Pergamon

Cement and Concrete Research 29 (1999) 407–415

CEMENT AND CONCRETE RESEARCH

Structure and properties of poly(vinyl alcohol)-modified mortar and concrete[1]

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Manuscript received 29 October 1998; accepted manuscript 11 December 1998

Abstract

The structure and properties of mortars and concretes containing up to 2 wt% (based on cement) of poly(vinyl alcohol) (PVA) were examined and compared with those without PVA. Among changes occurring with the addition of PVA were increases in air void content and apparent fluidity and a reduction in the bleeding of fresh mortar and concrete. The increased fluidity caused increased slump for fresh concrete. The microstructure was examined by polarizing optical microscopy and scanning electron microscopy in backscattered mode of cut surfaces after hardening. The porous interfacial transition zones around sand grains and coarse aggregate were significantly reduced, and the cement particles were uniformly distributed without significant depletion near aggregate surfaces. For mortars, using a prewetting mixing technique, the compressive strength was decreased moderately, but the flexural strength was unchanged. For concretes, with the same mixing technique, the compressive strengths after 28 days of hydration were relatively unchanged, but the postpeak area of the compression stress-strain curve was reduced, accompanying a change in fracture behavior from debonding to cohesive failure of the coarse aggregate. When concrete having the same air void content with PVA as without was made, the compressive strength was moderately increased.

Keywords: Interfacial transition zone; Compressive strength; Polymers; Concrete; Mortar

The strength of concrete is known to increase with an increase in the aggregate-cement bond strength [1–5]. Both silica fume [1] and polymer dispersions [2–5] have been used to increase concrete strength by improving the aggregate-cement bond. However, these materials need to be used at the rate of 10–20% based on cement to be effective, and at this rate, they can add considerably to the cost. Small amounts of poly(vinyl alcohol) (PVA) have been shown to significantly increase the aggregate-paste bond strength and reduce the thickness of the interfacial transition zone in an aggregate-paste bond model system [6,7]. If the increase in bond strength with PVA observed with this model system occurs in concrete as well, an increase in the strength of the concrete can be expected. On the other hand, water-soluble polymers like PVA have often been found to decrease the mechanical properties of mortar and concrete [5]. In addition to affecting the bond strength, PVA has long been known to affect the air content of paste and mortar. In the present study, the combined effects arising from PVA of paste-aggregate bond improvement and increased air content were examined with regard to the strength properties of mortar and concrete.

1. Experimental

1.1. Materials

The cement used was a commercial ASTM type I ordinary portland cement. The two sands used were ASTM graded sand (silica sand, ASTM C778, U.S. Silica Co., Ottawa, IL, USA, used to prepare mortars and vacuum-cast concretes, and river sand with a maximum grain size of 4 mm, used to prepare regularly cast concretes. Pea gravel with the size range of 6–13 mm (1/4–1/2 in) was used as the coarse aggregate for the concrete. To remove clay from the aggregate surface, the pea gravel was cleaned with silica sand and water in a drum mixer and dried in air. The PVA used was

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[1] This paper was originally submitted to *Advanced Cement Based Materials*. The paper was received at the Editorial Office of *Cement and Concrete Research* on 29 October 1998 and accepted in final form on 11 December 1998.

0008-8846/99/$–see front matter
PII: S0008-8846(98)00246-4

Airvol 805 (Air Products and Chemicals Inc. Allentown, PA, USA). This had a relatively low molar mass of 31,000–50,000 weight average, 15,000–27,000 number average, and was 87–89% hydrolyzed PVA. Airvol 805 is a low foaming grade. PVA powder was dispersed in cold water at a concentration of 20%, and this mixture was heated to 90°C with stirring to completely dissolve the PVA. Then the PVA solution was cooled to room temperature and used within 24 h.

