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Study on the molecular structure of epoxy resin without hardener in mortar

Nur Farhayu Ariffin[1], Nor Hasanah Abdul Shukor Lim[2], Sharifah Maszura Syed Mohsin[1], Mohd Warid Hussin[2], Abdul Rahman Mohd Sam[2], Han Seung Lee[3]

[1]Faculty of Civil Engineering & Earth Resources, Universiti Malaysia Pahang, Pahang, Malaysia
[2]School of Civil Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor, Malaysia
[3]School of Architecture and Architectural Engineering, College of Engineering Sciences, Hanyang University ERICA Campus, Republic of Korea

Email: farhayu@ump.edu.my

Abstract. The principal of molecular structure of cement mortar is important as it shows a component and interaction between cement and additive. By using a themogrativimetric analysis, the phase of mortar structure when exposed to high temperature can be determined. This paper presents the study on influence of epoxy resin without hardener on the microstructure of mortar. Mortar specimens were prepared with mass ratio of 1:3 (cement: fine aggregate), water-cement ratio of 0.48 and 5 to 20% epoxy resin of cement content. All tested specimens were subjected to wet-dry curing; where compressive strength, apparent porosity, thermogrativimetric analysis and fourier transformation infrared spectroscopy were measure. Result shows that, all strength properties of epoxy mortar were significantly higher than control sample and became constant at 10 % of epoxy resin ratio. Thermogrativimetric analysis shows the weight loss of epoxy mortar was almost similar for various percentage of epoxy resin while from fourier transformation infrared spectroscopy test, the component of epoxy mortar and normal mortar was significantly different.

1.0 Introduction

Epoxy resin is known as a repair material for concrete since years before. Usually, epoxy resin with the presence of hardener is used as a repair material or as an addition in concrete mixtures. In this paper, an epoxy resin will added in the mortar and concrete mixture without any hardener. It is believed that epoxy resin can be hardened in concrete because the epoxy resin ion will react with hydroxide ion, produce from the cement hydration process.

It is important to study the molecular behaviour of mortar when epoxy resin was added into the mixture. To study the microstructure of epoxy mortar, several techniques was apply. There is limited study on molecular behaviour on epoxy resin in concrete without hardener. Previous research was conducted with the epoxy mortar with addition of hardener. In this paper, the behaviour of epoxy resin without hardener in high temperature was observed and the decomposition of gases can be calculated.

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 [3] standard. The important constituent of cement was calcium, silica and alumina as these three component create a bonding within the mortar and concrete.

Fine Aggregates. Local river sand in with specific gravity of 2.62 and fineness modulus of 2.85 saturated surface dry conditions 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 in the range of 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 Epoxy Mortar

With reference to JIS A 1171-2000 [4], the hardener-free epoxy mortars were mixed with a mass ratio of cement to fine aggregates of 1:3; epoxy ratio 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 x 70 x 70 mm were casted for compressive strength test. The mixing procedure was basically same as the ordinary cement mortar. Table 1 shows the mix proportion of the epoxy mortar. In order to have an optimum percentage of epoxy resin, the various epoxy resin was used in initial experimental work. Normal mortar was prepared as a control specimens.

Table 1 Mix proportion of epoxy mortar

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

2.3 Curing Regime

Wet-dry curing and additional dry curing were applied to all 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 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 [5]. Three cubes of mortars 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 calculated for average. 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 epoxy mortar was conducted using a compression test machine at the Civil Engineering Material and Structure Laboratory 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 [6]. 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 and the calculated compressive strength was based on the average of three values. For strength development test, the compressive strength test was conducted after 28, 56, 90, 120, 180, 270, and 360 days.

2.4.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials were measured as a function of increasing temperature in time. TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of moisture. The temperature set for epoxy mortar was 30°C to 1000°C with the heating rate of 10°C/minute in nitrogenic atmosphere. Mortar specimen was crushed into powdered form and passed through 150 µm sieve. Various ratios of epoxy resin were tested to see the differences in decomposition pattern. The suitable aluminium pans for TGA analysers were filled with approximately 10 mg of mortar powder. Various ratios of epoxy-modified mortar were tested to observe and investigate the differences in decomposition pattern. Figure 1 shows the TGA machine used to conduct this test.

Figure 1. Thermogravimetric machine

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 ratios 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 day-28 while the compressive strength of the 10 % epoxy resin was 36 MPa, which was the highest strength among all epoxy ratios and higher than the strength of normal mortar. This was achieved due to the presence of alkalis from the hydration process to react with epoxy resin.

