of concrete. One of the new pozzolanic materials culminated from recent advances in nanotechnology was nano silica, which has been used to treat the problems of cracking in concrete. Crack appearance is due to change in volume from various reasons, but the most common is freezing and thawing, that may affect the strength and durability in the long term. Nano silica, due to having a high specific surface, constitutes a strong adhesion agent in hydrated cement and like pozzolans, fills the micro cracks and capillary pores, and thus increases the density of cement, reduces the permeability, and enhances strength and durability. But in the event of cracking of the already treated concrete, the nano silica treatment appears to perform poorly. However, the new advances in nanomaterial technology havecreated even new materials by enhancing the properties of nano silica through various modifications.

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The discovery of some of theadvantageousnano scale properties has led to widespread use of the new additiveswith increased specific surface for each particle, resulting in concretes with enhanced engineering qualities, improved hardness, and better flexibility (Ouhadi, 2012 and Ouhadi, 2011). The potential objectives of nanomaterial application are quite considerable - some of them are as follows (Ouhadi, 2011 and Lines, 2008):

- To solveenvironmental problems,
- To produce materials and products with exceptional properties, and
- To benefit the downstream applications.

Infact, in each of the resulting materials coming from theapplication ofnanomaterial technology, interestingnew properties have been realized (Ouhadi *et al*., 2012; Ouhadi, 2011 and Lines, 2008). Thus creating a new initial condition that spurs further development. Cementis a substancethatsticks together concrete components and has been widely used in civil engineering practices (Senff, 2009 and Hui, 2004). Cement is itself a nanomaterial as the strengthanddurabilityof

concretestructuresis determinedby themicrostructureandmass transportof materials at the nanoscale levels where thephysical and chemical propertiesof cementcansignificantlyimprove with the use of the additives (Hui, 2004; Monteiro, 2009; Ke, 2005). A decreaseinthe particle sizeof cementincreases the electrostatic force and specific surface area of the particle, resulting in a harder concrete (Ke, 2005; Aiu, 2006; Hanehara, 2001). Anincreaseinnano silica content in cementincreases the compressive strength, especially in the early age of curing (Ginebra, 2004; and Nazari, 2010). Studies also show that compressive and flexural strengthsof cementmortarsmodified withorganicnano silicaare better than the conventional cementmortars (Nazari, 2010 and Wen-YihKuo, 2006). Nano silica particles that are mixeduniformly incement paste during mixing enhances the hydration rate, contributing to an increased strength (Ye Qing, 2007). A concrete, prepared with nano silica additives is resistant to permeability, durable, and more resistant to penetration by sulfate ions (Byung-Wan Jo, 2007 and Hui Li, 2004). The formation of fracturesduring the lifetimeof aconcrete, however isinevitable and is the main contributor to the weakening process of the structure. Fracturescould come from excessiveloading, volume change, temperature change, cycles of freezing and thawing, creep, poorconstruction, deterioration mechanism, and improperdesign. The self-healing mechanisms brought about by nano silica additives are very much affected by fracture widths in concrete among others, which have become the subject of study in many researches (Hui Li, 2004 and Tao Ji, 2005). Hence itis highly desirable if such concrete that repairsitself from fractures can be developed. Inrecent years, research onself-healing concrete using poroushol low tubesorglasstubes has been carried out (Campillo et al., 2007 and Kanl, 2010; Yang, 2009 and Brown, 2004), but no attention has been paid to the self healing mechanisms brought by the additives. The purpose of the current paper istopresent some findings associated with the use of a new additive thatincreasesthestrengthanddurability of concretewhile healing fractures at the same time - the nanocapsule - and to describe itssynthesis.