1.2. Mixing, casting, and curing procedures

For the mortars, a cement:sand:water ratio of 1:2:0.5 was used. When PVA was added, the amount of water in the PVA solution was included in the water-to-cement ratio. The amounts of PVA added were 1% and 2% (solid) based on the weight of cement; these corresponded to 0.29 and 0.57 wt% based on the total weight of mortar. ASTM C305 mixing was used as the standard mixing procedure for the mortar, using a planetary mixer (Hobart Co., Troy, OH, USA). ASTM C305 mixing consists of a sequence of mixings that involve a total of 1.0 min at a paddle speed of 140 rpm followed by a total of 1.5 min at a speed of 285 rpm. The reference mortar was mixed following the ASTM C305 mixing procedure. When PVA was added, the prewetting technique described previously [8] was employed to minimize air void formation. In this technique cement, sand, and water were first mixed using the ASTM C305 procedure, and then the PVA solution was mixed with the prewetted mortar at a paddle speed of 140 rpm for 1 min. The fresh mortar was cast into plastic molds on a vibrating table. Plastic cylinder molds 76 mm (3 in) in diameter and 152 mm (6 in) high were used for compression tests, and square-bar molds 51 × 51 × 305 mm (2 × 2 × 12 in) were used for flexural strength tests. The volumes of each mold and the weights of the mortar in the molds were measured to determine the density of the mixtures.

For the concretes, a cement:sand:pea gravel ratio of 1:2:2.5 and two water-to-cement ratios (0.50 and 0.45) were used. The amounts of PVA added were again 1% and 2% (solids), based on the weight of cement. These correspond to 0.17% and 0.33% based on the total weight of concrete with a water-to-cement ratio of 0.50. The amounts of water in the PVA solution were included in the water-to-cement ratios. An omnimixer (Chiyoda Technical and Industrial Co., Tokyo, Japan) was used for concrete mixing. This had a moving bowl with a rubber wall and a mixing rod in the middle. To make the reference concretes, cement, sand, pea gravel, and water were mixed together for 2 min at a speed of around 350 rpm and then for another 1 min at a speed of around 250 rpm. To make the PVA-modified concretes, cement, sand, pea gravel, and water were first mixed for 2 min at 350 rpm, and then the PVA solution was mixed with the prewetted concrete for 1 min at 250 rpm to minimize air void formation [8]. The fresh concretes were cast into plastic cylinder molds 102 mm (4 in) in diameter and 203 mm (8 in) high with vibration for compression testing. The volumes of each molds and the weights of the concrete in the molds were measured to determine the densities of the fresh mixtures.

To examine the effect of PVA on the workability (or flowability) of concrete, slump tests were done for the fresh concretes. The test procedure followed ASTM C143 using a cone-shape mold, 203 mm (8 in) bottom diameter, 102 mm (4 in) top diameter, and 305 mm (12 in) high. Three slump tests were done for each mix and their average value was calculated.

To prepare PVA-modified concretes having the same densities as those of the unmodified concretes, the extra air voids in the PVA-modified concretes were removed by applying vacuum before casting into molds. For this, the fresh mixture of the PVA-modified concrete was placed in a plastic vacuum container, and the container was evacuated for 1–2 min. A small fraction of the water (approximately 0.4%) evaporated during the air evacuation, but an extra amount of water had been added before mixing the concrete to compensate for this. The concrete was vibrated during the evacuation and then cast into molds with vibration. The silica sand (rather than river sand) was used to prepare the vacuum-cast concretes.

The mortar and concrete specimens were demolded after 24 h and then stored in lime-saturated water at 20°C until tested (either 7 or 28 days).

1.3. Mechanical strength tests

The compressive strength of cylindrical specimens of mortar and concrete were measured with a hydraulic Instron Model 1336 (Instron Corp., Canton, MA, USA) equipped with a 2225 kN (500 kips) load-cell at a crosshead speed of 0.025 mm/s (0.001 in/sec). Four cylinder specimens, 76 mm (3 in) in diameter and 152 mm (6 in) high for mortar and 102 mm (4 in) in diameter and 203 mm (8 in) high for concrete, were tested for each mix. The load and machine displacement signals were recorded using a data acquisition system. Two hour before testing, the hardened specimens were taken out of the water bath where they had been for 7 or 28 days to dry the surfaces and cap both ends of the cylinder with sulfur mortar (ASTM C617).

