

EFFECT OF POLYVINYL ALCOHOL ON FLEXURAL STRENGTH AND SOME IMPORTANT PHYSICAL PROPERTIES OF PORTLAND CEMENT PASTE

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Abstract: Some water-soluble polymers have proved potentials for improvement in properties of Portland cements. This work was designed to investigate the simultaneous effect of both water-to-cement (W/C) and polymer-to-cement (P/C) ratios on flexural strength of type V Portland cement pastes containing polyvinyl alcohol. The obtained results confirmed the strong effect of W/C-ratio on the effectiveness of the added polymer so that there exist optimum values for both W/C and P/C-ratios. Pastes prepared at optimum W/C and P/C-ratios of respectively 0.30 and 0.016 exhibited the highest flexural strength which was more than two times the strength of unmodified pastes. Further measurements on hardened paste specimens prepared at W/C=0.30 show that increasing the P/C-ratio increases dry bulk specific gravity of the specimens and result in significant reductions in both total permeable pore volume and water absorption of the specimens confirming the effective packing caused by polyvinyl alcohol acetate.

Keywords: Polyvinyl, Alcohol, Portland Cement, Flexural Strength

1. INTRODUCTION

To satisfy the needs of modern civilization, continuous research works are devoted to development of new low cost materials with specific properties. Recent advances in the field of cement-based products are related to the use of admixtures like polymers added in small quantities to modify the properties of cement products.

Cement-polymer composites are materials, which are made by a very small replacement of hydraulic cement by polymeric binders. Continuous research activities [1–5] have resulted to development of various suitable polymers, which are now widely used. The properties of the composites are related to the nature and quantity of the polymer used. Melamine formaldehyde resin [6] and hydroxyl propyl methylcellulose [7], act as retarder for cement while other polymer/monomer e.g. furfuryl alcohol [8] act as accelerator. One important group of polymers is those which are soluble in aqueous media [9–15].

It is believed that some of the water-soluble polymers interact chemically with the hydration products of Portland cement, and the others just make a film around cement grains [14, 15]. The nature of the interaction therefore depends upon

the type and the amount of polymer used. For the case of chemically reactive polymers, like polyvinyl alcohol, the mechanism of the reaction is not yet completely understood due to the amorphous nature of the products. However, discussions were made based on studies on microstructure and molecular structure and it is proposed that calcium complexes formed by chemical interaction occupy the free place in the pore structure [10]. The new compounds formed fill the pores, thus, densifying the structure and improving properties of the cement paste.

The role of water in polymer-modified cement mixes is very important and not just hydrating the cement phases, but at the same time hydrolysis of polymer, dispersion of polymer around cement particles, and imparting rheological properties for a suitable workability. Water is also responsible for the total volume and size distribution of the pore system developing in the hardened cement paste, controlling its permeability and thus determining its durability. In spite of such important role, no individual research work has been devoted to the role of water. The present study is therefore devoted to the simultaneous effects of both W/C- and P/C-ratios on important physical properties of type V Portland cement paste containing polyvinyl alcohol. Polyvinyl alcohol is a water-soluble

polymer which has gained more attention in recent years due to its potential for industrial applications. In spite of its importance, it has been less studied as a cement modifying agent and there is very few literature devoted to cement-polymer composites based on which [10].

Flexural strength was measured and studied as the most important mechanical property of the polymer-modified cement paste and water absorption was also considered and studied as the most important physical property determining the material durability in penetrating aggressive environments. The hardened cement pastes prepared at the optimum W/C-ratio, i.e. 0.30, were also utilized to investigate the effects of P/C-ratio on their dry bulk specific gravity, total permeable pore volume and water absorption.

2. EXPERIMENTAL

The cement used was type V Portland cement prepared from Tehran cement company. Its properties are given in table 1.

Table 1. Properties of cement

Physical Properties	Value
Density (g/cm ³)	3.145
Blain Specific surface area (cm ² /g)	2950
Chemical composition (wt%)	
CaO	64.90
SiO ₂	22.42
Al ₂ O ₃	3.81
Fe ₂ O ₃	4.20
MgO	0.08
SO ₃	1.46
K ₂ O	0.42
LOI	1.61
Bouge's potential phase composition (wt%)	
C ₃ S	65.31
C ₂ S	18.15
C ₃ A	3.16
C ₄ AF	13.37

Polyvinyl alcohol (PVA), prepared from Merck company, 88% nominal hydrolysis was used without further purification. The molecular weight was 125000.