Preparation of the nanocapsule

The process of synthesizing a nanocapsulemainly involved embedding the styrene - a self-healing polymeric material – inside a silica coated sphere. The major steps followed were four, as given next and summarized in Fig. 1:

- First, in order to turn the self-healing material, i.e. styrene, into nano polystyrene, certain amounts of PVP and AIBA were mixed with acetone, with deionized water used as the reaction solvent. The mixture was brought to a good homogeneous suspension by 15 minutes of magnetic stirring. Next, styrene was added to the mixture and then kept for one hour at 24 °C. Then, the solution was further kept for 48 hours at 85 °C, during which the nano polystyrene core was formed. This step has involved an extensive program of trials and errors in producing the perfect nano polystyrene. All activities were carried out in an airtight chamber.
- Second, the formed nano polystyrene was isolated from water and acetone of the solution. The cellulose membrane with pores of various sizes, and shaped into small bags, was used in isolating nano polystyrene from the solution. Pure ethanol was added to the solution to assist the separation.
- Third, the TEOS was applied for coating the produced nano polystyrene particles. This stage was the most crucial as it involved the selection of a suitable coating, the outcome of which is the nanocapsule with silica coating
- Fourth, ammonia (NH_3) was added to the solution, followed gradually by more TEOS, and then kept for 3 hours at 50 °C. The obtained precipitate was isolated through centrifusion at 4000 rpm and was then washed 5 times with deionized water in order to remove the unreacted materials. The precipitate was kept in the oven for 250 minutes at 90 °C for drying. The obtained material was finally grinded by a ball mill.

Table 1. Components ofType II Portland cement of the Hegmatan Cement Factory, Iran

Components	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	LOI	C_3A
Mass by percent	21.37	5.03	3.88	63.15	1.55	2.17	0.65	0.45	1.95	6.76

MATERIALS AND METHODS

Materials

The commercially available materials namelythe styrene or St, thepoly (vinylpolypyrrolidone) or PVP, the tetraethyl lorthosilicate or TEOS, acetone, ethanol, and ammonia were obtained from an internationalchemical supplier –the Merck. The 2,20 Azobis (isobutyramidine) dihydrochlorideor AIBAandthe cellulose membranewere obtained from another supplier– the Sigma-Aldrich. The main cementitious material was Portland cement while the additive was thenewly synthesized nanocapsule. The Portland cement used was the Type II, of theHegmatan Cement Factory, Iran. The physical and chemical properties of the cement are shown in Table 1. Deionized water was used in the synthesis of nanocapsule and mixing of the concrete.

Preparation of Concrete specimens

The categories of specimens were as follows:

- Untreated, i.e. without the nanocapsule and intact, i.e. without the freezing and thawing cycles (SB)
- Untreated, i.e. without the nanocapsuleand fractured, i.e. with freezing and thawing cycles (SBC)
- Treated, i.e. with the nanocapsule and intact, i.e. without freezing and thawing cycles (SN)
- Treated, i.e. with the nanocapsule and fractured, i.e. with freezing and thawing cycles (SNC)

For each category, 10 specimens were prepared, thus there were 40 in all. Each specimen was a 10 cm by 10 cm by 10 cm cube. All were kept in a humidity chamber for a specified time at a temperature of 22±2 °C in order to avoid different temperature effects on the concrete strength (BS, 1881). In

order to evaluate the effect of using nanocapsule, specimens were prepared according the specification of Table 2.

by exposure to the surrounding air[24]. Once the 150 cycles of freezing and thawingcompleted, which took 150 days, the

