Isophorone Diisocyanate (IPDI) Microencapsulation for Self-Healing of Cementitious Materials

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Abstract:

Since cementitious materials are brittle, they are prone to cracking. Cracks could be healed via autogenous methods namely healing microcapsules.The objective of this study was twofold. First, microencapsulation of isophorone diisocyanate (IPDI) as a catalyst-free healing agent. Second, evaluation of microcapsules effect on promotion of cementitious materials healing capability. PU prepolymer was synthesized and smoth spherical microcapsules of IPDI with average diameter of 48-62 μm were produced successfully. The microcapsules shell wall thickness varied linearly with microcapsule diameter and so, the shell wall thickness to diameter ratio was constant ($\sim$0.04).The microcapsules weight loss in a 6 months period was $\sim$12.47% under ambient conditions. The mortars containg 3% of their cement weight IPDI microcapsules, had up to 74% recovery rate of compressive strength while this rate for control mortars (with no microcapsule) were less than 50%.

EDS analysis of healed mortars, showed noticable amount of carbon in the areas of ruptured microcapsules and healed cracks, confirming that healing process had been precisely accomplished according to the theory of self healing assumed.

Samples containig micocapsules had higher initial compressive strength in comparison with control ones, indicating that there had been an undesired rupture of portion of microcapsules during prepartion and molding of specimens. This demonstrated need of more studies and work on mechanical properties of microcapsules specially stiffness of those used in cementitious composites.

Keywords: Microcapsules, Microencapsulation, Isophorone diisocyanate (IPDI), Self-healing, Cementitious Materials.

1.Introduction

One of the major challenges of developed countries in recent years is unprecedented deterioration of infrastructures. In some cases, the annual expense of maintenance and repairment of such structures, has exceeded the cost of new infrastructures construction. In the U.S, its estimated that financial impact of maintaining, repairing or replacing deteriorating structures hits the record of $21 billion annually [1].Meanwhile more than half of funds were used for such issues in Europe [2]. Beside the large amount of financial resources needed for inspection, monitoring, maintenance and repairing of these structures, apply of such amount of workforce to accomplish these affairs just in time, has become a great challenge due to pandemic and social riots.

Deterioration of Concrete, as the most widely applied material in construction of infrastructures, is of great concern. It could be the result of several environmental factors which attack the material chemically or physically. Development of cracks would ease

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penetration of harmful substances into the structure and accelerate deterioration as the result [3].

Several approaches have been proposed to elevate cementitious materials' stability and durability through healing systems. These approaches may be broadly classified into five major categories : (1) chemical encapsulation, (2) bacterial encapsulation, (3) mineral admixtures, (4) chemical in glass tubing, and (5) intrinsic self-healing with self-controlled tight crack width [1].The concept of microcapsule healing is based on encapsulation of a healing agent and embedding microcapsules in the concrete [4].As the crack propagates and hits the microcapsule, microcapsule breaks and the healing agent gets released. Penetration of healing agent into the crack starts healing process of the concrete.

Different materials, as healing agent, have been evaluated in encapsulation process in recent decades, including methyl methacrylate, ethyl cyanoacrylate, sodium silicate, polyurethane, epoxy [5-10]. Despite the promising results achieved in some of the studies, most of these materials are not applicable, since they are so expensive and/or there are difficulties in production, transfer and use of them in real scale.

1-1- Objectives

The objective of the study was twofold. First, an experimental program was run to investigate the potential of encapsulation of diisocyanate monomer via interfacial polymerization, and to study and monitor the effects of preparation parameters (namely agitation rate) on size, morphology of microcapsules. Second, microcapsules effect on concrete's healing was evaluated in order to identify effectiveness of such microcapsules application in promotion of cementitious material's healing capability.

1-2- Background

Among so many proposed autonomic healing systems, chemical encapsulation is appealing due to three main characteristics it has: (1) its versatility, this approach facilitates apply of variety of healing agents in wide range of sizes between micrometer to nanometer and use of them in variety of infrastructures, because the healing process is independent of the external ambience;(2) its potential of a long shelf life, although it also depends on the specifics of the agent encapsulated and physical properties of shell wall; and (3) its pervasiveness which provides capability of adding capsules directly to the mixture, remaining intact during mixing process [1].

Self-healing of polymer composites based on microcapsules first proposed in 2001 [11].After that many researchers adopted the idea for promoting self-healing capability of cementitious composites .The concept of self-healing of cementitious materials using catalyst-free, polymer base microcapsules is illustrated in Fig.1.When a crack develops and hits the microcapsules, microcapsules break and healing agent releases. Released healing agent fills the crack, and in contact with the moisture of the ambience, healing agent becomes polymerized.