The flexural strength of the square mortar bars, with the dimensions of 51 × 51 × 305 mm (2 × 2 × 12 in), was measured by four-point bending with a span length of 229 mm (9 in) using an Instron Model 4206 (Instron Corp., Canton, MA, USA) equipped with a 44.5-kN (10 kips) load-cell at a crosshead speed of 0.0212 mm/s (0.05 in/min). The specimens were taken out of the water bath just before testing and their surfaces were maintained wet during the test to prevent surface drying cracks. Six specimens from each mix were tested.

1.4. Observation of interfacial transition zone and fracture surface

To examine the microstructure, the tested mortars and concretes were sectioned with a diamond saw, and their cut surfaces were observed with a polarizing optical microscope (Olympus BH-2, Tokyo, Japan) and a scanning electron microscope in backscatter mode. For backscatter microscopy, the sectioned pieces were immersed in a low-viscosity epoxy resin after drying in air to allow the specimens to become impregnated with the resin. The resin was then hardened at room temperature for one day, and the specimen surface was polished with #1000, #2400, and #4000 silicon carbide grinding papers. The nonpolar liquid (kerosene) was used as a coolant for the polishing and for washing the specimens in an ultrasonic cleaner between polishing steps. The polished specimens were dried under vacuum for two days and thinly coated with Au-Pd. The specimens were examined with a scanning electron microscope (Hitachi S-520, Hitachi Ltd., Tokyo, Japan) equipped with a backscattered electron detector.

The fracture surfaces of the tested concrete specimens were also observed visually and with an optical stereo microscope.

2. Results

2.1. Mortar

2.1.1. Fresh mortar properties

The addition of PVA to mortar was found to cause the mass density to decrease, and the decrease was greater with greater PVA content. For example, the density had decreased about 5% with 2 wt% PVA (based on cement mass). With 2.0 wt% PVA, the density was 2.04 mg/m^3; without PVA, the density was around 2.17 mg/m^3.

The viscosity and the bleeding of mortar were both found to be reduced with the addition of PVA, as had been observed in PVA-modified cement pastes [7].

2.1.2. Mortar microstructure

The cut surfaces of the hardened mortar specimens were examined with both polarizing optical microscopy and scanning electron microscopy in backscattered mode. Typical micrographs are shown in Fig. 1 and Fig. 2. The cement particles are seen as small dark spots in the optical micrographs and as the brightest spots in the backscattered electron micrographs; the sand grains are the larger objects. In the optical micrograph without PVA (Fig. 1a), distinct white bands 30–80 μm wide are seen to surround each sand grain. Neighboring bands tend to overlap or connect be-

