

MECHANICAL PROPERTIES AND SELF-HEALING MECHANISM OF EPOXY MORTAR

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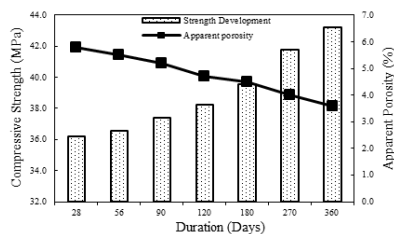
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Graphical abstract



Abstract

Crack deformation in concrete start with hairline crack or micro-crack which can lead to major crack if not prevented. Crack can cause a major deterioration to the structure as liquid can penetrate inside and cause damage as a result; the durability of concrete will decrease. Self-healing concrete was introduced to automatically repair hairline crack or micro-crack without external intervention. Previous study had shown that by introducing bacteria into the concrete, the crack will heal itself. This paper presents the study on self-healing mortar by using epoxy resin without hardener as a self-healing agent. The self-healing process was evaluated using Ultrasonic Pulse Velocity measurements up to 180 days. Mortar specimens were prepared with mass ratio of 1:3 (cement: fine aggregate), water-cement ratio of 0.48 and 10% epoxy resin of cement content. All tested specimens were subjected to wet-dry curing; where compressive strength, flexural strength, and tensile splitting strength and self-healing mechanism were measured. The results obtained shows that, all strength properties of the self-healing epoxy mortar were significantly higher than the control sample and became constant at 10 % of epoxy resin content. Based on the pulse velocity measurements, after 60 days the cracks of the mortar healed automatically as a result of the reaction between the unhardened epoxy resin and hydroxyl ion from cement hydrate. This shows the ability of the epoxy to be used as self-healing agent.

Keywords: Self-healing, self-healing epoxy mortar, cracks; self-healing agent

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1.0 INTRODUCTION

Micro-crack caused by earthquake, wind load, shock and other reasons can leads to deterioration of concrete which can allow water to penetrate into the concrete. The penetration of water can cause many problems such as corrosion of rebar, reduce a strength and many more. In actual concrete structure, a lot of micro-cracks are difficult to be detected, observed, and measured directly due to the limitation of current technology [1]. Micro-crack can leads to major crack which can lead to collapse of structures.

Consideration of this problem led to the introduction of self-healing concrete. Self-healing concrete was studied long time ago by using bacteria as a healing agent. The purpose of self-healing concrete is to automatically repair a crack without using additional materials. Generally, the phenomenon comprises of two major mechanisms. For internal crack healing, the process is based on further hydration or swelling of unreacted particles [2]. Previous researches on the used of bacteria as a healing agent had demonstrated that the micro-cracks in cementitious materials are able to heal under certain circumstances [3, 4]. When water access into the cracks, it can be healed by the precipitation of calcium carbonate [5] by further hydration of unhydrated cement particles.

There are quite a number of healing agents introduced by many researches such as bacteria, micro capsule and hollow tube. However, on the use of polymer as a healing agent, only few studies have been conducted. The use of bacteria as a self-healing agent has some disadvantages such as its dangerous nature if contact to human body. Similarly, even though bacteria are free organism, but the process of getting the right bacteria was harder as it mixed with many other types of bacteria. Others method of self-healing agent was usually expensive. Therefore, this paper focused on self-healing mortar by using epoxy resin without hardener as a healing agent. The mechanical properties and strength development of self-healing mortar was investigated as well as a self-healing mechanism.

2.0 EXPERIMENTAL PROGRAM

2.1 Materials

Cement. The cement used in the study was ordinary Portland cement (OPC) conforming to ASTM C150 / C150M-12 [6]. The important constituent of cement are calcium, silica and alumina as these three components create a bonding within the mortar and concrete.

Fine Aggregates. Local river sand with specific gravity of 2.62 and fineness modulus of 2.85 in a saturated

surface dry condition was used. The fine aggregate was oven-dried and wetted until saturated surface-dry condition was reached.

Epoxy Resin. Diglycidyl Ether of Bisphenol A-type epoxy resin was used in the mix proportion and stored in room temperature to avoid damage. The amount of epoxy resin added in the mix was 10 % of the cement content. The viscosity of epoxy resin chosen was high as to create a bonding between epoxy resin and hydroxyl ion.