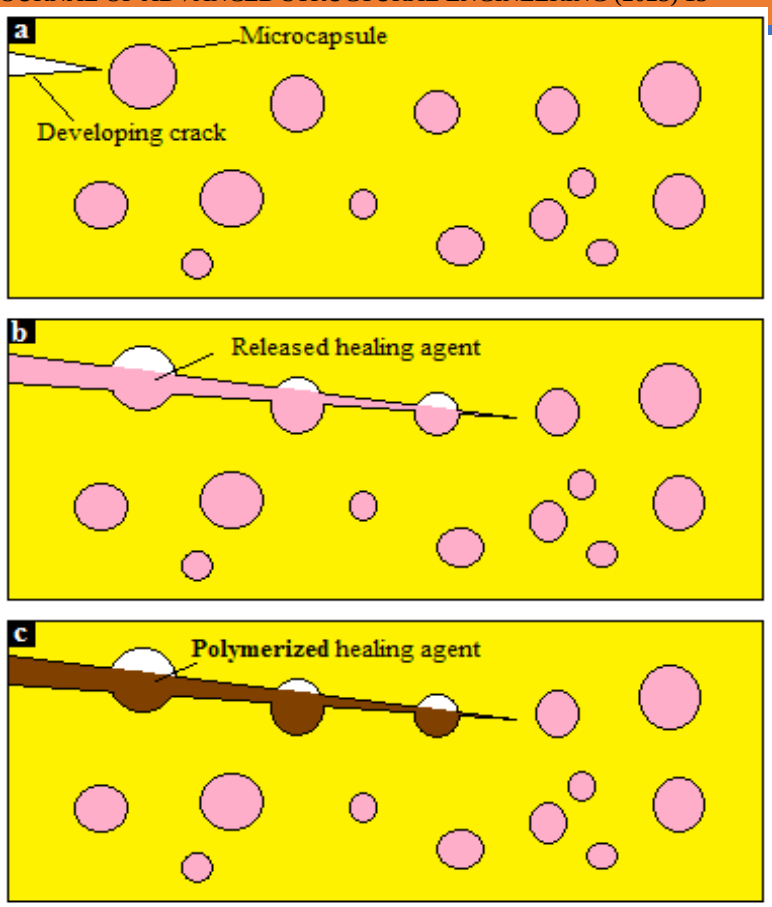
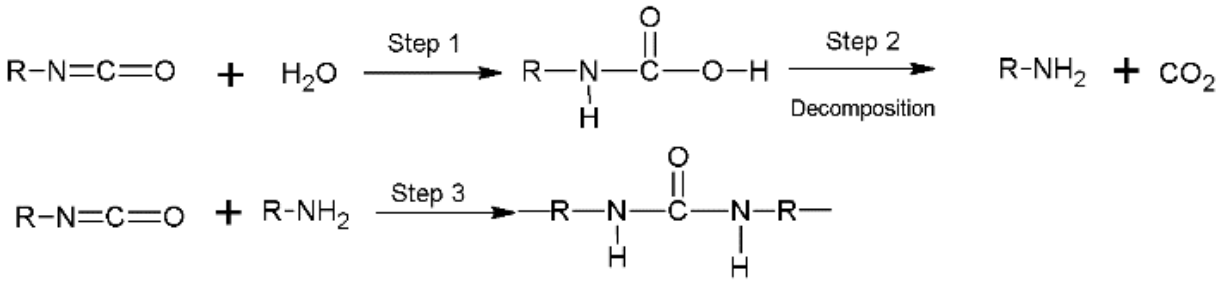


Fig.1. Schematic illustration of the self-healing concept of cementitious materials using catalyst-free polymer-base microcapsules: (a) Microcapsules dispersed in cementitious material while crack is developing, (b) The crack hits the microcapsules and the healing agent releases and fills the crack, (c) In contact with the moisture of the ambience, the healing agent becomes polymerized.

Du encapsulated TDI in composite shell for self- healing of cementitious materials [12]. Beglarigale encapsulated sodium silicate in polyurethane shell to apply in self-healing of cementitious materials [13].Giannaros encapsulated sodium silicate solution in gelatin-gum Arabic shell and solid sodium silicate in polyurethane shell to seal cracks in cement [14].Milla evaluated the effects of calcium nitrate microcapsules on concrete properties [15] . Dong applied urea-formaldehyde/epoxy microcapsules for self-healing of cementitious materials [9]. Yang prepared oil core/silica gel shell microcapsules to apply for self-healing in cementitious composite[10].



.Fig.2. Chemical reaction scheme of isocyanate with water.

In this research, we synthetized isophorone diisocyanate (IPDI) core/PU shell microcapsules as the healing agent. Encapsulation of liquid-phase diisocyanate accomplished via interfacial polymerization in stabilized aqueous emulsion. Chemical reaction scheme of isocyanate with water, is shown in Fig.2. The main reason persuaded us toward choosing this material as healing agent was that, despite many other healing agents applied in previous studies, IPDI is a monomeric aliphatic diisocyanate which is reactive with water and, therefore, there is no need to a catalyst to be added to the matrix either directly or through encapsulation [16]. Synthesis of polyurethane prepolymer using 1,4-butanediol and synthesis of polyurethane microcapsule shell using 1,4-butanediol are demonstrated in Fig.3. Characteristics of prepolymer and microcapsules were studied and microcapsules capability of recovering mechanical properties of damaged mortar was evaluated.

