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Effect of polyvinyl alcohol on the hydration of cement with rice husk ash

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Abstract

Effect of 3.0-wt.% polyvinyl alcohol (PVA) was studied on the hydration of ordinary Portland cement in the presence and absence of 10% rice husk ash (RHA) by employing different techniques. The results have shown that PVA increases the strength and decreases the porosity. The increase in strength is due to the interaction of PVA with cement, forming some new compounds that fill the pores or improve the bond between the cement. The two cements behave in a similar way, and hence, replacement of cement by 10-wt.% RHA is beneficial. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer; Polyvinyl alcohol; Portland cement; Rice husk ash; Differential thermal analysis

1. Introduction

Polymers have been used to improve the durability properties of concrete [1–7]. Some of the polymers interact chemically with the hydration products of Portland cement, and the others make film. Calcium complexes formed by chemical interaction occupy the free place in the pore structure. If the new compounds formed are insufficient to fill the pores, they seal them, thus, densifying the structure. The permeability decreases even if there is no significant decrease in the porosity. Consequently, the durability properties improve. The nature of interaction depends upon the type of polymer used. Water soluble polymers, such as polyvinyl alcohol (PVA), has been used in cement mortars and concrete for improving the durability properties and strength.

In this paper, the effect of 3.0-wt.% PVA has been studied on the hydration of cement with and without rice husk ash (RHA).

2. Experimental

2.1. Materials

2.1.1. Cement

Portland cement clinker made from Vikram Cement plant was used for the hydration studies. The clinker was mixed with gypsum and RHA. The details of the two cements used are given in Table 1.

The chemical and mineralogical compositions of the cement are given in Tables 2 and 3, respectively. The composition of the RHA is also given in Table 2.

PVA from SD Fine-Chem was used. The molecular weight was 125 000. The concentration of the polymer given here is with reference to the weight of cement.

2.2. Preparation of PVA solution

About 6.0 g of PVA was boiled in 50-ml distilled water until the entire amount was dissolved. The solution was kept overnight and then was made up to 100 ml.

2.3. Preparation of hydrated samples

About 20 g of cements (RD-11 and -63) were weighed in polythene bags separately and allowed to hydrate in the presence and absence of 3.0-wt.% PVA for different periods

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Table 1
Cement composition and Blaine surface area

Cement no.	Clinker (wt.%)	Gypsum (wt.%)	RHA (wt.%)	Blaine surface area (m^2/kg)
RD-11	95	5	–	280
RD-63	86	4	10	387

of hydration, in such a way that w/c ratio was 0.5, i.e. by adding 10 ml of the PVA solution prepared above. The hydration was stopped at different intervals of time by using isopropyl alcohol and ether. The samples were dried at 105°C in an oven and then sealed in polythene bags and stored in a desiccator.

Free lime of the hydrated samples was determined by modified Franke method.

About 1 g of the hydrated samples was heated first at 105°C for 1 h and then at 1000°C in ceramic crucibles. From the weight loss, the nonevaporable water contents were determined. Presence of 3.0-wt.% PVA will also contribute to this value, however, it will be insignificant.

X-ray diffraction patterns of some of the hydrated samples were recorded at BARC, Mumbai with the help of a DIANO X-ray diffractometer having Cu target X-ray tube using Cu K_α radiation ($\lambda = 1.5418$ Å).

DTA of PVA and some samples hydrated for 7 days were done at BARC under ambient conditions from room temperature to 1000°C at a heating rate of 10°C/min.

Scanning electron microscopic (SEM) studies of cement RD-11 hydrated for 1 day in the presence and absence of 3.0-wt.% PVA were done at DMSRDE Kanpur.

The two cements (RD-11 and -63) were mixed with PVA solution at w/c ratio of 0.3 in the presence of 3.0-wt.% PVA. The mixtures were made in a blender and then shifted to $5 \times 5 \times 5$-cm^3 molds. The molds were then vibrated for 5 min on a Crompton Greaves machine, and the cubes were then left for 1 day in the molds. After 1 day, the cubes were demolded and immersed in water until compressive strengths test. AIM-304 compressive strength testing machine was used. For each test, three molds were made, and the values are the average of three values.