2.2 Preparation of Self-Healing Epoxy Mortar

With reference to JIS A 1171-2000 [7], the hardener-free self-healing epoxy mortars were mixed with a mass ratio of cement to fine aggregates of 1:3; epoxy content of 5, 10, 15, and 20 % of cement; and a water-cement ratio of 0.48. The flow spread diameter was in the range of 170 ± 5 mm. Mortar cube specimens of $70 \times 70 \times 70$ mm were cast for compressive strength test and $100 \times 100 \times 100$ mm for self-healing evaluation. Prism specimens of $40 \times 40 \times 160$ mm were cast for flexural test and for tensile splitting test; the cylindrical specimen with the size of 150 mm in height and 70 mm in diameter was used. The mixing procedure was basically the same as the ordinary cement mortar. Table 1 shows the mix proportion of the self-healing epoxy mortar. In order to have an optimum percentage of epoxy resin, the various epoxy resin was used in the initial experimental work. Normal mortar was prepared as a control specimen.

Table 1 Mix proportion of epoxy self-healing mortar

Sand	Cement (kg/m ³)	Water	Epoxy content (%)	Water /Cement	Sand: Cement
			0		
1517	506	228	5		
			10	0.48	3:1
			15		
			20		

2.3 Curing Regime

Wet-dry curing and additional dry curing were applied to all self-healing epoxy mortar without hardener specimens. For initial curing, wet-dry curing was applied to the specimens where the specimens were placed under wet burlap for two days followed by five days in water. After that, the specimens were taken out and placed at a room temperature for 21 days. After the specimens matured and crack was initiated, prolong dry-curing was applied. The normal mortar went through water curing.

2.4 Tests

2.4.1 Apparent Porosity

Determination of apparent porosity of mortars was done according to ASTM C1403-13 [8]. Three cubes of mortar were oven-dried at 85°C for 24 hours and then immersed in water for 48 hours. The cubes were further suspended in water and weighted. The data were recorded and average value was determined. The percentage of apparent porosity was determined at 28, 56, 90, 120, 180, 270, and 360 days of curing period.

2.4.2 Compressive Strength

The compressive strength test for self-healing epoxy mortar was conducted using a compression test machine at the Material and Structure Laboratory in the Faculty of Civil Engineering, Universiti Teknologi Malaysia, with maximum load of 2000 kN and the loading rate was 0.3 N/mm²/s after 28 days of curing. The test was conducted according to BS EN 12390-3: 2009 [9]. An increasing compressive load was applied to the specimen until failure occurred to obtain the maximum compressive load.

The cube size was 70 x 70 x 70 mm as in accordance to BS EN 998-1:2010 and the calculated compressive strength was based on the average of three values. For strength development test, the compressive strength test was conducted at the ages of 28, 56, 90, 120, 180, 270, and 360 days.

2.4.3 Flexural and Tensile Splitting Tests

The prism specimen was tested for flexural strength after 28 days in accordance with ASTM C348-08 [10]. The size of the mortar prism was 40 x 40 x 160 mm and tested for various percentages of epoxy resin content. This test was conducted to study the ability of the specimen to resist deflection under load.

For tensile splitting test, cylindrical specimen with the size of 150 mm in height and 70 mm in diameter was cast and tested at the age of 28 days. The test was carried out according to ASTM C496M-11 [11].

2.4.4 Self-Healing Test

2.4.4.1 Preloading and Dry Curing

After the initial curing, the cracks are created by using compression machine at loading rate of 0, 50 and 80% of the maximum load. Then, after the crack was developed, the specimens were dry cured at room temperature for 28 days, 1 month, 3 month and 6 month. The production of crack was checked by using non-destructive test equipment, Ultrasonic Pulse Velocity (UPV) machine. The mechanism of crack production is shown in Figure 1.