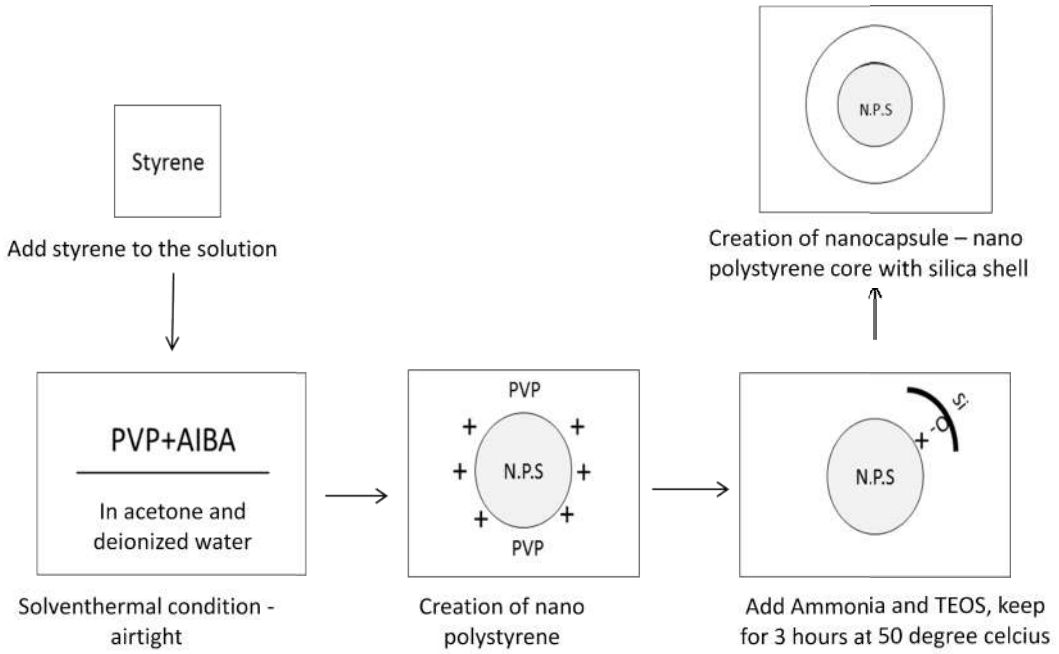


Figure 1. The synthesis of nanocapsulewith polymer core and silica coating

Table 2. The summary of mixture design for 1 m^3 of concrete

Material	Sand	Gravel (surface dried)	Superplasticizer	Water	Nano Capsule	Type II Portland cement of Hegmatan, Iran
Mass, kg	882.6	874.4	2.85	157.5	35	315

Table 3. A summary of tests carried out on the concrete specimens

	Categories			
	SB	SBC	SN	SNC
All specimens	10	10	10	10
Specimens put under UPV tests	10	10	10	10
Specimens put under compression tests	10	10	10	10
Specimens put under FESEM imaging	0	2 tests (before and after fracture on a specimen)	1	2 tests (before and after fracture on a statement)
FESEM imaging		For nanocapsule only (1)		
TEM imaging		For nanocapsule only (1)		

The nanocapsuleis a material with very high specific surface area for each particle unit and therefore there is a tendency for strong aggregation and dehydration, thus the naphthalene sulfonate was used as the superplasticizer. The aggregate used was gravel, with a maximum size of 5.12 cm while the sand was one passing sieve #4; both were saturated but surface dried. The specific gravity of gravel was 2.63 g/$cm^3$and of sandwas 2.51 g/cm^3.The mixture designs were in accordance to ACI211.2-98 with asand-to-gravel ratio of 1:1 and water-to-cement ratio of 0:45. The density of cement was 350 kg/m^3 and the nanocapsule addition into the mix was by replacing 10% of the mass of cement. The superplasticizer used was about 0.85% of the total mass of cementitious materials.

Testing of the specimens

In order to determine the durability of the specimens against cycles of freezing and thawing, 20 specimens – 10 with nanocapsule and 10 without nanocapsule - were subjected to the cycles of freezing, at between -14 and +4 °C, and thawing

specimens were tested for Ultrasonic Pulse Velocity (UPV). The UPV test is non-destructive, low cost, and easy to carry out. In the tests, pulses were sent out with a frequency of 54 kHz and the transmission time was displayed on a digital screen,accurate to 0.1 microsecond. For each specimen, 5 readings of the pulseswere carried out through different points on the cube adjacent surfaces in order to cover the entire specimen volume. The average of the results was recorded with UPV measured in km/s. The equation used was:

$$V=L/T \quad \text{……...(1)}$$

Where V being the velocity of pulse transmission in km/s, L being the length of transmission route in km, and T being the time of pulse transmission through the cube in second. In order to determine the strength of the specimens at 7 and 28 days, 5 specimens from each category were subjected to compression tests for each of the 7 and 28 days curing time.Finally, FESEM images were taken of a specimen, each from the SBC and SNC categories. The summary of tests on the specimens is given in Table 3.