Table 2
Oxide composition (wt.%)

	RHA	RD-11
LOI	1.32	2.41
SiO_2	88.73	21.86
Al_2O_3	2.03	4.40
Fe_2O_3	1.99	4.20
CaO	2.93	61.70
MgO	0.77	1.29
SO_3	0.46	2.49
Mn_2O_3	0.04	0.10
TiO_2	0.31	0.18
Na_2O	0.27	0.20
K_2O	1.20	0.50
IR	55.88	1.36

Table 3
Mineralogical composition of RD-11

Phase	C_3S	C_2S	C_3A	C_4AF
Composition (wt.%)	49.4	25.4	4.6	12.8

Pore size measurements of the samples were made with an Aminco porosimeter.

About 10 ml of 0.1% PVA solution in water was mixed with 1-g RD-11 cement, shaken for 1 min and filtered. The UV-visible spectra of this solution and 0.1% PVA solution were recorded with the help of Hitachi U.2000 UV-visible spectrophotometer in the wavelength range of 190–500 nm.

3. Results and discussion

The variation of nonevaporable water contents with hydration time in the presence and absence of 3% PVA is shown in Fig. 1. The values increase with the hydration time, indicating an increased hydration. In the case of RD-11 cement, the values of W_n are lower in the presence of PVA at all the ages of hydration, indicating that the extent of hydration is lower in the presence of PVA. In the case of RD-63 (control), the values are lower up to 3 days, but at 7 and 28 days, W_n values are higher as compared to that of RD-11. The lower value may be due to the dilution effect in presence of RHA. Besides, pozzolanic reaction might have not started up to 3 days of hydration. However, after 3 days of hydration, the pozzolanic reaction might have occurred and more C–S–H were formed. This causes an increase in the nonevaporable water content values. In the presence of PVA, the W_n values are lower indicating lesser hydration.

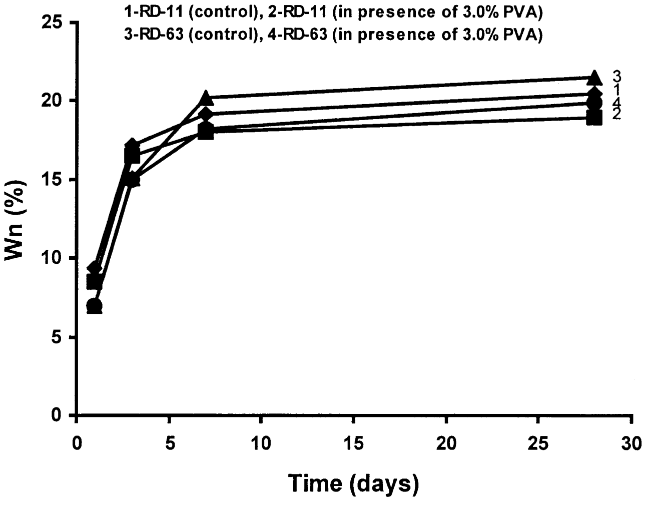

Fig. 1. Variation of nonevaporable water contents with hydration time.

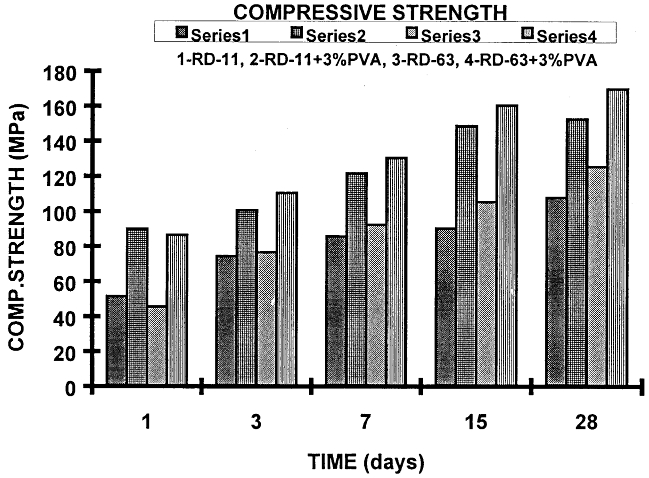

Fig. 2. Variation of compressive strength with hydration time.

The variation of free lime with hydration time for the two cements in the presence and absence of 3.0-wt.% PVA was determined. The values increase in all the cases with hydration time. In the case of RD-11, the free lime values are lower in the presence of 3.0-wt.% PVA at all the ages of hydration as compared to that of control. This shows that PVA retards the hydration. In the case of RD-63 cement, the free lime values are lower than that of RD-11. In the presence of RHA (RD-63), the lower values of free lime may be due to following two reasons: dilution effect and pozzolanic reaction between RHA and $Ca(OH)_2$. In the presence of PVA, the values are further decreased. PVA, a polymer, coats the surface of hydrated and unhydrated grains of cement, hindering the approach of water molecules to come in contact with cement particles resulting into retardation of hydration.