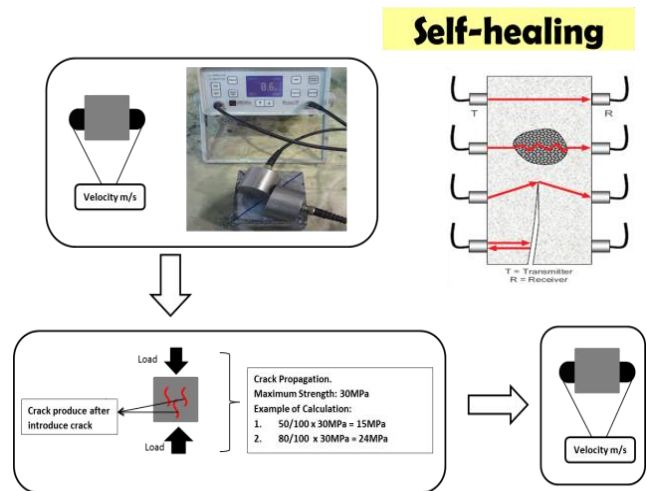


Figure 1 Crack production to epoxy self-healing mortar

2.4.4.2 Determination of Degree of Hardening of Epoxy Resin

The testing procedure adopted in this test was similar to the one used by Masahiro [12]. The matured cube specimens were crushed and ground into powders and sieved through 1.2 mm sieve. After that, 5 gram of the powder was diluted with 30 gram of 1-methoxy-2-propanol solution and stirred for 10 minutes. The hardened epoxy was extracted by using glass microfiber filter paper for 2 hours. The filter sample was heat at temperature of 100°C for 60 minutes. The percentage of degree of hardening (DoH) of the epoxy was calculated by the following equation.

$$\text{DoH (\%)} = [(E_{ui} - E_{ue}) \times 100] / E_{ui} \quad (1)$$

Where

E_{ui} = mass (g) of unhardened epoxy resin

E_{ue} = mass (g) of unhardened epoxy resin extracted

3.0 RESULTS AND DISCUSSIONS

3.1 Optimum Mix Proportion

The optimum mix proportion was selected based on compressive strength of the specimen. Figure 2 exhibits the different contents of epoxy resin in mortar under wet-dry curing, which has been added to the mortar to study its effect on compressive strength. The compressive strength of normal mortar was 30 MPa at 28 days while the compressive strength of the 10 % epoxy resin was 36 MPa at the same curing period, which was the highest strength among all the epoxy contents and that of the normal mortar. This was achieved due to the presence of alkalis from the hydration process to react with epoxy resin.

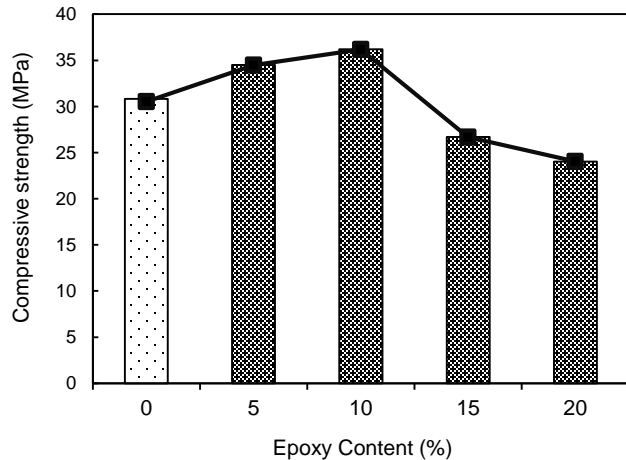


Figure 2 Relationship between compressive strength and epoxy content at 28 days for wet-dry curing

The increase in epoxy content beyond 10 % has decreased the compressive strength probably due to the presence of epoxy resin that was not hardened and disturbs the bonding between hydroxyl ion and epoxy resin, which had been previously reported by Ohama *et al.* [13]. According to Ohama and Takahashi [14-16], the reductions in the flexural and compressive strengths of the polymer-modified mortars using epoxy resin without the hardener at polymer-cement ratios of 10 % or more may be explained by the presence of considerable amount of epoxy resin which cannot harden in the polymer-modified mortars. The unhardened epoxy resin become excessive and lowers the compressive strength of the mortar. Therefore, 10 % epoxy content was taken as the optimum content to be use without hardener which gives higher compressive strength.

3.2 Flexural Test

The flexural test was conducted to investigate the material's ability to resist deformation under load. The result of the 28 days curing self-healing epoxy mortar is shown in Figure 3.

