Modification of microstructure of cement mortars by water-soluble polyvinyl alcohol

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Abstract. The scanning electron microscopy (SEM) was used to describe the morphology and condition of hydrate crystals. This work is designed to investigate the simultaneous effect of both polymers to cement ratio (p/c) and water to cement ratio (w/c) ratios on flexural strength of type I ordinary Portland cement mortar containing PVA. The obtained results confirmed the effect of the added polymer and an optimum value for p/c equal to 1.6% at optimum w/c of 0.30 was recommended due to highest obtained flexural strength, which is two times of the strength of unmodified mortar. SEM images present an abundant crystal of cement mortar growth noticed at the air void surfaces of the modified mortars where the presence of water-soluble polymers is expected. Possible film formation on the surface of cement grains due to PVC addition was studied by examining the influence of the curing conditions on the flexural strength.

1. Introduction
Polymer has gained more attention in recent years because of its possible use for many manufacturing demands. It is used as a modification agent for cement. The effect of low volume amount of Polyvinyl Alcohol (PVA) as water-soluble on cement mortar microstructure and reaction of hydration cement was considered. The polymer molecules provided on the Nano scale improve bonding for the relatively large cement grains. Polyvinyl alcohol (PVA) (sometimes referred to as PVOH PVAL or POVAL) was the principal artificial colloid ready in 1924 [1], followed by hydrolysis of acetates clusters of (PVAc to PVA) [2]. Continuous researches focused on the improvement of novel little budget material by limited features [3]. Cement polymer materials can be manufactured by a right slight auxiliary of cement by polymeric materials [4, 5 & 6]. Polymer soluble molecule provided on the molecular scale, can improve the comparatively great cement granules through polymers. The enhancement of the material properties was stated with nonappearance of agents taking place at surfaces, and the creation of the films on the hydrate’s crystal can be easier and uniform [7]. Adding of actual slight amounts of water-soluble polymers improves strength of adhesion and the durability to cementitious materials [8 & 9]. Water is also responsible for the total size and distribution of pore size system developed in cement paste, controlling its permeability and thus determining its durability [10]. Despite this important role, no individual research has been devoted to the role of water.

2. Water soluble polymers in cement mortars
Water-soluble polymer is usually used with very little p/c ratio, the fresh mix workability was significantly improved compared to normal cement mortar mixtures due to the impact of polymeric materials on plasticizers and air-entraining. The modified mortar structure demonstrates greater water holding capacity than normal cement structures [11]. Moreover, well spreading of cement mortar [12]
&13] and increase in direct tensile strength is achieved due to improvement in bond strength between cement grains and aggregate among cement mortar [14]. An important decrease in interfacial transition zone (ITZ) thickness nearby aggregate particles, and meaningful reduction in Ca (OH)₂ crystal could be achieved due to the use of polymers and by potentially replacing those with C-S-H phase. Although, it was found that the use of water-soluble polymers increases specific properties of mortar, for example, workability and adhesion; making them suitable as adhesive mortar, the study of this in a micro structural way is needed. Thus, this work aims to investigate the impact of these polymers on the cement hydrates that are formed, in particular at micro and Nano scales.

3. Materials
Materials used for experimental works in this study were verified to conform with the Iraqi specifications (IQS), the tests were performed in the laboratory of Babylon University, College of Material Engineering, and these materials are:

3.1 Ordinary Portland cement (O.P.C) Type (I)
This corresponds to IQS No. 5/1984 [14]. The cement was stored in air – tight plastic containers to avoid exposure to the atmosphere.

3.2 Natural fine aggregate:
All fine aggregate was passing through 1.18mm sieve, and fineness modulus to 1.64 was used, its grading conforms to IQS No. 45/1984 (zone 4) [15]. The sand was spread out and left in air for surface dry before use.

3.3 Polyvinyl alcohol (PVA):
With molecular weight of 125000 gm/mol, 88% nominal hydrolysis was used without further purification as shown in Figure 1. The polymers concentration is specified here according to the weight of the cement for the preparation of the PVA solution. The solution was prepared using approximately 10g of PVC in 300 ml of boiled water until it dissolved completely. The solution was saved overnight in an open-air atmosphere to reduce its volume to 100 ml.

3.4 Super plasticizer (SP):
Modified poly-carboxylates was used as super plasticizer (SP) to control the excellent flowability properties of fresh mortar and it conforms to the requirements of ASTM C494- 14 [16].

![Figure 1. Polyvinyl alcohol.](image)

A) Powder (PVA). B) After completely dissolved.

4. Mixing, casting, curing and specimens preparation
PVA powders are first dissolved in mixing water before being added to the sand and cement in the
laboratory mixer for mortar, a good homogeneous mix was achieved according to ASTM C305-14 [17]. Table 1 shows the mixing ratios for all the mortar mixtures used in this study. Curing was achieved by two procedures applied after the removal of molds. First, part of specimens was immersed in water in moist room for 2 days (under 20°C, 90-95% R.H.), followed by dry curing till the day of testing at 20°C and 63% relative humidity. Water immersing causes certain compounds of cement hydration and the PVA film-coated to be leached out, leading to increase in porosity of the cements mortar and decrease in strength, as shown in Figure 2; therefore, dry curing was preferred [12].