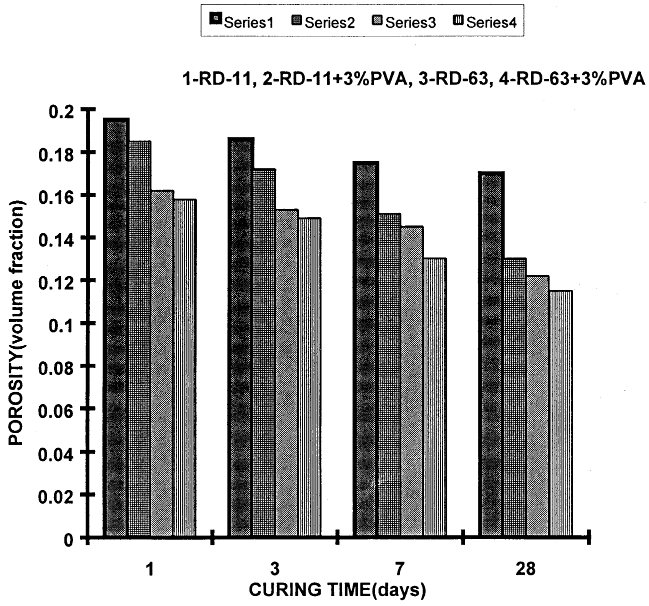

Fig. 3. Variation of porosity with hydration time.

The compressive strengths of the two cements (RD-11 and -63) with hydration time are given in Fig. 2. The values increase with hydration time and are higher in the case of RD-63 except at 1 day of hydration. The higher values of strength in the case of RD-63 may be due to pozzolanic reaction between amorphous silica of RHA and $Ca(OH)_2$ produced during hydration of cement, giving more C–S–H. However, the lower value of strength at 1 day of hydration may be due to dilution effect, and the pozzolanic reaction might have not taken place during this period. The compressive strength values in the presence of 3.0-wt.% PVA are also given in Fig. 2. The values are higher as compared to that of control.

The change in total porosity with hydration time is given in Fig. 3. The values decrease with time and are lower in the case of RD-63, indicating that as the quantity of the hydration products increase, the porosity decreases. The lower values of porosity in the case of RD-63 is due to

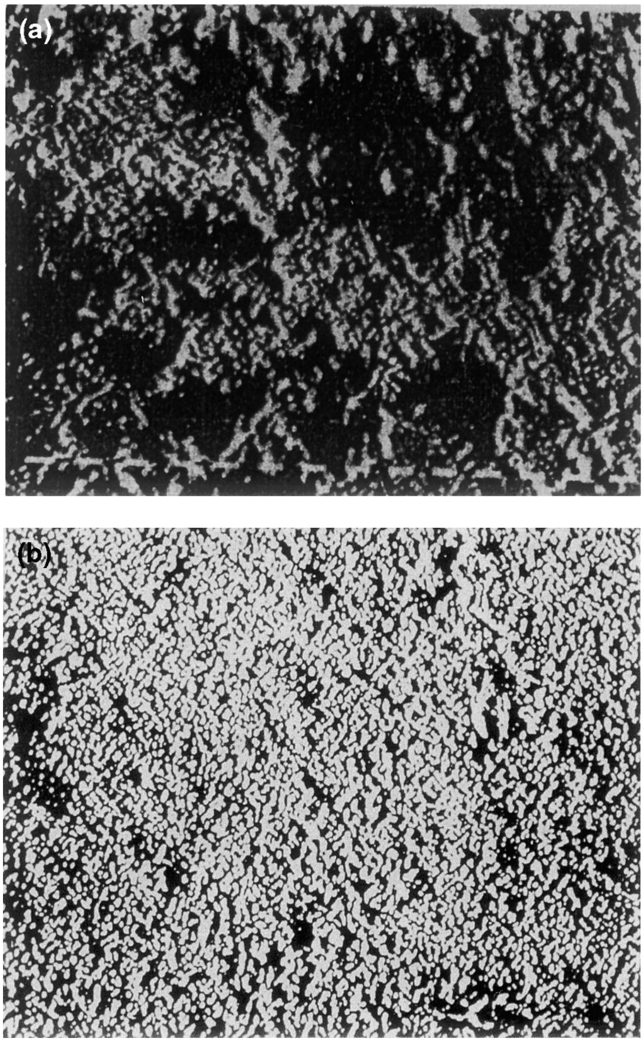

Fig. 4. (a) SEM picture of RD-11 hydrated for 28 days (w/c = 0.3); (b) SEM picture of RD-11 hydrated for 28 days in the presence of 3.0 wt.% PVA (w/c = 0.3).