The increase in epoxy ratio 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. [7]. According to Ohama and Takahashi [8-10], 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 ratio was taken as the optimum content as to use without hardener which gives higher compressive strength.
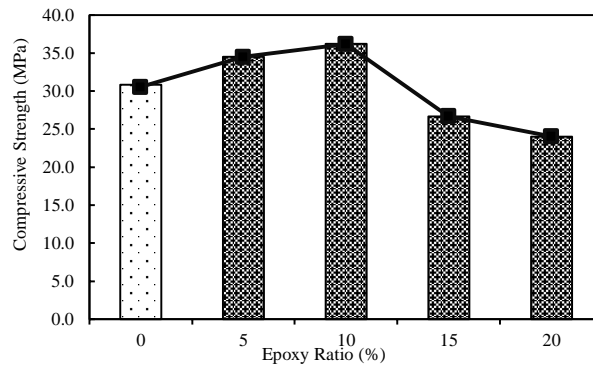

Figure 2. Relationship between compressive strength and epoxy ratio in 28 days with wet-dry curing

3.2 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 make a concrete and mortar denser [11]. The figure shows the result of strength development and apparent porosity of 10% epoxy ratio with wet-dry curing. This ratio and curing regime was selected as it gives a higher compressive strength and suitable condition for hydration and polymerization process. As shown in Figure 3, 28 days apparent porosity was recorded at 6 % while the strength was 36 MPa.
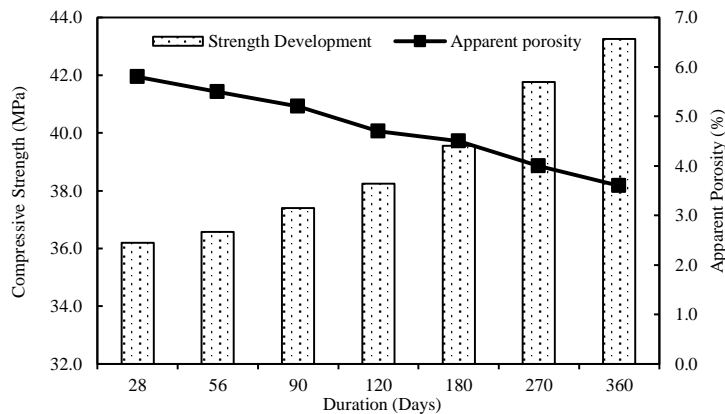

Figure 3. Relationship between compressive strength and porosity of 10% epoxy ratio with duration

   Prolonged curing period has shown to lower the porosity and increases the strength of mortar. After 365 days curing, the porosity was 3.7 % and the compressive strength was 44 MPa. The decreasing of porosity at 365 days was recorded almost 40 % of its initial porosity. In the meantime, the compressive strength increased 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.

3.3 Thermogravimetric analysis (TGA)

The result in Figure 3 was simplified in Tables 2 and 3. Figure 4 shows the results for TGA and Differential thermal analysis (DTA) where the decomposition of component in high temperature was measured. The percentage of element decomposition was calculated based on DTA graph and shown in Table 5. At 30°C to 200°C, the decomposition of CSH gel contains in epoxy mortar was occurred. Then, the decomposition of polymer and $Ca(OH)_2$ happened at 200°C to 400°C and 400°C to 500°C, respectively. The decomposition of $CaCO_3$ gases was occurred at 500°C to 700°C [12]. The percentage of gases decomposition can be calculated based on TGA and DTA graph.

Table 2 Result of thermogravimetric analysis

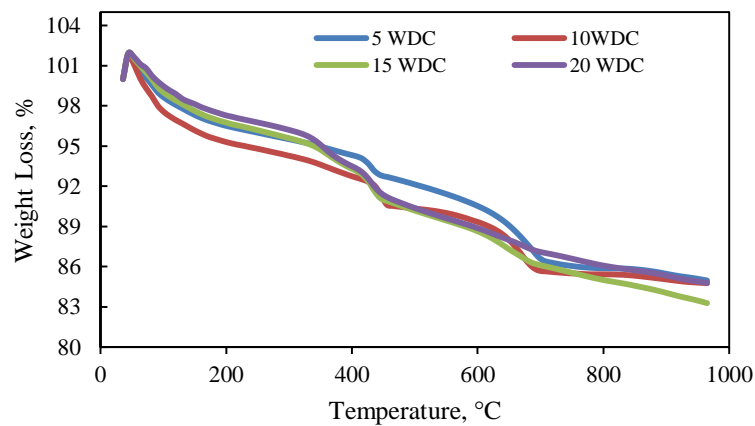|	Decomposition of CSH gel, (%)	Decomposition of polymer, (%)	Decomposition of $Ca(OH)_2$ (Portlandite) , (%)	Decomposition of carbonate phases, (%)		Residue (%)
	30°C – 200°C	200°C – 400°C	400°C – 500°C	500°C – 750°C	700°C – 850°C	850°C
5 % WDC	3.47	2.16	2.28	6.19	0.89	85.81
10 % WDC	4.67	2.52	2.43	4.83	0.57	85.39
15 % WDC	3.37	3.26	3.10	4.63	1.46	84.57
20 % WDC	2.70	3.73	3.26	3.76	1.31	85.72