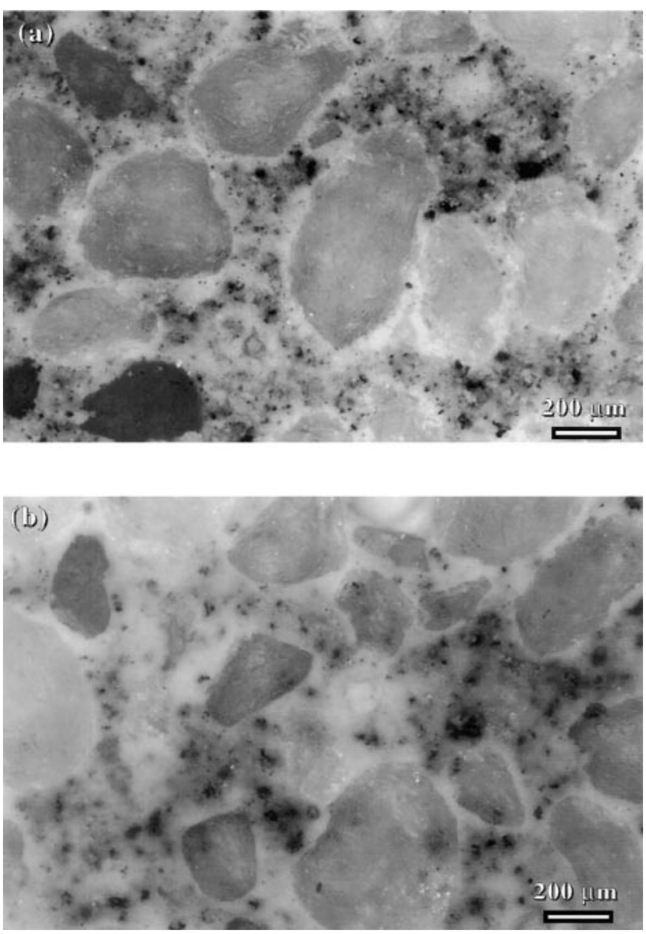

Fig. 1. Polarizing optical micrographs of the cut surfaces of mortars showing distributions of cement particles around sand grains. (*a*) Without PVA, (*b*) with 2 wt% PVA (based on cement). Hydration time, 28 days; w/c ratio, 0.5.

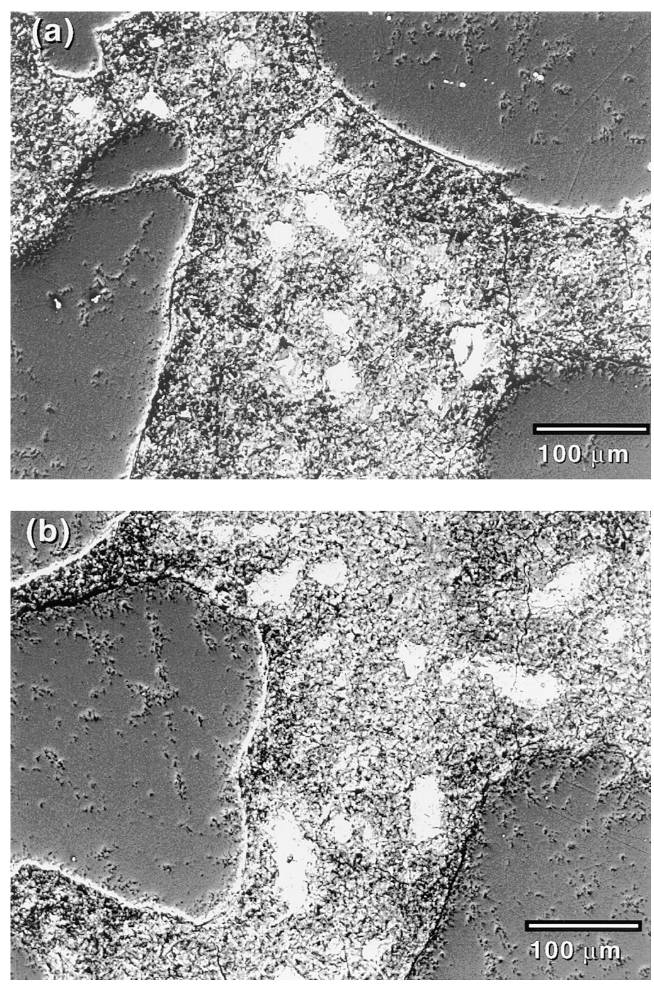

Fig. 2. Backscattered electron micrographs of the cut surfaces of mortars showing distributions of cement particles around sand grains. (*a*) Without PVA, (*b*) with 2 wt% PVA (based on cement). Hydration time, 28 days; w/c ratio, 0.5.