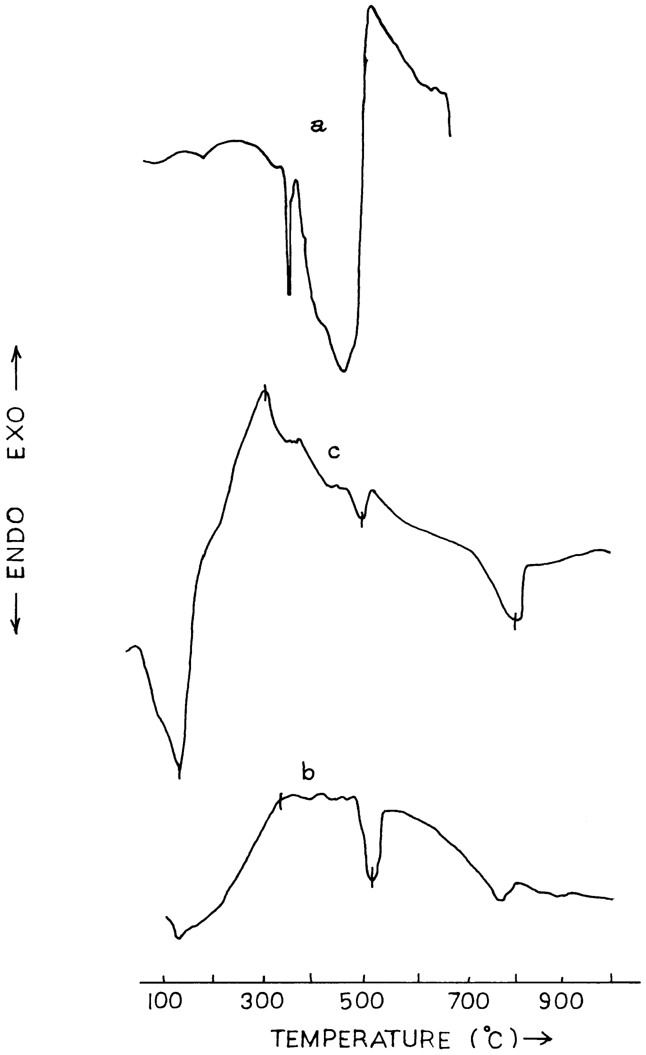

Fig. 5. DTA of (a) PVA, (b) RD-11 hydrated for 7 days, (c) RD-11 hydrated for 7 days in presence of 3.0 wt.% PVA; w/c = 0.5.

larger amount of hydration products formed in the presence of RHA. At 1-day hydration, RHA might be acting as a filler. However, in the presence of 3.0-wt.% PVA , the total porosity values are decreased further, indicating the compactness of the structure.

SEM micrographs of cement RD-11 hydrated in the absence and presence of 3-wt.% PVA at 28 days are shown in Fig. 4. Results have shown that addition of polymer reduces the total porosity and decreases variation in pore size distribution (Fig. 4b). Such reduction of porosity without polymer cannot give such compact structure.

The XRD pattern of RD-11 and -63 are almost similar, showing strong peaks due to the presence of gypsum, C_3S and C_2S. However, the relative intensities are slightly different. When the cements were allowed to hydrate in the absence of PVA, the peak due to gypsum (d = 7.4683 Å) disappeared, and a strong new peak due to the formation of portlandite appeared at d = 4.93557 Å. The intensities of the peaks due to C_3S and C_2S phases also decreased, indicating the hydration of cement. In the presence of 3.0-wt.% PVA, the intensity of the peaks due to the formation of portlandite is lower, whereas, the intensity of the peaks due to C_3S and C_2S phases are higher as compared to that of the control. This simply indicates that PVA retards the hydration. Although the XRD patterns in the presence of 3.0-wt.% PVA are slightly different but definite, conclusions could not be made for the formation of any new compound.