RESULTS AND DISCUSSION

Morphology of Nanocapsule particles

FESEM analysis

The formation of polymeric nanocapsule, 30 to 50 nm in diameter, was verified by the Field Emission Scanning Electron Microscope (FESEM) image of Fig. 2 of the synthesized sample. Most of the particles had a fully spherical surface and a fully closed shell. However, it should be noted that the lengthened period of sulfonationhas led to theincreased polarity and symmetry of the surface, which in turn might have reduced the surface area of a particle that has collided with another.

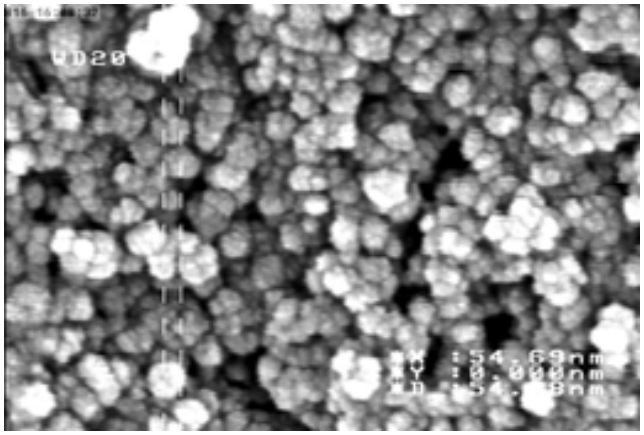


Figure 2. FESEM of the synthesized nanocapsule

TEM analysis

The Transmission Electron Microscope (TEM) has found widespread application across the scientific disciplines due to its unparalleled ability in providing structural and chemical information over a range of scales down to the level of atomic dimensions, thus has been used to investigate the properties of nano-structured materials (Smith, 1997 and Ernst, 1997). Thus the TEM imaging of synthesized nanomaterial was carried out resulting in the image given in Fig. 3, where the formation of polymer core is shown by the opaque centers and of the silica shell by the transparent surrounding. The size of a nanocapsule also shows the appropriateness of its name.

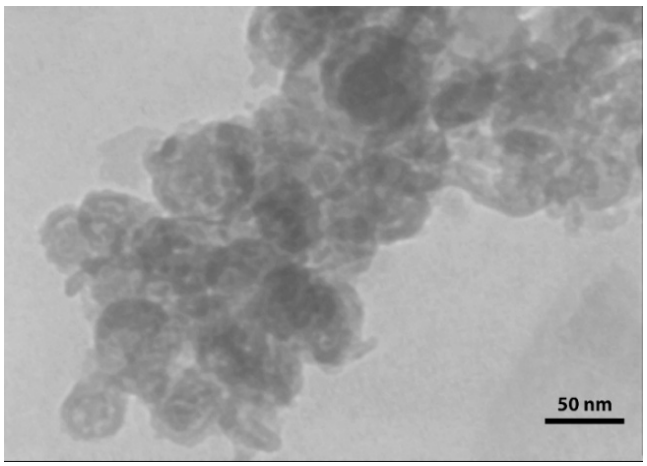


Figure 3. TEM of the synthesized Nanocapsules

Ultrasonic pulse velocity (UPV) tests onconcrete specimens

TheUPV of treated and untreated specimens are given in Table 4 and Fig 4. Each of the velocities given is the average out of readings on 10 specimens from each category. Specimens were either intact or fractured, and for each, either treated or untreated.

Table 4. Ultrasonic pulse velocity (UPV)

	7 days, km/s	28 days, km/s	Division product between 2 specific UPVs
SB	3.551	3.783	SB28days/SB7days=1.065
SBC	3.131	3.443	SBC28days/SBC7days=1.100
			SBC7days/SB7days=0.882
			SBC28days/SB28days=0.910
SN	4.266	4.429	SN7days/SB7days=1.201
			SN28days/SB28days=1.171
			SN28days/SN7days=1.038
			SN7days/SNC7days=1.060
			SN28days/SNC28days=1.027
SNC	4.025	4.314	SNC7days/SBC7days=1.286
			SNC28days/SBC28days=1.254
			SNC28days/SNC7days=1.072