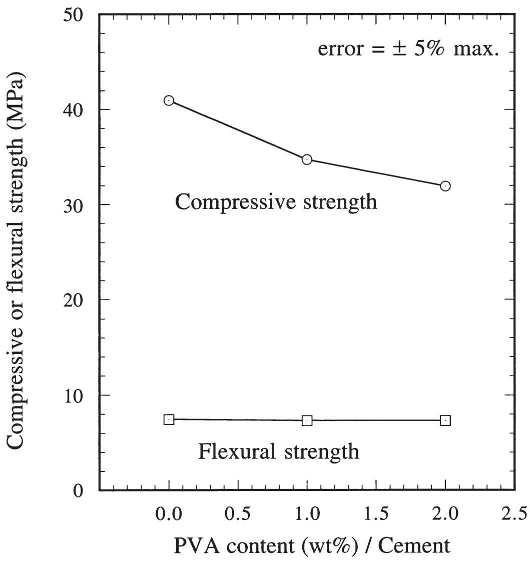

Fig. 3. Effect of PVA on the compressive and flexural strengths of mortar. Hydration time, 28 days; w/c ratio, 0.5.

cause of the width of the bands and the closeness of the sand grains. In the backscattered electron micrograph of the mortar without PVA (Fig. 2a), a degree of darkness is seen in the regions surrounding the sand grains within 30–80 μm of the grains. Because the backscattered brightness is proportional to material density, the darkness suggests higher porosity in these regions. In both the optical and backscattered electron micrographs of mortar without PVA, the cement particles that are visible tend to be distributed nonuniformly in the cement paste and to concentrate in the paste-rich regions between the sand grains and away from the sand grain surfaces. In the mortars with 2% PVA/cement (Figs. 1b and 2b), such bands surrounding the sand grains were less common, and when they did occur, they were thinner. As a result, neighboring bands tended not to overlap or connect but to be isolated. Also, the cement particles tended to be more uniformly distributed through the paste and were found adjacent to the sand grains as often as away from the grains. Macroscopically, PVA-modified mortar looked lighter in color and had more air voids, and both were observable with optical microscopy.

2.1.3. Mechanical strength tests

The compressive and flexural strengths of mortar with different amounts of PVA are shown in Fig. 3. The compressive strength of the mortar, measured with specimens 76 mm (3 in) in diameter and 152 mm (6 in) high, tended to decrease with PVA. The compressive strength decreased about 20% with 2% PVA/cement. The flexural strength of the mortar, measured by the four-point bending of square bars with the dimensions of 51 × 51 × 305 mm (2 × 2 × 12 in) and a span length of 229 mm (9 in), however, did not show any significant change with PVA content.

2.2. Concrete

2.2.1. Fresh concrete properties

Consistent with PVA-modified mortar, PVA-modified concrete had more air voids and lower density. Typical density changes with the addition of PVA are shown in Fig. 4. The density is seen to have decreased about 1% per 1 wt% PVA (based on cement mass).

The slump value of fresh concrete is shown in Fig. 5. It is seen to have increased with PVA. For fresh concrete with a w/c ratio of 0.50, slump increased from 32 mm (1.25 in) for

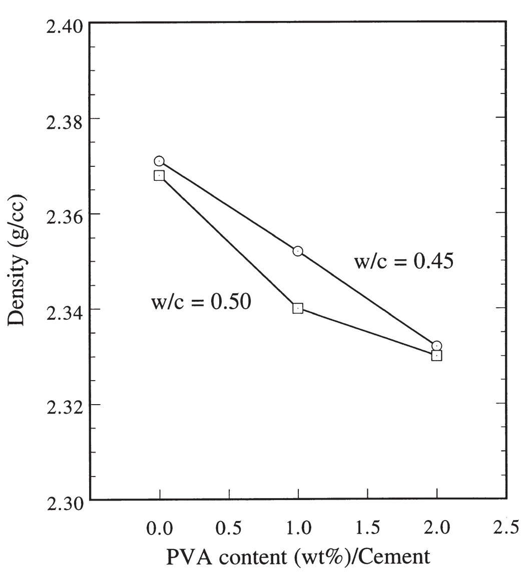

Fig. 4. Typical densities of fresh concrete mixtures with different PVA contents and w/c ratios.