DTA curve of PVA is shown in the Fig. 5 and shows a number of endothermic peaks. The DTA of RD-11 cement hydrated for 7 days in the presence and absence of 3.0-wt.% PVA at w/c = 0.5 are also given in Fig. 5. In the case of control, three endothermic peaks at 105°C, 520°C and 750°C are observed, which are due to loss of adsorbed water, decomposition of $Ca(OH)_2$ formed during hydration and small amount of $CaCO_3$ formed as a result of carbonation, respectively. In the presence of 3.0-wt.% PVA, there

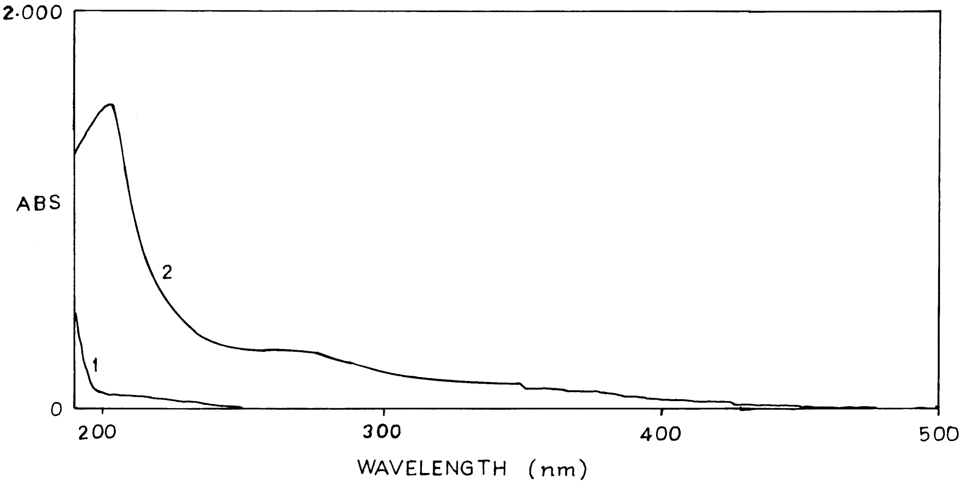

Fig. 6. UV-visible spectra of (1) 0.1% PVA in water, (2) filtrate of RD-11 cement shaken with 0.1% PVA for 1 min (w/c = 10).

are again three endotherms at around 110°C, 500°C and 780°C. The peak area for the endotherm at 110°C is much higher than that of the control, indicating that more adsorption of water has taken place in the presence of PVA. The peak area of the endotherm at 500°C due to decomposition of $Ca(OH)_2$ is much lower as compared to that of the control, indicating that in presence of PVA, the hydration is either retarded or PVA reacts with $Ca(OH)_2$ in some way. The endothermic peak at 780°C may either be due to decomposition of $CaCO_3$ or some other new compounds formed, and the peak area is much higher than that of the control. In addition to the endothermic peaks in the presence of PVA, there are number of exothermic peaks in the temperature range of 200–500°C. These peaks are absent both in the case of PVA and control sample. The presence of these peaks very clearly shows that some new compounds are formed as a result of interaction between PVA and RD-11 cement during hydration. However, X-ray diffraction studies did not give any information regarding the formation of compounds between PVA and the cement. This may be due to formation of amorphous compounds, which could not be detected by X-ray diffraction technique.

The UV-visible spectra of 0.1% PVA solution and its interaction product with RD-11 cement are shown in Fig. 6. In the case of 0.1% PVA solution, there is very little absorption in the region of 190–500 nm, with a small peak at about 225 nm. However, when RD-11 cement was allowed to interact with 0.1% PVA solution for 1 min, the spectra is completely changed. The absorption is much higher with three peaks at about 200, 280 and 350 nm. This confirms that there is a strong interaction between PVA and cement, forming some compounds. The compound formed is amorphous in nature, as it was not detected by X-ray diffraction technique.

4. Conclusions

The overall results have shown that the two cements behave in a similar way, and hence, replacement of cement by 10% RHA is beneficial. PVA retards the hydration, but at the same time increases the compressive strength and decreases the porosity. These effects are due to chemical interaction between PVA and cement . New compound formation cannot add to the increase in strength. It may improve the bond between the cement particles, thereby increasing the strength.

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