![Image](image_url)

**Figure 2.** Leached of polymers in water tank while specimens curing.

| No. mix | Concentration of addition PVA (%) | Cement kg/m³ | Sand kg/m³ | w/c | SP (%) | p/c |
|---------|----------------------------------|--------------|------------|-----|--------|-----|
| Mix1cc* | 0                                | 1.0          | 0.50       | 0.45| 0      | 0.008 |
| Mix1sc** | 0.7                             | 1.0          | 0.50       | 0.30| 0.5    | 0.01 |
| Mix13  | 0.7                              | 1.0          | 0.50       | 0.30| 0.5    | 0.01 |
| Mix14  | 0.7                              | 1.0          | 0.50       | 0.30| 0.5    | 0.02 |
| Mix21  | 0.7                              | 1.0          | 0.50       | 0.30| 0.5    | 0.008 |
| Mix22  | 0.7                              | 1.0          | 0.50       | 0.30| 0.5    | 0.01 |
| Mix23  | 0.7                              | 1.0          | 0.50       | 0.30| 0.5    | 0.01 |
| Mix24  | 0.7                              | 1.0          | 0.50       | 0.30| 0.5    | 0.02 |
| Mix31  | 2                                | 1.0          | 0.50       | 0.30| 0.5    | 0.008 |
| Mix32  | 2                                | 1.0          | 0.50       | 0.30| 0.5    | 0.01 |
| Mix33  | 2                                | 1.0          | 0.50       | 0.30| 0.5    | 0.01 |
| Mix34  | 2                                | 1.0          | 0.50       | 0.30| 0.5    | 0.02 |
| Mix41  | 2                                | 1.0          | 0.50       | 0.30| 0.5    | 0.008 |
| Mix42  | 2                                | 1.0          | 0.50       | 0.30| 0.5    | 0.01 |
| Mix43  | 2                                | 1.0          | 0.50       | 0.30| 0.5    | 0.01 |
| Mix44  | 2                                | 1.0          | 0.50       | 0.30| 0.5    | 0.02 |

CC* = conventional curing.  SC** = Self-curing
5. Testing program

5.1 Flowability (diameter) Test:
Standard consistency of plain cement mortar composite or modified cement mortar with PVA related with amount of water essential for giving good workability was determined by the flow test. The test of flow table was performed according to (ASTM C230 - 14) [18].

5.2 Compression test:
The compressive strength test is performed according to ASTM C109-16[19] on 50 mm cubes. The average of three cubes was adopted at each test.

5.3 Direct tension test:
Samples were prepared conferring to BS 6319-7:1985 [20], for direct tensile strength tests.

5.4 Flexural test:
The flexural bending strength of the mortar was determined by prisms with 40× 40× 160 mm dimension, in agreement with ASTM C 348-18 [21].

5.5 Scanning Electron Microscope (SEM):
Sample of fracture surface from mortar specimens subjected to both type of curing is inspected by a VEGA3 TESCAN type of SEM.

6. Results of mechanical strength

6.1 Fresh properties (flow test):
It was indicated that PVA develops the cement mortar workability significantly as shown in the figure 3. This improvement was indicated up to a certain limit (at any specified w/c); comparatively greater values of p/c act adversely and result in decreased workability.

![Figure 3. Spread diameter of unmodified and modified cement mortar by PVA at different concentration (C=PVA powder % of cement weight).](image)

6.2 Hardened properties:
The results of all mortar specimens are listed in Table 2; it indicates the average results for 28 days.

6.2.1 The compressive strength: at 28 days with dry curing for modified mortar and moisture curing for all mortar specimens are indicated in Figure 4. The results showed a decrease in strength with the increase in the amount of PVA within the cement mixture, possibly due to the air voids formed during mixing [10]. Mix23 has low compressive strength with increasing p/c ratio at 1% concentration due to increased void due leaching at wet curing as can be seen in Figure 2.

6.2.2 Direct tensile strength: results are indicated in Figure 5. Depending on the hydration and films formation, it was noticeable that the rate of increase in direct tensile strength has decreased gradually with respect to increment p/c ratio for all mix proportions. These results were corresponding to the findings of the other researcher [22]. P/C ratio in the hydration products in matrix was reduced; thus, negatively affecting the mechanical properties of modified cement mortar [13].

6.2.3 Flexural strength: results of average three prisms at 28 days under flexural one-point load are shown in Figure 6. PVA solution has proved potential enhancement in the flexural strength of cement mortar composite, it reached up to twice the strength of the unmodified cement mortar. Polymer film development increases the strength of flexural, but with water curing and when PVA film leached out, the specimen surfaces become rough and caused high porosity so the flexural strength decreased, this is clear with the type of curing shown in Figure 2. Curing effect indicated that the flexural strength of modified mortars with PVA was increased by about half in wet curing and twice in dry curing, respectively, which is confirmed by other researches [12 & 22]. According to all results above the optimal dose of PVA (equal to 0.016) with 1% concentration could be recommend, which gave good workability and mechanical strength.