To prepare PVA solution, about 7.0 g of PVA was boiled in 300 ml water until the polymer was entirely dissolved. The solution was kept overnight in an open-air atmosphere to reduce its volume to an exact value of 100 ml.

A number of cement-polymer mixes were designed by varying both P/C- and W/C-ratios. The P/C-ratio was adjusted at six different values of 0.004, 0.008, 0.012, 0.016 and 0.020 covering relatively low and high values. Based on some preliminary experimental results, three different W/C-ratios including 0.28, 0.30 and 0.32 were also considered.

Before casting, PVA solution and water were mixed first. The mixture was then added to cement and was mixed for 5 minutes. The mixed polymer-modified pastes were cast into molds under very fine vibration to prepare prism specimens of the size 5×32×150 mm. The specimens were demolded approximately 24 hours after casting and then subjected to the following curing regime:

1 day moist curing at 20°C and more than 95% relative humidity and then 27 days dry curing at 20°C and 50-60% relative humidity.

After curing the specimens were used to measure their flexural strength. Flexural strength was determined according to ASTM C 78 testing method. For each measurement three specimens were used and the average value was reported as the result. A number of cylindrical paste specimens of the size 5×10 cm were also prepared at the constant W/C-ratio of 0.30 to investigate the effects of polymer on dry bulk specific gravity, total permeable pore volume and water absorption of hardened cement paste. These specimens were also cured in the same way.

To evaluate the effect of polymer on paste workability, spread diameter was according to ASTM C230 testing method.

Dry bulk specific gravity, total permeable pore volume and water absorption were determined according to the following procedure:

- a) Specimens were weighed and dried in an oven at a temperature of 100 to 110 °C for 48 hr. the specimens were then allowed to cool in dry air to the temperature of 25 °C and weighed again. This procedure was repeated until the difference between any two successive weights was less than 0.5% of the lowest one. This last weight was designated by A as the oven-dried weight.
- b) After final drying, cooling, and weighing, the specimens were immersed in water at 25°C for 72 hr. They were weighed after removing their surface moisture with a towel. This procedure was repeated until the difference between any two successive weights was less than 0.5% of the heavier weight. The final surface-dry weight after immersion was designated by B as the saturated weight after immersion.
- c) The specimens were placed in a receptacle, covered with tap water, and were boiled for 5 hr. They were then allowed to cool and their surface moisture was dried with a towel. The soaked, boiled, surface-dried weight was designated by C as the saturated weight after boiling.
- d) After immersion and boiling, the specimens were suspended in water at 25 °C by a wire and again weighed. This weight was designated by D as the immersed weight.

Using the above determined weights, dry bulk specific gravity, total permeable pore volume and water absorption of specimens were calculated as follows:

$$\text{Dry bulk specific gravity} = \frac{A}{(C-D)} \quad (1)$$

$$\text{Volume of permeable pore space, \%} = \frac{(C-A)}{(C-D)} \times 100 \quad (2)$$

$$\text{Water absorption after immersion, \%} = \left[\frac{(B-A)}{A} \right] \times 100 \quad (3)$$

3. RESULTS AND DISCUSSIONS

3.1. Workability

Figure 1 represents the results obtained for spread diameter. As seen, PVA improves the cement paste workability considerably. This effect however is observed up to a certain limit and at any given W/C-ratio, relatively higher values of P/C-ratios behave adversely and result in reduced workability. For the three studied W/C-ratios of 0.28, 0.30, and 0.32, the limits for P/C-ratios are 0.012, 0.016, and 0.016 respectively. The positive effect of PVA on cement paste workability is mainly interpreted in terms of improved consistency due to both the 'ball bearing' action and the dispersing effect of polymer. Relatively high P/C-ratios, however, reduce the paste workability due to increases in