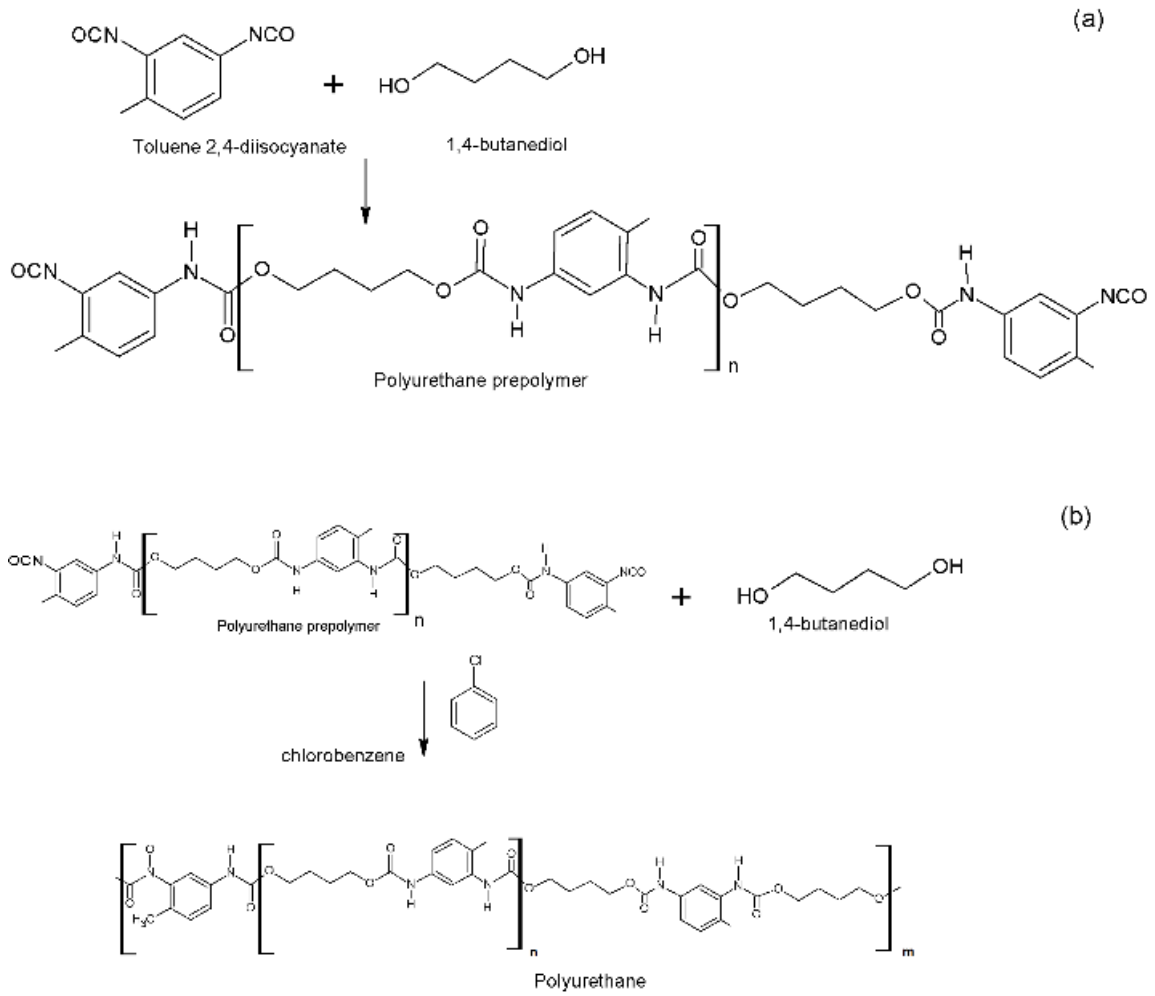


Fig.3. Synthesis of: (a) polyurethane prepolymer using 1,4-butanediol, (b) polyurethane microcapsule shell using 1,4-butanediol.

1. Experimental

Microcapsules were fabricated via interfacial polymerization of polyurethane (PU). Toluene diisocyanate (TDI) prepolymer was first prepared as constituent material of shell wall and then microcapsules were synthesized. All chemicals were purchased at reagent grade and no further purification were done.

2-1- Materials

Toluene 2,4-diisocyanate (TDI), cyclohexanone, 1,4-Butanediol (BD), isophorone diisocyanate (IPDI) and cholorobenzene were supplied from Merck KGaA. Gum arabic was provided from Sigma Aldrich Co.

2-2- Preparation of prepolymer

(1) Toluene 2,4-diisocyanate was dissolved into cyclohexanone; (2) the mixture was suspended in an 80℃ oil bath and 1,4-Butanediol was slowly added; (3) the mixture was purged with N_2 and let to react for 24 h; (4) the mixture was distilled at 100℃ under 15 Torr for 4-5 h, leaving a yellowish, viscous prepolymer .

The molecular weight was 1270 for number-average ($\bar{M}_n$) and 1690 for weight average ($\bar{M}_w$) by gel permeation chromatography [17].

2-3- Synthesis of microcapsules

(1) deionized water and gum arabic surfactant were mixed at room temperature and the solution was agitated for 3 h; (2) the prepolymer was dissolved into cholorobenzene at 68℃ and IPDI was added and mixed; (3) the mixture was poured into the gum arabic solution and heated to 70℃; (4) at 50℃, 1,4-butanediol was added as chain extender and agitated for 45 min; (5) once cooled to ambient temperature, the suspension was rinsed with deionized water and vacuum filtered; (6) microcapsules were air-dried for 48 h.
Formation of PU shell at the interface between the aqueous phase and oil phase is schematically demonstrated in Fig.4 [18].

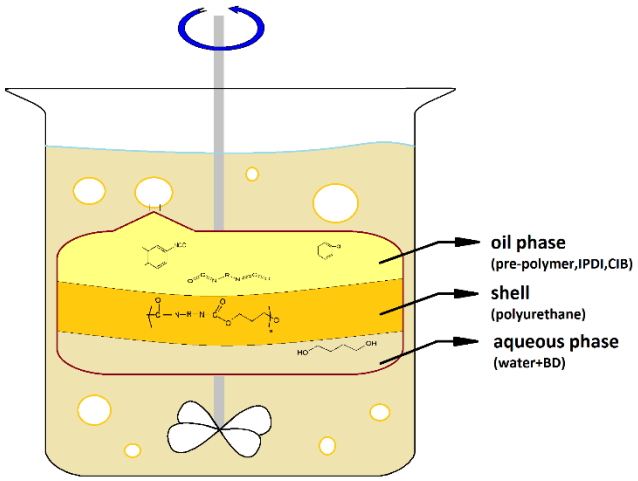


Fig.4. schematic diagram of shell wall formation.

2-4- Measurement and characterization of pre-polymer and microcapsules

Physical and chemical characteristics of pre-polymer and microcapsules were measured as belwo:

2-4-1- NCO content of pre-polymer

NCO content was determined through titration: (1) the synthesized pre-polymer was dissolved in dry toluene using a mechanical agitator; (2) di-n-butylamine solution was added and after a while, isopropyl alcohol and bromphenol blue indicator were added respectively; (3) titration was performed with hydrochloric acid to a yellow end point; (4) blank titration was run including all reagents but omitting prepolymer. The NCO content was defined as follows:

$$NCO,\% = \frac{[(B-V)\times N\times 0.042]}{W}\times 100 \qquad (1)$$

In which, *B* and *V* are the volumes of HCl for titration of the blank and prepolymer respectively, *N* normality of HCl, and *W* grams of prepolymer.

2-4-2- Microcapsules size distribution

Microcapsule size distribution was studied using SEM images and image analysis software. Statistical outputs were extracted through data sets of at least 300 measurements.

2-4-3- Morphology of microcapsules

Morphology of microcapsules and shell thickness were observed and studied using a scanning electron microscopy (ESEM, Vega\\ Tescan) (Figs.6 and 7). In order to reduce charging voltage, samples were sputtered with a thin layer of gold. All SEM images were taken at 10.00 kV voltage.

2-5- Mortar preparation

Table 1 illustrates mix design of each group. Twenty four cube specimens with dimension of 50*50*50 mm were prepared for each mix design.

For preparation of each batch of mortar, sand, cement (and microcapsules) were agitated for 120s by agitator. After that, water were added to the mixture, letting mixture be stirred again for 120s with higher speed. Mortar were poured into molds and compacted based on ASTM C192-06. Cubes were cured for 24 h in a temperature-controlled and humidity-controlled chamber and then demolded. Specimens were cured for 28 days before testing.

2-6- Pre-damaging of specimens

Specimens testing were accomplished based on ASTM C39 and maximum compressive strength of mortar were determined for each mix design. In order to pre-damage specimens and induce cracks, specimens of each mix design were divided into three groups, as shown in Table 2, and were subjected to 30%,45% and 60% of maximum compressive load respectively. Soon after, specimens were left in the curing room for 7 d to heal. After healing, specimens were tested again using the same protocol and maximum compressive strength of healed mortar were recorded. Recovery rate of compressive strength for each group were determined as follows:

$$\eta = \frac{f_c}{f_{ci}}\times 100\% \qquad (2)$$

Where η is recovery rate of compressive strength, f_{ci} and f_c (both in MPa) are initial compressive strength of mortar and compressive strength of damaged mortar after healing.