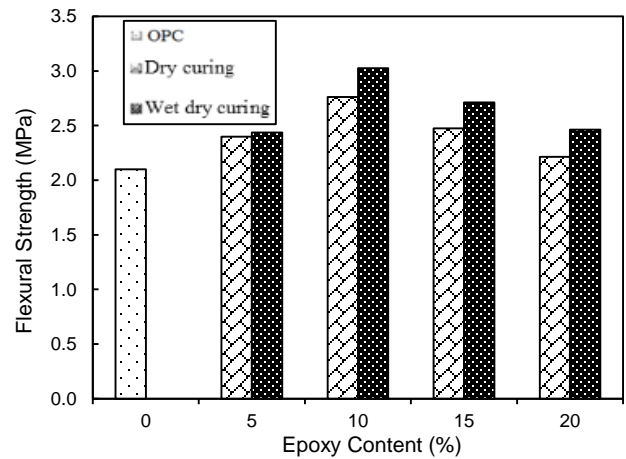


Figure 3 Relationship between flexural strength and percentage of epoxy content

From the Figure, it can be seen that mortar with 10 % epoxy content gave the highest flexural strength for both curing regimes compared to 5 %, 15 %, and 20 %. The 10 % epoxy content with wet-dry curing gave a 3 MPa of flexural strength while with dry curing the flexural strength was 2.8 MPa. The self-healing epoxy mortar had the highest flexural strength due to the epoxy resin had reacted well with the hydroxyl ions from cement hydrate, which ultimately produced a denser and more durable mortar [17].

3.3 Tensile Splitting Test

The results of the tensile splitting strength test of all the specimens are shown in Figure 4. From the Figure, the tensile strength of normal mortar is lower than that of the epoxy self-healing mortars. The 10 % epoxy resin shows the highest tensile strength for specimens that were exposed to wet-dry curing condition, but any addition beyond 10 % had lowered the tensile strength. Again, this was attributed to the improvement in cement hydrate and polymer.

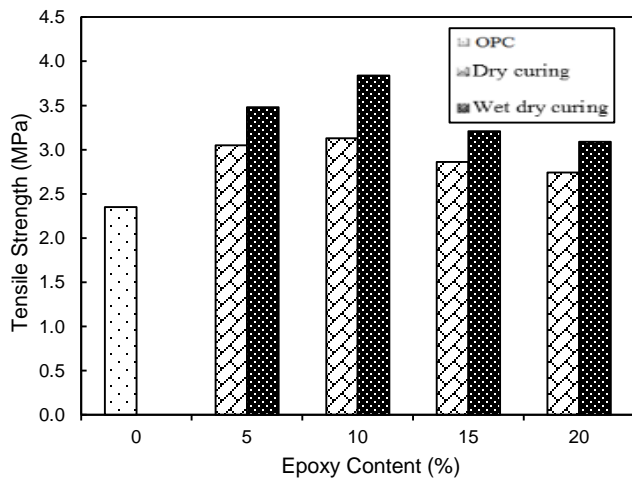


Figure 4 Relationship between tensile splitting strength and epoxy content

3.4 Strength Development vs Porosity

Porosity of the mortars highly influences the strength of mortar. The reduction of porosity in concrete will increase its strength as it makes a concrete and mortar denser [18]. Figure 5 shows the result of the strength development and apparent porosity of 10% epoxy content with wet-dry curing. This content and curing regime was selected as it gives a higher compressive strength and suitable condition for hydration and polymerization process. As shown in Figure 5, the 28 days apparent porosity was recorded at 6 % while the strength was 36 MPa. Prolonged curing period has shown to lower the porosity and increases the strength of the mortar. After 365 days curing, the porosity was 3.7 % and the compressive strength was 44 MPa. The decrease in the porosity at 365 days was recorded almost 40 % of its initial porosity. In the meantime, the compressive strength increased by 20 % from initial strength. The epoxy resin without hardener added into the mortar mixture was active even in dry condition that produces higher compressive strength and closes the pores within. The results of the test indicated that the epoxy resin without hardener can be used as an additive in mortar.

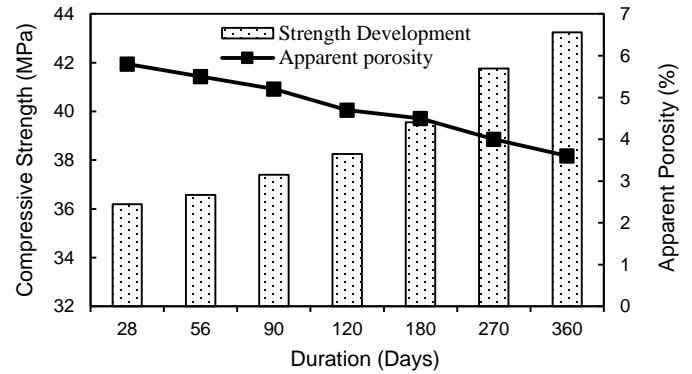


Figure 5 Relationship between compressive strength and porosity of 10% epoxy content with duration

3.5 Degree of Hardening

The degree of hardening of epoxy resin with different percentage was determined at 28 days, 90 days and 180 days. Figure 6 shows the result for specimens under wet-dry curing.