Note: SB: intact and untreated
SBC: fractured by freezing and thawing and untreated
SN: intact and treated
SNC: fractured by freezing and thawing and treated

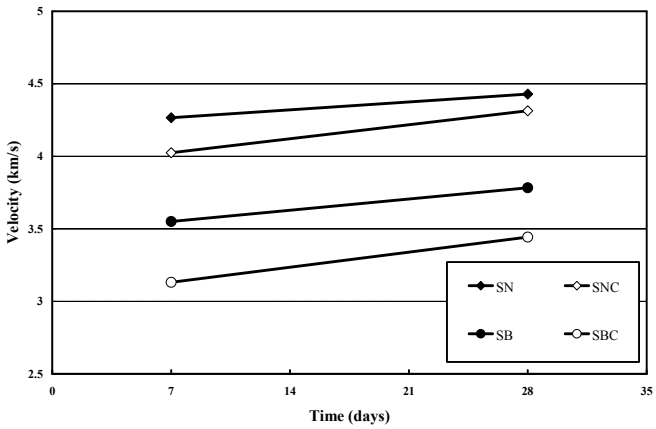


Figure 4. The results of UPV tests on specimens

For the intact, treated specimens, on Day 7, the UPV was faster by 20.1% and on Day 28, by 17.1% as compared to the untreated specimens, thus indicating the overall merit of the treatment. For the fractured, treated specimens, on Day 7, the UPV was intensified by 28.6%, while on Day 28, the velocity intensified by 25.4% as compared to the untreated specimens; thus also showing the treatment advantage although affected by the fracture from freezing and thawing. Overall, with curing time increasing from 7 days to 28 days,the UPV was found in general to have increased by 3.8 % in case of the intactand treated to 10.0 % in case of the fractured and untreated.For the fractured and untreated, on Day 7, the UPV waslesser at 88.2% of the intact and untreated; whileon Day 28, the UPV of the fractured and untreated was lesser at 91.0% of the intact and untreated. The development of micro-fractures in specimens due tocycles of freezing and thawingapparentlyhas led to the reduced overall UPV when compared to normal specimens. However, there was a small recovery in relative quality due to the curing as reflected by the slightly narrowing of the gap between the two bottom curves in Fig. 4 as time increases. For the fractured and untreated, the UPV on Day 28 was 10.0%

more than on Day 7, indicating an increased absolute quality with increasing time. In other words, with increasing curing time, the hardened concrete has caused a slightly faster UPV travel through the same fractured specimens. On Day 7, the UPV of the intactand treated was higher by 6.0% in comparison to the fractured and treated. On Day 28 however, the UPV of intact and treated was higher only by 2.7% in comparison to the intact and fractured. These results are portrayed by the topmost 2 curves in Fig. 4.With increasing time, the difference between the performances of the two categories of specimens has narrowed, thus verifying the exceptional treatment brought by the nanocapsule fracturedfractured concrete. Again by comparison, on Day 28, the fracturinghas reduced the UPV by about 9.1% for the untreated; such reduction in the treated was only 2.7%.

The progress of pozzolanic reactions and the formation of calcium silicate hydrate or CSH and calcium alumina hydrate or CAH have led to the decreasing concrete pores and therefore increased UPV for the treated specimens in general. Then, for the fractured, the UPV wasgenerally reduced. During the curing period, however, while the cement hydrates, the silica-coating of the nanocapsulescontributed to the pozzolanic reactions by having active silica in the concrete, the SiO_2, to react with calcium hydroxide or $Ca(OH)_2$,from the solution released into the capillary pores by the cement paste. The insoluble calcium silicate crystals formed in the pores created the dense structure of the cement paste, leading to areduced permeability and increased UPV. The proper activity of the nanocapsule core as a self-healing material can be realized as soon as the micro or nano cracks appeared during freezing and thawing cycles. In these circumstances, the nano-styrene repairment mechanism was released by the nanocapsule. The nano-styrene preventedfrom enlargement of the transverse and longitudinal opening of the fractures while repairing them. Based on the results, the hypothesis of self-healing can be further explained as follows: Throughout the process of cement hydration at nano scale level, the nanocapsule was involved in the first place leading to the reduced permeability of the hydrated cement. The silica-coating of the nanocapsule engaged in pozzolanic reactions of the cement hydration. Strong linkage between nanocapsule and blended cement can be traced to the large contact surface between the two. After undergoing freezing and thawing cycles, conditions that have created the micro-cracks, the nanocapsule released the repair material in response to the creation of the cracks. The concrete, therefore wasrepaired in a smart way when the proper opportunity for engagement was made available.