Table 1. Mix Designs of Mortars (Mass Ratios)

Mix	Sand	Water	Cement	Microcapsule
M0	300	50	100	0
M1-1100	300	50	100	1(1100rpm)
M3-1100	300	50	100	3(1100 rpm)
M1-1300	300	50	100	1(1300 rpm)
M3-1300	300	50	100	3(1300 rpm)

3. Results and discussion

3-1- NCO content of pre-polymer

The NCO content of synthesized pre-polymer was determined through titration.
The average NCO content was 19.8±0.8 wt %, which was higher than commercial pre-polymers (5-15%) .The NCO content plays the main role in formation of a high quality shell.

3-2- Microcapsules processing and characterization

Isophorone diisocyanate (IPDI) as healing agent, encapsulated via interfacial polymerization in an oil and water emulsion. After preparing pre-polymer, it was dissolved into chlorobenzene.1,4-Butanediol played the role of a chain extender for the shell wall, since the relative rate of reaction of diol/NCO is considerably higher than that of water/NCO. The large difference in reactivities of IPDI and TDI led to stable shell wall formation and formation of capsules with a high IPDI fill content [18].

3-3- Formation of microcapsules and viability of core materials

Formation of microcapsules was initially assessed through a simple test. A small amount of air dried capsules was poured on a piece of paper and was pressed with a spoon. Paper became wet indicating that microcapsules had been formed and broke as the result of external pressure. To control viability of the encapsulated IPDI, following test was conducted. A small amount of microcapsules was crushed. Ethylamine was added to the contents of microcapsules. The released liquid from microcapsules gelled, showing that IPDI had been encapsulated and was chemically active. Crushed microcapsules were subjected to water, core material got hydrated and solid polymer got formed, indicating ability of reaction in wet environment.

3-4- Size distribution

There are several factors which affect the size of microcapsules namely: geometry of the mixing design, blade hydrodynamics, viscosity, interfacial tension of the media, shear/agitation rate, temperature ,and surfactant [18].Size distribution of microcapsules in two different agitation rates (1100,1300 rpm) were measured

while other affecting factors were constant (Table 3). As the results presented in Fig.5 show, increasing the agitation rate would lead to smaller products.

Table 2. Pre-damaged Specimens Classification

Code	Mix	Preloading (ratio)
M0-30	M0	30%
M0-45		45%
M0-60		60%
M1-1100-30	M1-1100	30%
M1-1100-45		45%
M1-1100-60		60%
M3-1100-30	M3-1100	30%
M3-1100-45		45%
M3-1100-60		60%
M1-1300-30	M1-1300	30%
M1-1300-45		45%
M1-1300-60		60%
M3-1300-30	M3-1300	30%
M3-1300-45		45%
M3-1300-60		60%

Table 3. Geometric Parameters of Synthesized Microcapsules

Agitation Rate (rpm)	1100	1300
D, Diameter (μm)	62±21	48±19
t, Wall Thickness (μm)	3±1	2±1
t/D	0.04	0.04

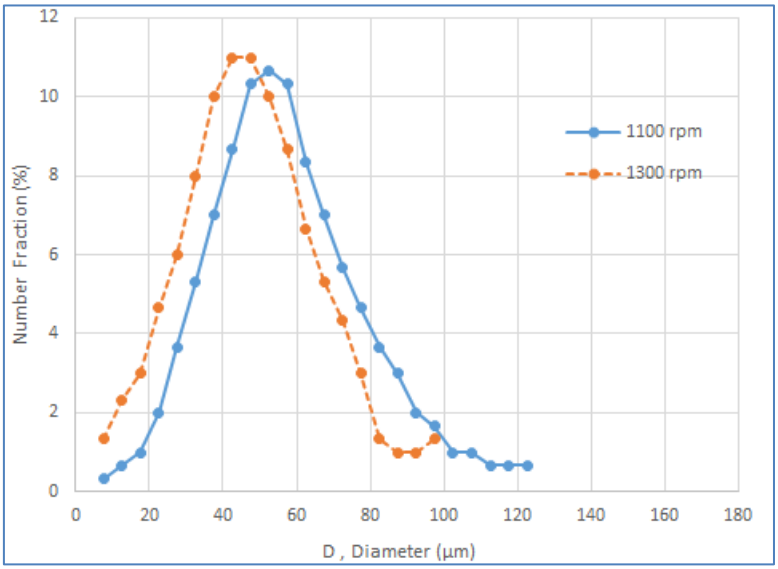


Fig.5. Size distribution at different agitation rates

Shear forces and interfacial tension of oil droplets are in balance in a definite agitation rate [19].As the agitation rate increases, shear forces become stronger and large droplets break into smaller ones.

3-5- Surface morphology of microcapsules

The surface morphology of microcapsules in different agitation rates was studied using SEM microscope (Figs.6(a) and 7(a)).

It was recognizable that the inner surface of microcapsules shell wall was smother than the outside (Figs.6(c) and 7(c)). It could be explained as the result of less shear flow inside the microcapsule during the formation of wall, comparing the amount of that outside. Ratio of shell wall thickness to dimeter of microcapsules was relatively constant. This constancy at these agitation rates had mean value of 0.04.