Figure 4. Weight loss of specimen after exposed to high temperature

Table 3 shows the percentage of gases derived from the graph. From the table, 10 % epoxy ratio recorded lower decomposition of components because the polymer interfere the behaviour of hydroxide calcium and its content. By addition of the epoxy resin, the interaction between polymer and hydroxide ion became active and the $Ca(OH)_2$ that was reacted with epoxy resin cause a polymerization process to occur. The amount of $CaOH_2$ was reduced as the polymer became reactive. From the TGA analysis, the composition of $CaCO_3$ was highest in 10 % of epoxy ratio. When epoxy resin reacts with the hydroxyl ion, $CaCO_3$ was

produced. Beyond 10 % of epoxy resin ratio, the hydration process takes place and the polymer did not react with hydroxyl ion. This is the reason for the higher percentage of component when TGA test was conducted. As stated before, addition of more than 10 % epoxy resin cause the resin to be excessive and lowered the compressive strength.

Table 3 Percentage of gases decomposition

	H_2O (%)	$Ca(OH)_2$ (%)	CO_2 (%)	$CaCO_3$ (%)
5 % WDC	6.62	27.23	4.26	9.68
10 % WDC	4.4	18.08	5.59	13.51
15 % WDC	6.13	25.19	5.99	12.87
20 % WDC	6.5	26.73	5.65	12.83

3.4 Fourier Transformation Infrared Spectroscopy (FTIR)

Figure 5 presents the Fourier transformation infrared spectroscopy (FTIR) for epoxy mortar and normal mortar. FTIR is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. The goal of any absorption spectroscopy is to measure how well a sample absorbs light at each wavelength which later will determine the material's molecular composition and structure. In Figure 4, absorption bands within the range of 4000-1500 wavenumbers indicates the stretching of OH ion from calcium hydroxide, $Ca(OH)_2$, in the cement hydrates. The bands were the same for normal and epoxy mortars. At 1000 wavenumbers, the epoxy ring was stretched in epoxy mortar while in normal mortar, the CO_3 ion appeared in higher percentage. The summary of composition and structure is shown in Figure 4 and Table 4.
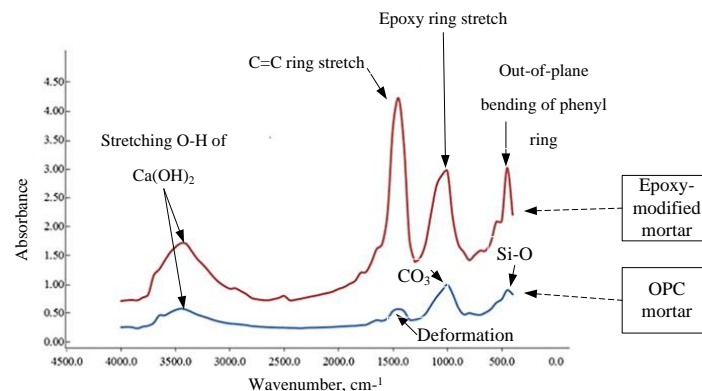

Figure 5. FTIR between epoxy mortar and normal mortar

Table 4 Comparison of composition and structure of normal and epoxy mortars

Wavelength	Composition	
	Normal mortar	Epoxy mortar
3000-4000	Stretching O-H of $Ca(OH)_2$	Stretching O-H of $Ca(OH)_2$
1200-1700	Deformation H-O-H	C=C ring stretch
800-1200	CO_3	Epoxy ring stretch
300-700	Si-O	Out-of-plane bending of phenyl ring

By comparing the profile of self-healing epoxy-modified mortar and normal mortar, it is interesting to note that the positions of main bands in the profile of epoxy-modified mortar shift to 1110 cm^{-1}, which can be attributed to CSH gel. Moreover, the sharp peak around 3650 cm^{-1} is due to the hydroxyl stretching band, which shows that there is calcium hydroxide in healing products [13].

4.0 CONCLUSIONS

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 36MPa, 3MPa and 3.8MPa, respectively.

ii. The trend of strength development of the 10 % epoxy mortar kept increasing after 360 days of curing and the decreasing of porosity recorded almost 40 % of reduction.

iii. With the increased of epoxy content, the degree of hardening started to decrease due to the insufficient amount of hydroxyl ion to react with the excessive epoxy.

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