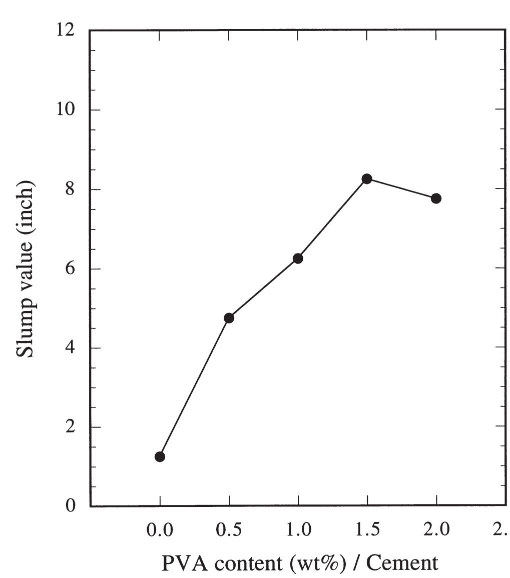

Fig. 5. Effect of PVA on the slump values of concrete for the w/c ratio of 0.50.

concrete without PVA to about 203 mm (8 in) with 2 wt% PVA. The bleeding of water to the surface of the concrete was significantly reduced with PVA, as was also observed with PVA-modified mortars and pastes [7].

2.2.2. Concrete microstructure

Optical and backscattered scanning electron micrographs near the coarse aggregate of cut surfaces of specimens are shown in Fig. 6 and Fig. 7. In the concrete without PVA, distinct bands with higher porosity (appearing white in optical micrographs (Fig. 6a) and darker in backscattered electron micrographs (Fig. 7a) are again observed around the pea gravel and sand grains, and their width or thickness is again 30–80 μm. The cement particles exist more densely away from the surfaces of the sand grains and are seldom found near the surfaces of the pea gravel.

In the concrete with 2% PVA/cement (Figs. 6b and 7b), porous bands surrounding the pea gravel and sand grains were less common, and when they did occur, they were thinner. Also, the cement particles were uniformly distributed through the cement paste, right to the aggregate surfaces. These microstructural features are essentially the same as those for the mortars mentioned above.

2.2.3. Fracture surface

Macrophotographs of the fracture surfaces of concretes containing pea gravel aggregate after compressive failure are shown in Fig. 8. (The coarse aggregate seen ranges in width from 13 to 25 mm.) Without PVA (Fig. 8a), many of the stones can be seen protruding from the surface (the darker objects with shadows); many indentations (appearing white) where stones had been are also seen. Thus, the fracture path tended to go around the coarse aggregate, suggesting that most of the coarse aggregate was easily debonded. When observed with a microscope, the debonded stones were found to have on their surfaces thin layers of the same white powdery deposit seen on the opposite fracture sur-