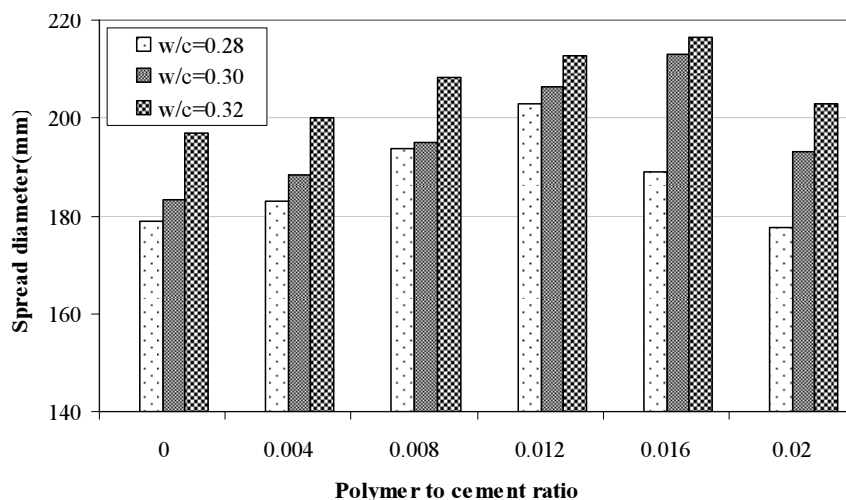


Fig. 1. Spread diameter of cement pastes modified by polyvinyl alcohol at different W/C- and P/C-ratios

paste viscosity. The W/C-ratio of the Portland cement paste at a given consistency (flow or slump) can therefore be markedly reduced by modifying it with a suitable proportion of PVA. This water reduction effect is found to contribute to a strength development and drying shrinkage reduction [2].

3.2. Flexural Strength

The flexural strength (FS) of the specimens was measured in accordance with ASTM C 78 and using the equation (4).

$$FS = \frac{P.L}{b.d^2} \quad (4)$$

In this equation P is the maximum applied load, L is the span length, b is the average width of specimens, and d is the average depth of the specimens.

The obtained results are presented graphically in figure 2. As seen, at the lower W/C- ratio of 0.28, addition of polymer not only does not provide any improvement in flexural strength, but also decreases the flexural strength slightly. Such a decrease in flexural strength is due to the relatively low W/C- ratio [3]. Relatively lower amounts of water probably can not result in complete hydrolysis of polymer and/or an effective dispersion of which around cement particles [13]. Increasing W/C-ratio from 0.28 to 0.30 resulted in significant improvement in

flexural strengths especially at P/C-ratios around 0.016. As seen, flexural strengths as high as twice the strength of unmodified paste can be obtained at optimum W/C- and P/C-ratios. Higher W/C-ratios, e.g. 0.32, are less effective on flexural strength. Lower flexural strengths at relatively higher W/C-ratios can probably be attributed to the effect of excess water addition producing a relatively large total pore volume in the hardened pastes which weakens the flexural behavior. Detailed experimental work along with utilization of suitable laboratory techniques including mercury intrusion porosimetry are however necessary to support such a claim.

3.3. Dry Bulk Specific Gravity

The effect of polymer on dry bulk specific gravity of polymer-modified hardened paste was also studied. The variations of dry bulk specific gravity due to changes in P/C-ratio are shown in figure 3. According to this figure, it can be concluded that any increases in P/C-ratio in the given range result in a significant increase in dry bulk specific gravity. Such a positive effect of PVA on hardened Portland cement paste can be simply attributed to the lubricating effect of which facilitating both dispersion and close packing of cement particles which are then held tightly together by the binding properties of both hydration products of cement phases and the polymer matrix produced [4].