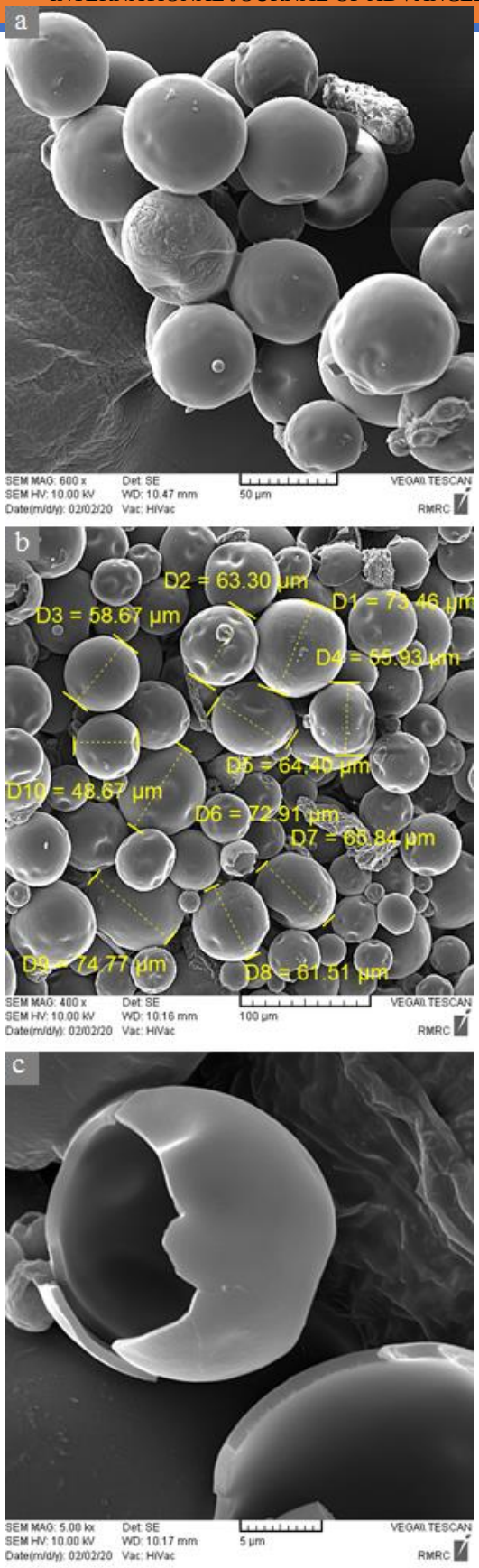


Fig.6. SEM photos of: (a) morphology, (b) size distribution, and (c) inner surface of microcapsules produced at agitation rate of 1100 rpm

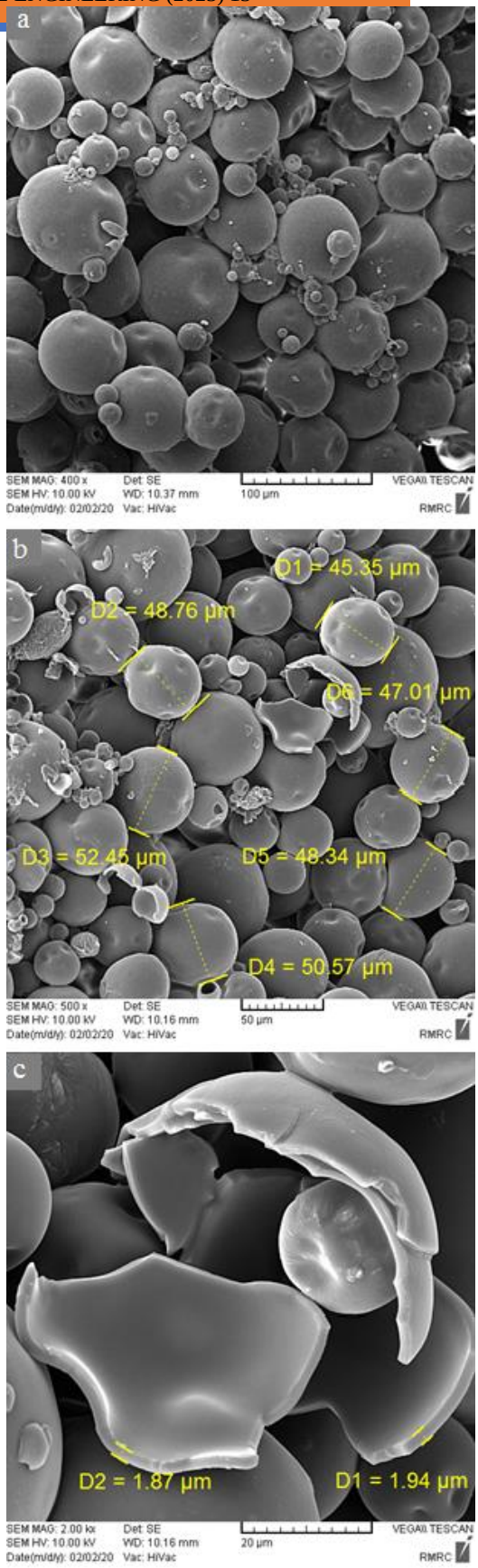


Fig.7. SEM photos of: (a) morphology, (b) size distribution, and (c) inner surface of microcapsules produced at agitation rate of 1300 rpm

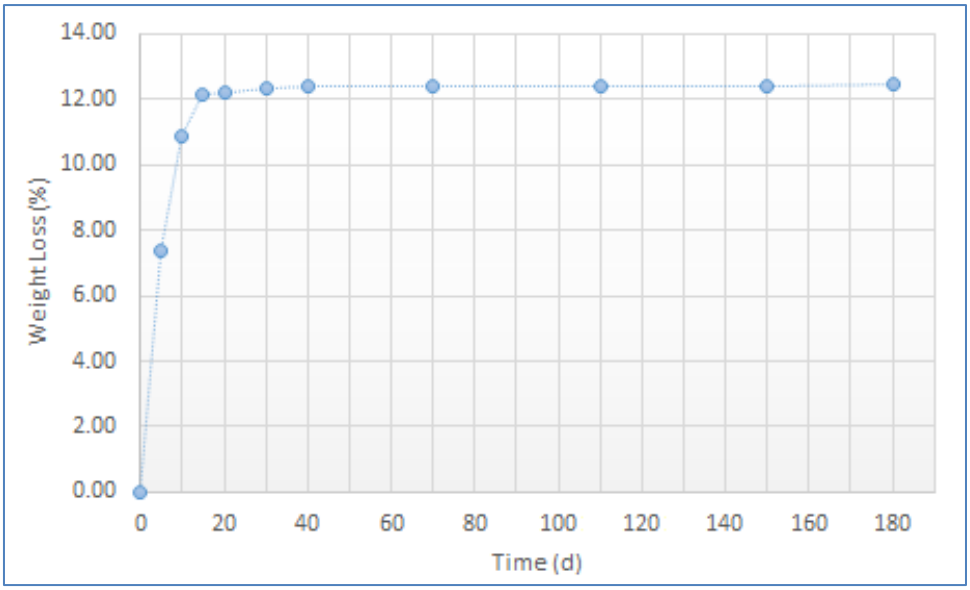


Fig.8. Weight loss over time

3-6- Shelf life

Unlike many manufactured products, Civil infrastructures have a relatively long service life. It is impossible to predict when damage will occur over the period of service, So any self-healing functionality must also possess a long shelf life. To investigate the shelf life of synthesized microcapsules, weight loss of microcapsules produced at 1300 rpm were monitored for a period of 6 months. Microcapsules were kept in a glass vial at room temperature in this period. Results were demonstrated in Fig.8.