Compressive strength tests on concrete specimens

The compressiontests were carried out on treated and untreated specimens that have been cured for 7 and 28 days, the results of which are given in Fig. 5. On Day 7, the strength of the treated specimen was 78.3% higher than the untreated specimen, while on Day 28 the strength of the treated specimen was only 54.8% higher. In these cases of intact and treated concrete, the nano-silica, through pozzolanic reactions, has performed efficiently by filling tiny pores. The active silica was combined with the released calcium hydroxide from the cement paste in the capillary pores producing insoluble calcium silicate crystals, which ultimately lead to the dense structure of the cement paste and increased the compressive strength. For the fractured and untreated, on Day 7, the compressive strength was lesser, at 77.3% of the intact and untreated. On Day 28, the compressive strength of the fractured and untreated was 82.2% of the intact and untreated.

Table 5. Compressive strengths

	Day 7, MPa	Day 28, MPa	Division product between 2 specific Compressive Strengths
SB	22.4	31.83	SB28days/SB7days=1.421
SBC	17.31	26.15	SBC28days/SBC7days=1.511
			SBC7days/SB7days=0.773
			SBC28days/SB28days=0.82.2
SN	39.94	49.26	SN7days/SB7days=1.783
			SN28days/SB28days=1.548
			SN28days/SN7days=1.233
			SN7days/SNC7days=1.055
			SN28days/SNC28days=1.033
SNC	37.86	47.67	SNC7days/SBC7days=2.187
			SNC28days/SBC28days=1.823
			SNC28days/SNC7days=1.259

Note: SB: intact and untreated
SBC: fractured by freezing and thawing and untreated
SN: intact and treated
SNC: fractured by freezing and thawing and treated

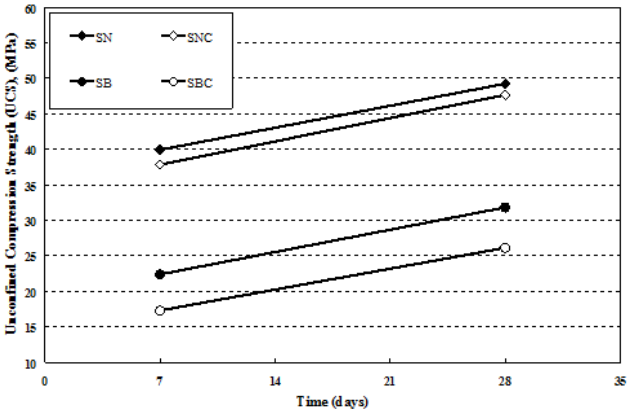


Figure 5. The unconfined compressive strength of the specimens tested

In contrast, for the fractured and treated, on Day 7, the compressive strength was higher at 169% of the intact and untreated. On Day 28, the compressive strength of the fractured and treated was not as high but at 150% of the intact and untreated. Thus, the desirable outcome of using the nanocapsule was demonstrated even in fractured concrete.

Observation of a microcrack by SEM

SEM images were captured of treated and untreated specimensbefore and after fracturing by cycles of freezing and thawing. Fig 6 shows the image of atreated specimen surface showing the inactive nanocapusule unitsdue to specimen lacking a crack. In this case, the nanocapsule has only contributed to the hydration process and the cement pozzolanic reactions, contributing to the formation of hydrated calcium silicate gel. The fractured surface of a treated specimen after exposure to 150 cycles of freezing and thawing is given in Fig. 7(a). The self healing progression, i.e. the release of nano polystyrenes and their structural growth into extended plumes, can be seen to have taken place. The nanocapsule at first crowded the fracture zone by creating intense pozzolanic activity characterized by the presence of a dense calcium

silicate hydrated gel structure on the one hand and the extremely high microfilling property of these particles on the other.