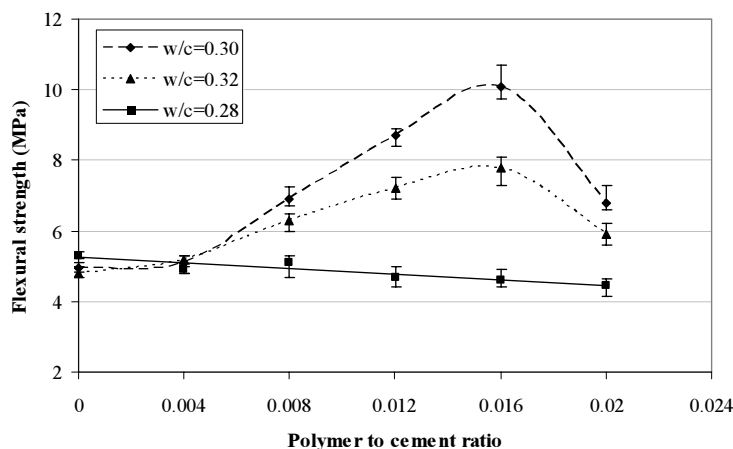


Fig. 2. Flexural strength of cement pastes modified by polyvinyl alcohol at different W/C- and P/C-ratios.

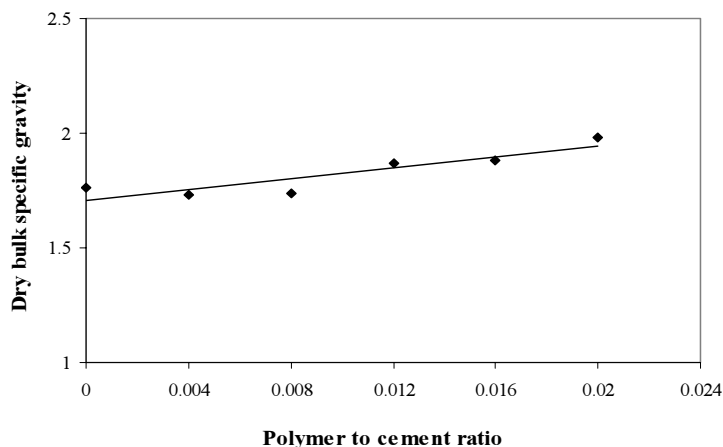


Fig. 3. Effect of polymer addition on dry bulk specific gravity

3.4. Total Permeable Pore Volume

The obtained results show that total permeable pore volume of the cement pastes modified by PVA varies with the inclusion of polymer, as shown in figure 4. The higher the P/C-ratio, the lower the total permeable pore volume.

Since permeable pore volume is the key-factor in determining the durability performance of cement-based materials when exposed to penetrating aggressive environments, any decrease in which could result in significant improvement in durability performance. Pore volume reduction due to polymer addition can also be attributed to its dispersing and close packing effects on cement particles. In such a case, formation of the polymer matrix along with

progress of hydration reactions of cement phases can result in a denser microstructure with a higher dry bulk specific gravity and of course a lower pore volume.

3.5. Water Absorption

When brought in contact with water, cement paste absorbs water because of its porous microstructure. The lower the water absorption, the lower the permeable pore volume. Measurement of water absorption of cement pastes modified by PVA is therefore a simple way to confirm the results obtained for dry bulk specific gravity and total permeable pore volume [11].

The effect of polymer addition on water

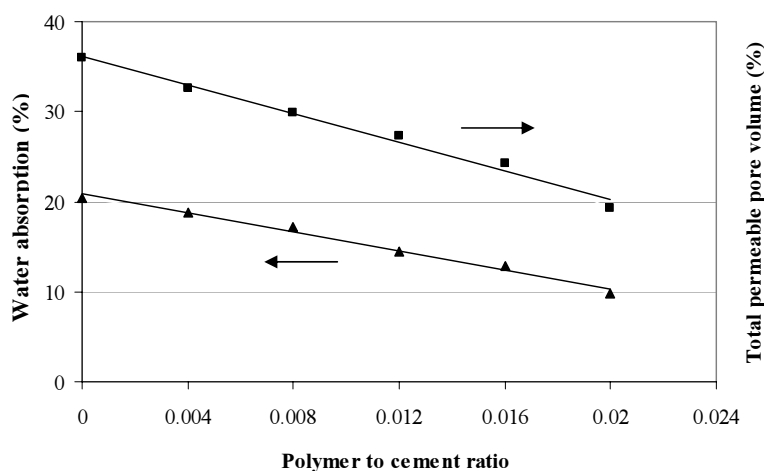


Fig. 4. Effect of polymer addition on total permeable pore volume and water absorption