3-7- Compressive strength of mortars

Fig.9 demonstrates the compressive strength of mortars with different percentages of microcapsule. The results were obtained from testing 50× 50×50 mortar cubes which were cured for 28 d, based on ASTM C39.As shown, the compressive strenght of M0, M1-1100, M3-1100, M1-1300, M3-1300 was 29.36 Mpa, 31.70 Mpa, 39.25 Mpa, 30.17 Mpa and 33.25 Mpa respectively. In comparison with M0 which had no microcapsule, there is 8%, 34%, 3% and 13% increase in compressive strenght of microcapsule-containing samples indicating that, there had been an undesired rupture of portion of microcapsules during preparing and molding of specimens, which had affected the compressive strength of mortars.

3-8-Pre-damaging samples,healing and evaluating compressive strength again

In order to investigate strength recovery capability of mortars containg microcapsule and compare it with plain mortar, mortars of each group divided into 3 sub-group and each were subjected to 30%, 45% and 60% of their respective compressive strength load. After preloading, specimens were cured in a temperature and humidity controlled chamber for 7 d and then compressive strength were examined. Results are shown in Fig.10.

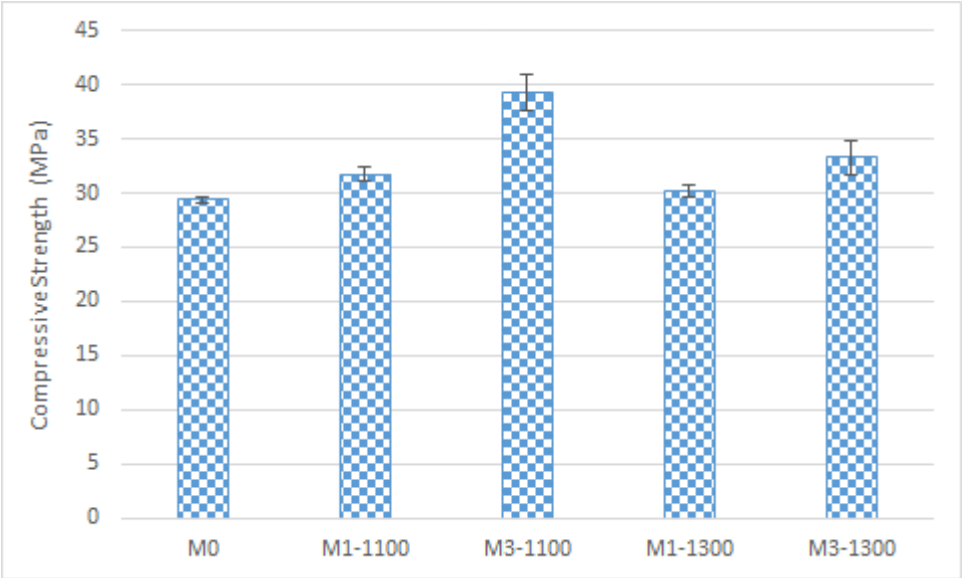


Fig.9. Compressive strength of mortars containg different percentages of microcapsules

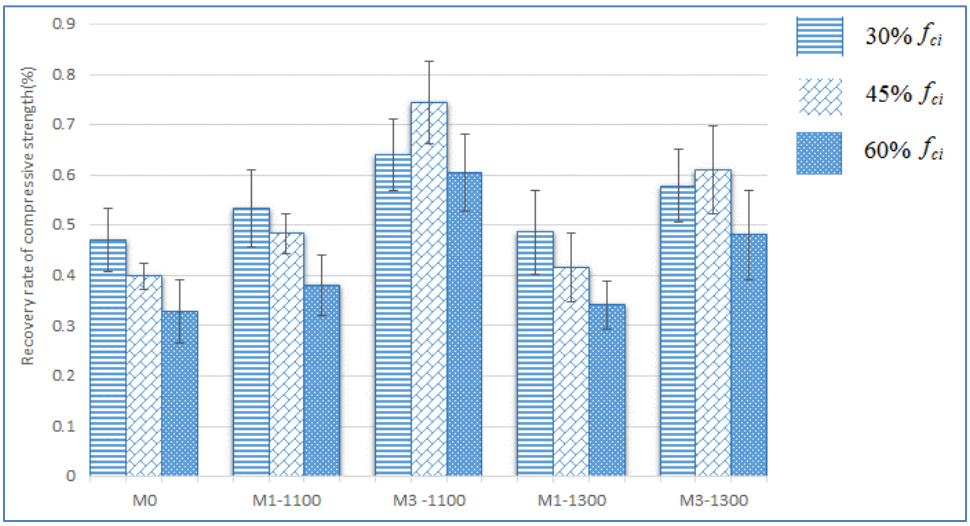


Fig.10. Compressive strength recovery rate of mortars containing different amount of microcapsules

As shown, for samples with no microcapsule (M0), the recovery rate of compressive strength, as pre- loading increased, decreased. That's because there was no healing mechanism for induced cracks in these samples.For specimens containing low amount of microcapsule (M1-1100, M1-1300), the recovery rate of compressive strength was higher than control samples, but since the amount of healing agent which released after rupture of microcapsules during pre-loading was low, in comparison with volume of induced cracks, there was no considerable increase in compressive strength recovery of samples, as pre-loading increased.In mortars containg more microcapsules (M3-1100, M3-1300), increase in recovery rate of compressive strength up to when preloading reached to 45% f_{ci}, was observed.Since microcapsules built at the agitation rate of 1100 rpm are bigger in size and have more healant and less impurity (mostly chlorobenzene) in comparison with those built at the agitation of 1300 rpm, for samples containing the same amount, but with different agitation rates, those containing microcapsules built at the agitation of 1100 rpm have higher recovery rates both at 30% f_{ci} and 45% f_{ci} pre-loadings. For samples with pre-loading rate of