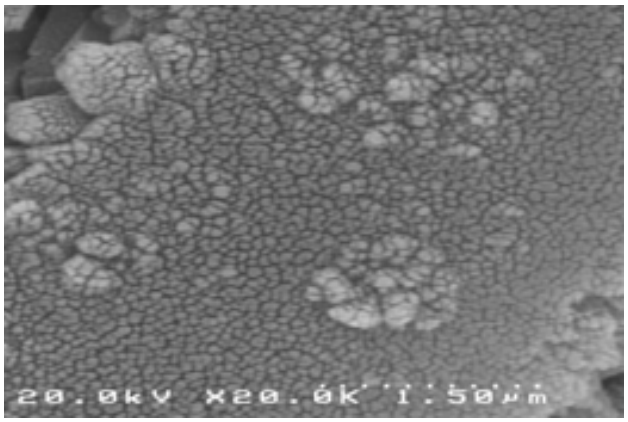
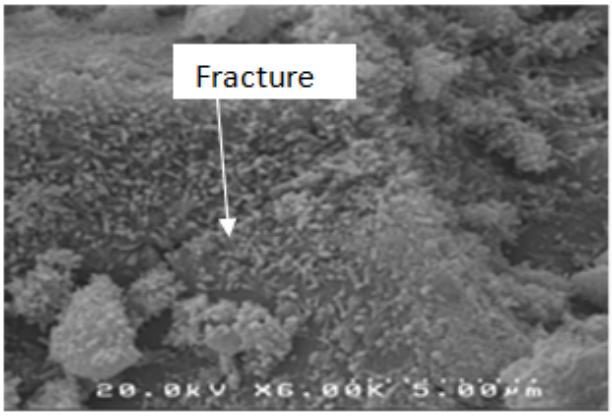
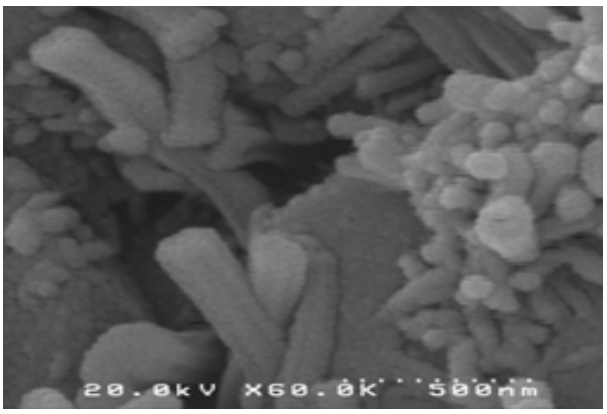


Figure 6. The surface of an intact and treated specimen

The nano polystyrenes can be clearly seen in Fig 7(b) in the form of extended plumes crowding a crack.



(a)



(b)

Figure 7. a) The fractured surface of a treated specimen after exposure to 150 cycles of freezing and thawing showing release of nano polystyrenes at the onset of a nanocapsuleactivityb) Formation of extendednano polystyrene plumes inside a crack

Conclusions

The following conclusions were derived from this study:

- The use of nanocapsule brought two sequential benefits. In the first stage, it improved the strength and durability of the concrete. In the second stage, under specific circumstances, it delivered the remedial materials to the cracks in the concrete.
- The merit of using nanocapsule was proven by both, higher compressive strength and higher UPV, even for the fractured specimens as compared to the intact, untreated specimens that were kept under normal condition.
- The specific surface area was an influential factor contributing to the pozzolanic reaction rate. This aspect has caused the nanocapsuleto react strongly with the limestone content of the cement, especially during the early period of curing.
- The production of cement with nanocapsule content may require a great deal of investment in terms of acquiring the special and new machineries, but the potential return could also be equally immense due to the unique property of the material.

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