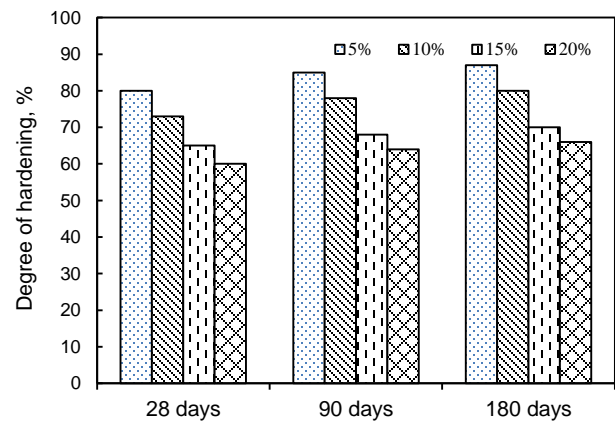


Figure 6 Degree of hardening of epoxy resin with wet-dry curing

From the Figure, the 5% epoxy content gives a higher degree of hardening at every period of testing. The degree of hardening of 5% epoxy resin was above 80% for every period of time. With the increased of epoxy content, the degree of hardening started to decrease. This is due to the excessive amount of epoxy that reacts with the hydroxyl ion. The amount of hydroxyl ion must be almost the same as the amount of epoxy resin needed for the polymerization reaction [18]. The degree of hardening of epoxy resin is important as it determines the strength and performance of epoxy self-healing mortar. If the epoxy resin not hardens, it will reduce the compressive strength of the mortar.

3.6 Self-Healing

The self-healing performance of epoxy self-healing mortar was observed by non-destructive test and compressive strength test. The non-destructive test conducted was ultrasonic pulse velocity (UPV) test. First, after the concrete was matured, pre-loading stress was applied and UPV time travel was measured. Figures 7 and 8 shows the results of self-healing mechanism in terms of UPV test and compressive strength test after 6 months dry-curing. The epoxy self-healing mortar present as epoxy mortar (EM) while normal mortar present as normal mortar (NM) in the Figures. As mention in the text, two types of load were applied to produce crack which are 50% and 80%. From the compressive strength test, the optimum strength was showed by 10% of epoxy content. With this consideration, only 10% of epoxy resin mortar was tested for self-healing evaluation.

Figure 7 shows a time travel of the pulse for epoxy self-healing mortars and normal mortar after pre-loading. From the Figure it can be seen that the normal mortar did not show any change in time travel even after 6 months. However, the 10% epoxy content mortar shows a better time travel after 6 months. The lower time travel indicates that the mortar is dense and less porous. From this result, it can be said that the self-healing process inside the mortar is functioning well and epoxy resin without hardener can be used as a self-healing agent.

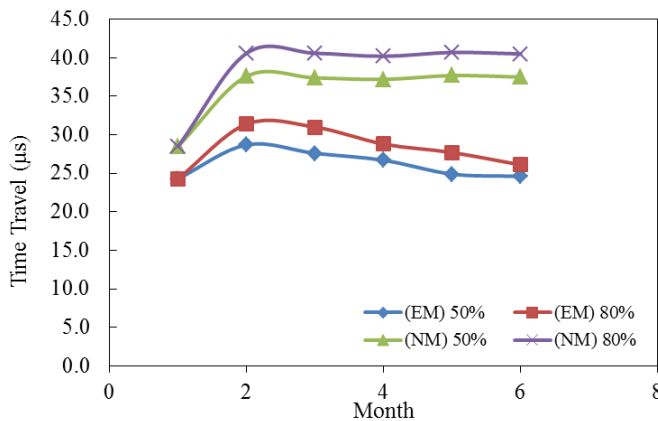


Figure 7 Time travel of epoxy self-healing mortar and normal mortar after pre-loading

Figure 8 shows the trend of compressive strength after propagation of crack and dry-curing. From the Figure, the 10% epoxy content added inside the mortar tends to increase the compressive strength. This shows that the epoxy resin can automatically repair cracks inside the mortar and improve the strength of the specimens. After 6 months, the compressive strength regains to its original compressive strength without external intervention. In contrast with normal mortar, the compressive strength is reduced. This is due

to the water penetration that can deteriorate the mortars.