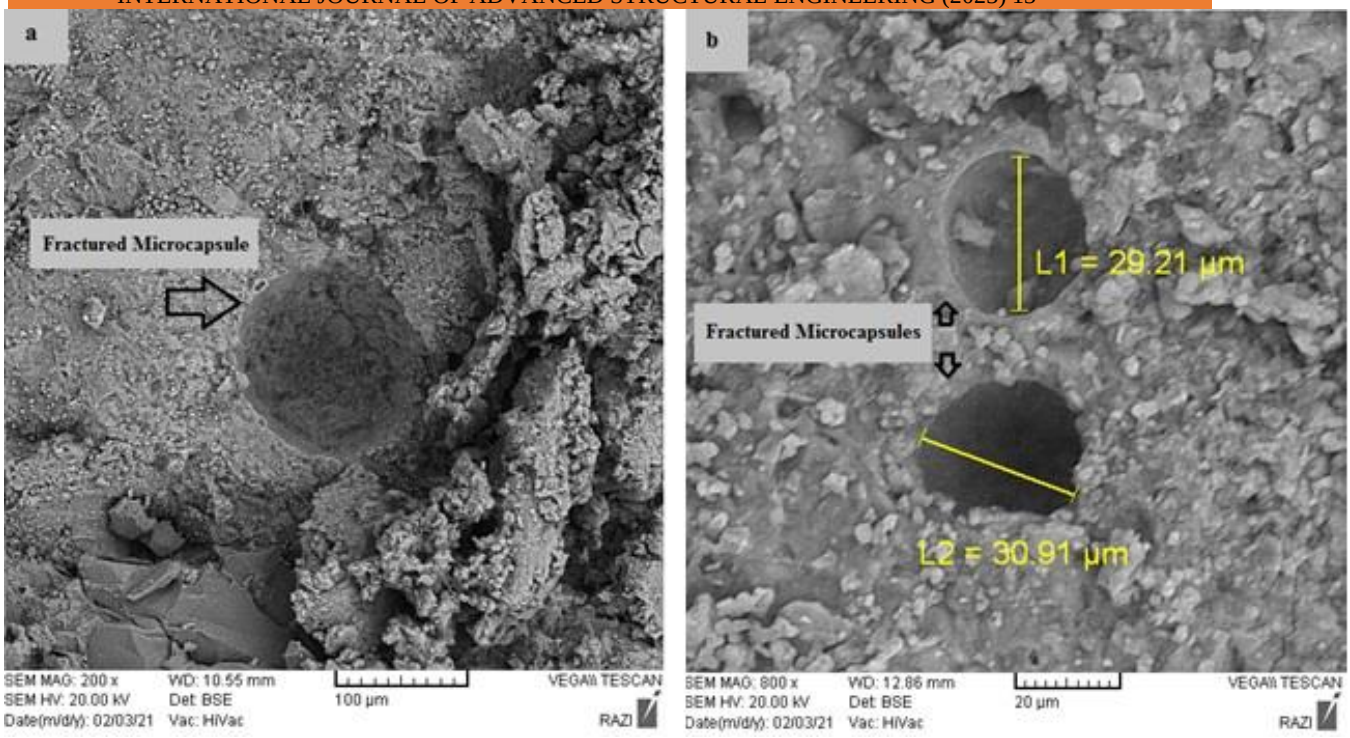


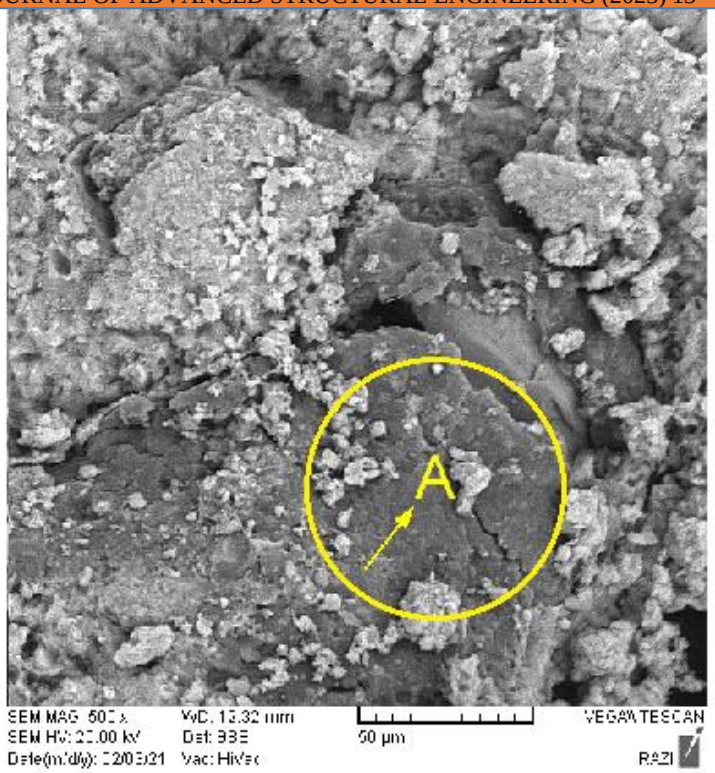
Fig.11. Fractured microcapsules in the matrix

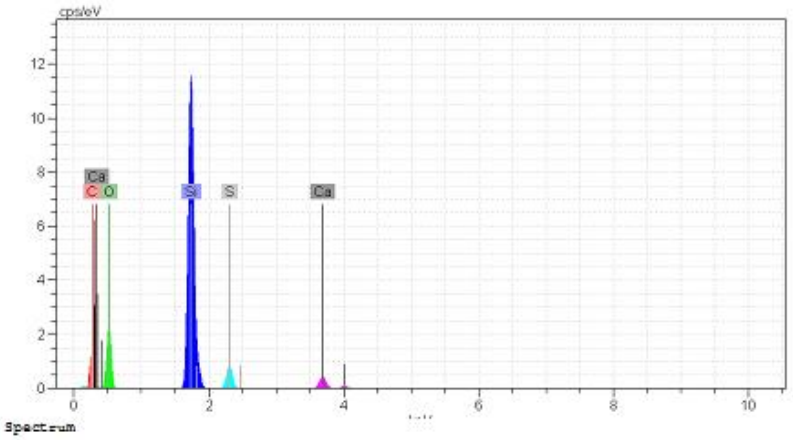
60% f_{ci}, there was an obvious decrease in recovery rate, indicating insufficience of microcapsules content to fill cracks.