absorption of hardened cement paste is shown graphically in figure 4. It is evident that water absorption reduces considerably with increase in P/C-ratio. As seen, a 2 wt% polymer addition can reduce the water absorption to half of the value obtained for the unmodified paste. This indicates that the polymer addition results in reduction of the porosity of the pastes. Other studies also showed that the polymer fills the voids in the cement matrix [12,13]. Polymer-modified cement pastes are therefore expected to be more resistant towards penetrating aggressive environments than control cement paste.

4. CONCLUSION

The results of this study show that flexural strength and important physical properties of Portland cement paste including permeable pore volume and water absorption can be significantly improved by addition of polyvinyl alcohol. The study confirms the important role of W/C-ratio on the effectiveness of the polymer, so that relatively low W/C-ratios can even provide inverse effect. To achieve the maximum possible improvement in properties, both P/C- and W/C-ratios must be optimized together.

REFERENCES

1. Ohama, Y., "Recent research & development in concrete-polymer composites", Proceedings of the 8th CANMET/ACI Int. Conf. on Recent Advances in Concrete Technology, ed. V. M. Malhotra, Montreal, Quebec, 1994, 753-783.
2. Ohama, Y., *Polymer-based admixtures*. J. Cem. Con. Composites., 1998, 20, 189.
3. Bright, R., Mraz, T. and Vassallo, J., "The influence of various polymeric materials on the physical properties of a cementitious patching compound", ASTM publication on Polymer-modified Hydraulic-cement mixtures, ed. L. A. Kuhlman, and D. G. Walters, 1999, 155-162.
4. Wang, R. and Gui, L., *Physical and mechanical properties of styrene-butadiene rubber emulsion modified cement mortars*. J. Cem. Con. Research., 2005, 35, 900.
5. Sickles, L. B., "Organics versus synthetics: their use as additives in mortars", Proceedings of Symposium on Mortars and Grouts Used in the Conservation of Historic Buildings, ICCROM, Rome, Italy, 1981, 387-392.
6. Singh, V. K., Khatri, S. D. and Singh, R. K., "High strength cement-melamine formaldehyde resin products", Proceedings of the 11th Int. Cong. on Chemistry of Cement (ICCC), Durban, South Africa, 2003.
7. Singh, N. K., Mishra, P. C., Singh, V. K. and Narang, K. K., *Effect of HPMC on the properties of cement*. Indian J. Chem. Technol., 2003, 9, 112.
8. Singh, V. K., Singh, R. K. and Khatri, S. D., *Effect of furfuryl alcohol on the properties of hydrated cement mortar*. J. Mater. Res., 2003, 5, 1131.
9. Brooks, S. A., Sinclair, W., Groves, G. W. and Double, D. D., *Effects of an organotitanate cross-linking additive on the processing and properties of macro-defect-free cement*. J. Mater. Sci., 1985, 20, 285.
10. Singh, N. B. and Sarita Rai., *Effect of polyvinyl alcohol on the hydration of cement with rice husk ash*, J. Cem. Con. Research, 2001, 31, 239.
11. Singh, R. K. and Rai U. S., *Effect of polyacrylamide on the different properties of cement and mortar*, J. Mater. Sci. Eng., 2005 A, 392, 42.
12. Ohama, Y., *Principle of latex modification and some typical properties of latex modified mortar and concrete*, J. ACI Mater., 1987, 86, 511.
13. Shaker, F. A., *Durability of styrene butadiene latex modified concrete*, J. Cem. Con. Research, 1997, 27(5), 711.
14. Gopinathan, K. and Rao R., "Influence of some water soluble polymers on the mechanical properties of cement polymer composites", Proceedings of the 9th Int. Cong. on Chemistry of Cement (ICCC), New Delhi, India, 1992, 538-543.
15. Kim, J. H., Robertson, R. E. and Naaman, A. E., *Structure and properties of poly (vinyl alcohol)-modified mortar and concrete*, J. Cem. Con. Research, 1999, 29, 407.