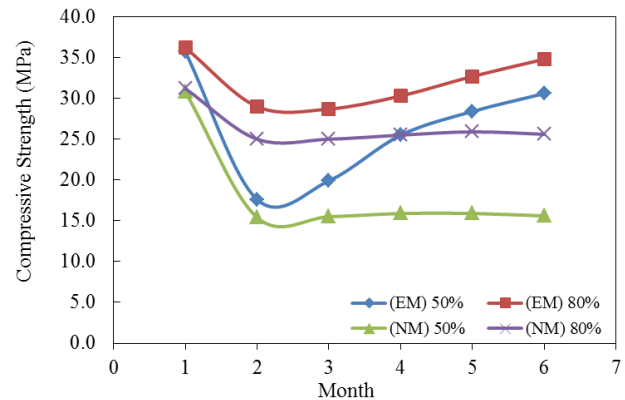


Figure 8 Compressive strength of epoxy self-healing mortar and normal mortar after pre-loading

3.7 Morphology

Figure 9 displays the Field Emission Scanning Electron Microscopy (FESEM) morphology of the 10% epoxy content in mortar that indicates the bonding between hydroxyl ion and epoxy resin. The bonding is important to produce a strong mortar and serves as a proof that the epoxy resin has reacted well with hydroxyl ions even without hardener.

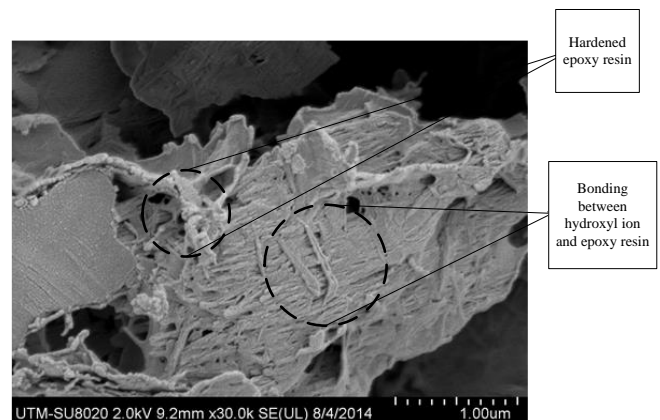


Figure 9 FESEM morphology of 10% self-healing epoxy mortar

The microscopy and Energy-dispersive X-ray spectroscopy (EDX) of self-healing epoxy mortar was observed after 365 days of dry curing. From Figure 10 it can be seen that the Ca^{++} was produced when epoxy resin react with hydroxyl ion. The Ca^{++} will react with others components to fill the pores and produced a denser mortar. The Ca^{++} ion was the important component that makes the self-healing of mortar functioning. Study by Musarrat [19] indicated that the Ca^{++} have the hexagonal faces crystals and was confirmed by EDX analysis. The porosity of self-healing epoxy mortar became less and increased the

compressive strength maybe due to the cleavage among themselves built up by individual layers are jointed together in a parallel way [20].

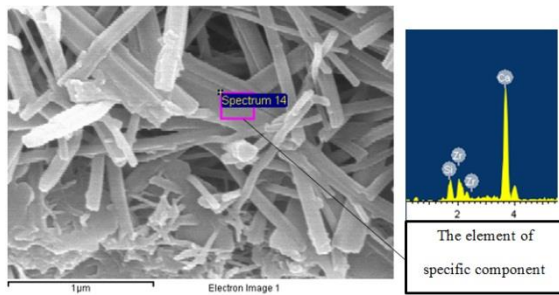


Figure 10 EDX morphology of 10 % self-healing epoxy mortar after 365 days curing

4.0 CONCLUSION

The conclusions that can be drawn from the study are as follows:

- i. The optimum amount of epoxy content that produced the highest compressive strength, flexural strength, tensile strength and strength development was 10%. The recorded compressive strength, flexural strength and tensile strength at 28 days were 36 MPa, 3 MPa and 3.8 MPa, respectively.
- ii. The trend of strength development of the 10 % epoxy self-healing mortar kept increasing after 360 days of curing and the decreasing of porosity recorded almost 40 % of reduction.
- iii. With the increase of epoxy content, the degree of hardening started to decrease due to the insufficient amount of hydroxyl ion to react with the excessive epoxy.
- iv. The self-healing process of epoxy resin is functioning well based on the UPV and compressive strength test results.

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