3-9- SEM/EDS analysis of healed mortars

After the completion of healing process, one specimen of healed mortar of M3-1100 and one of M0 (control) were cut to perform SEM/EDS analysis. The SEM images presented in Fig.11 show fractured microcapsules in the matrix, admitting that there had been a complete bond between microcapsules and cementitious matrix.This guarantees fracture of microcapsules and release of helant in cracks due to external stimulations.

To evaluate formation of healing products near cracks, EDS analyses were conducted both on control sample (M0) and on the zones of crushed microcapsules near cracks on M3-1100 sample .Typical analyses are presented in Figs.12 and 13.The results showed that there is a meaningful diffrence between carbon ratio of control specimen and microcapsules containing one, indicating that healing products were successfully formed in microcapsule containing samples.

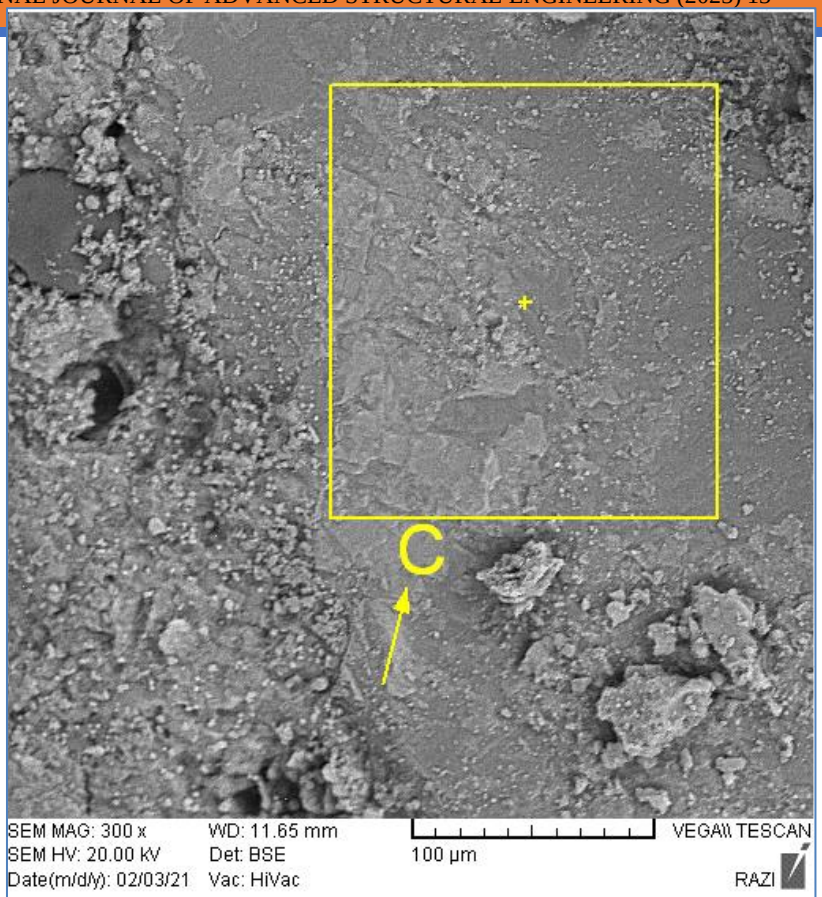


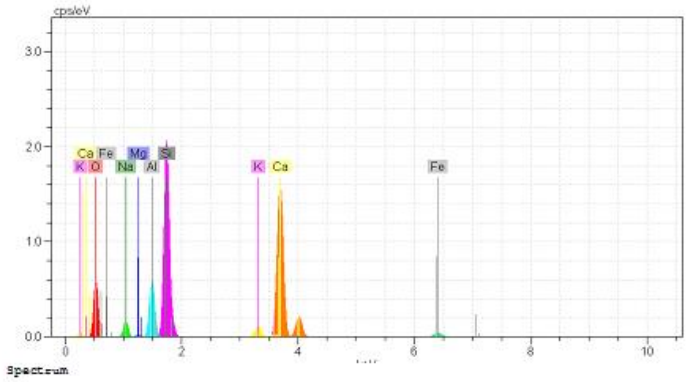


Spectra: A

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Carbon	K series	21.63	22.12	31.40
Oxygen	K series	46.56	47.60	50.73
Silicon	K series	25.40	25.97	15.77
Sulfur	K series	2.43	2.49	1.32
Calcium	K series	1.79	1.83	0.78
	Total:	97.8 %		

Fig.12. EDS analysis of fractured M3-1100 sample





Spectra: C

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Oxygen	K series	39.38	50.35	67.21
Sodium	K series	1.90	2.43	2.26
Magnesium	K series	0.17	0.21	0.19
Aluminium	K series	4.28	5.47	4.33
Silicon	K series	13.84	17.70	13.46
Potassium	K series	1.19	1.53	0.83
Calcium	K series	16.58	21.19	11.29
Iron	K series	0.88	1.12	0.43

Fig.13. EDS analysis of fractured control sample

2. Conclusions

The goal of this study was to evaluate the effects of PU microcapsules on elevating self healing capability of cementiotious composites. Isophorone diisocyanate (IPDI) core/PU shell microcapsules as healing agent were successfully synthesized via interfacial polymerization.The NCO content of prepolymer were measured and the morphology and size distribution of microcapsules were investigated.Self-healing capability of mortars containing microcapsules were also studied and the following conclusions were made:

1) The NCO content of synthesized prepolymer was 19.8 wt %, which was higher than commercial pre-polymers.
2) Adjusting agitation rate over 1100-1300 rpm, spherical microcapsules with average diameter of 62-48 μm were produced.The microcapsules surface were rough both inside and outside.The average ratio of shell wall thickness to microcapsule diameter was 0.04.Weight loss of microcapsules for a period of 6 month was 12.47%.
3) The mortars containg 3% of their cement weight IPDI microcapsules, had up to 74% recovery rate of compressive strength while this rate for mortars containg 1% microcapsules were less than 54% and for control mortars less than 50%.
4) SEM analysis results represented that microcapsules are fully bonded to the matrix and perfectly react with external stimulations. EDS analysis also performed that healing products are formed in caracks and the areas of microcapsules rupture.
5) The samples containig micocapsules had higher compressive strength in comparison with control ones, indicating that there had been an undesired rupture of portion of microcapsules during preparing and molding of specimens.This demonstrated need of more studies and work on mechanical properties of microcapsules specially stiffness of those used in cementitious composites.

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