6.2.4 SEM Investigation: At these surfaces, the existence of PVA film is predictable for the reason that of convergence is strong during the air void and water phase as shown in Figure 7. The fracture surfaces of the unmodified and modified mortars samples by polymers are compared in SEM images. Unhydrated cement granules appear as bright regions in SEM images, crack and pores in the form of black spots. Water-soluble polymers are added on a molecular scale to allow film formation to develop easily and at lower rates as indicated in Figure 7-b.

The shape of the film is formed as shown in Figure 8-b. After two days of wet curing followed by dry curing because of starting polymerization which is likely to happen after 7 days of curing, the Polyvinyl alcohol film increases significantly with increased relative humidity. Through SEM images in Figure 7-b and 8-b, it can be concluded that there is an abundance of Ca(OH)₂ crystals on the aerobic margin of the modified mortar, creating a moisture balance due to the formation of films that have increased the moisture level of the cement and hydrate formation. The cement grains can be recognized as the shining spots in the SEM; fine sand particles are the bigger bodies. Mortar without PVA in SEM appears as a grade of blackness and the areas neighboring the particles of sand are 0.6 mm of the particles. In SEM of cement mortar free of PVA, grains of cement are observable incline to disperse non-uniformly in the matrix. The dispersion of polymers for the purpose of PVA film formation was found in the matrix and through SEM images of 1.6% of PVC addition which acts as a mixture in cement mortar.
Table 2. Average strength at age 28 days of all mixes used.

| Mix No. | Concentration of addition PVA (%) (Powder/cement weight) | p/c | Compressive Strength (MPa) | Direct tensile Strength (MPa) | Flexural Strength (MPa) |
|---------|----------------------------------------------------------|-----|---------------------------|------------------------------|------------------------|
| Mix1cc* | 0                                                        | 0   | 30.95                     | 3.50                         | 7.95                   |
| Mix1sc**|                                                          |     | 38.80                     | 5.20                         | 5.60                   |
| Mix21   | 0.008                                                    |     | 35.70                     | 2.49                         | 6.20                   |
| Mix22   | 0.012                                                    |     | 35.15                     | 4.03                         | 7.16                   |
| Mix23   | 0.016                                                    |     | 47.38                     | 3.79                         | 7.95                   |
| Mix24   | 0.02                                                     |     | 33.95                     | 2.98                         | 7.95                   |
| Mix21cc*| 0.016                                                    |     | 43.00                     | 2.70                         | 7.30                   |
| Mix21sc**| 0.016                                                   |     | 43.65                     | 5.43                         | 11.78                  |
| Mix22cc*| 0.02                                                     |     | 33.65                     | 3.05                         | 7.18                   |
| Mix22sc**| 0.02                                                    |     | 33.65                     | 3.05                         | 7.18                   |
| Mix23cc*| 0.008                                                    |     | 51.93                     | 4.37                         | 6.83                   |
| Mix23sc**| 0.012                                                   |     | 37.85                     | 3.39                         | 8.27                   |
| Mix24cc*| 0.016                                                    |     | 34.65                     | 2.60                         | 8.90                   |
| Mix24sc**| 0.02                                                    |     | 34.75                     | 3.20                         | 7.23                   |
| Mix23cc*| 0.008                                                    |     | 55.50                     | 4.88                         | 7.60                   |
| Mix23sc**| 0.012                                                   |     | 37.00                     | 3.11                         | 8.45                   |
| Mix24cc*| 0.016                                                    |     | 45.25                     | 3.66                         | 10.83                  |
| Mix24sc**| 0.02                                                    |     | 29.70                     | 4.00                         | 7.41                   |

CC* = conventional curing. SC** = Self-curing

Figure 4. Average Compressive strength at 28 days for composite cement mortar.
Figure 5. Average direct tensile strength for all mortar specimens.

Figure 6. Flexural strength of cement mortar composite.
Figure 7. SEM image demonstrates of cement mortar composite phases and crack. 
(a) Cement mortar without PVA conventional curing (b) Cement mortar with 1% PVA self-curing
Figure 8. SEM image demonstrates, C-S-H fibers cover the walls of the air voids by self–curing. (a) Crack or void in cement mortar without PVA (b) Cement mortar with 1% PVA.

7. Conclusions
The results of inducing the PVA solution with cement mortar and the SEM images were studied and the following conclusions are drawn:

- The strength was significantly increased by the addition of small amounts of PVA, and the optimal dose of PVA equal to 0.016 with 1% p/c concentration could be recommend, which gave good workability and mechanical strength.
- PVA film creation is expected in modified mortars as the consequence of mechanical strength tests. The PVA film has a main influence on the compression, flexural and direct tension strength of mortar mixes cured in dry condition. Also, for modified cement mortar, SEM image showed that an efflorescence abundant of Ca(OH)$_2$ crystals was observed on the air voids surfaces.
- Modification of cement mortar by PVA solution affects the micro-structural features for
mortars in several ways; the rate of hydration, nature and morphology of hydrates and forming film polymers. Examination of SEM illustrates an efflorescence abundant of Ca(OH)$_2$ crystals next to the air void boundaries of modified mortar.

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