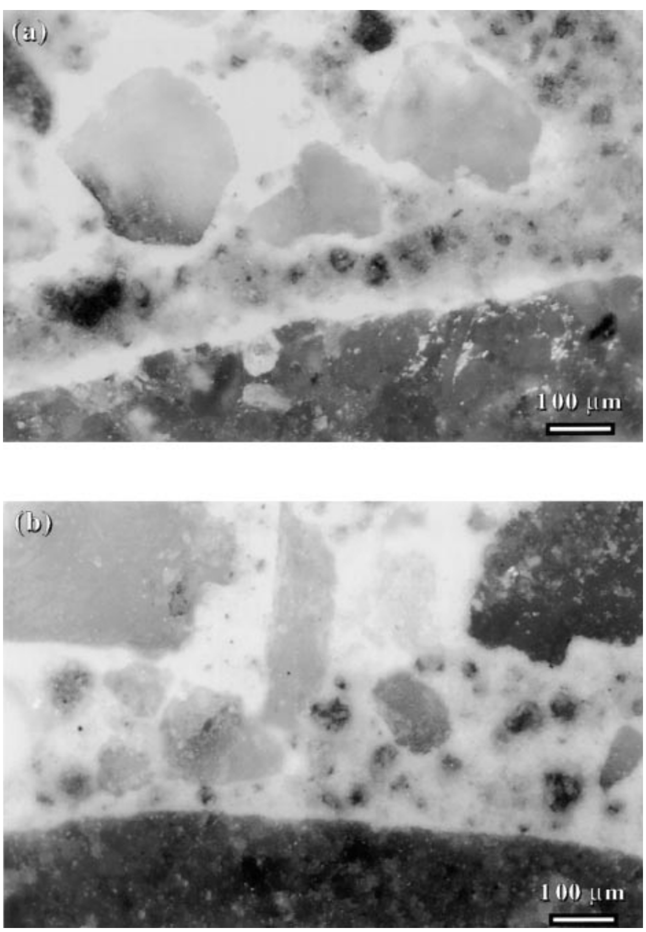

Fig. 6. Polarizing optical micrographs of the cut surfaces of concrete showing the distributions of cement particles around sand grains and pea gravel. (The pea gravel is seen at the bottom of the micrographs.) (*a*) Without PVA, (*b*) with 2 wt% PVA (based on cement). Hydration time, 28 days; w/c ratio, 0.5.

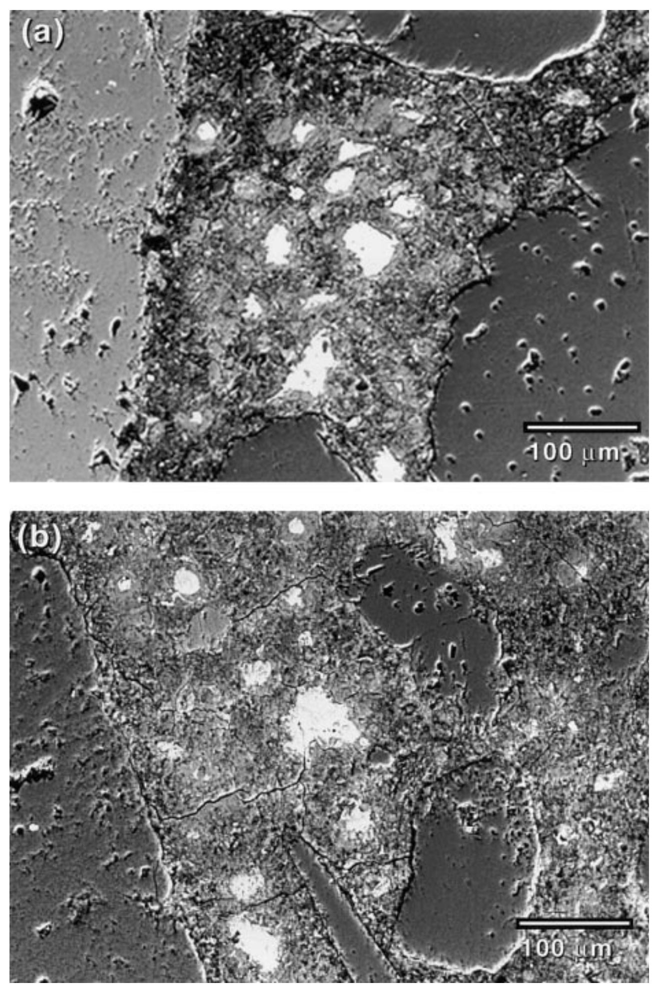

Fig. 7. Backscattered electron micrographs of the cut surfaces of concrete showing the distributions of cement particles around sand grains and pea gravel. (The pea gravel is seen along the left side of the micrographs.) (*a*) Without PVA, (*b*) with 2 wt% PVA (based on cement). Hydration time, 28 days; w/c ratio, 0.5.

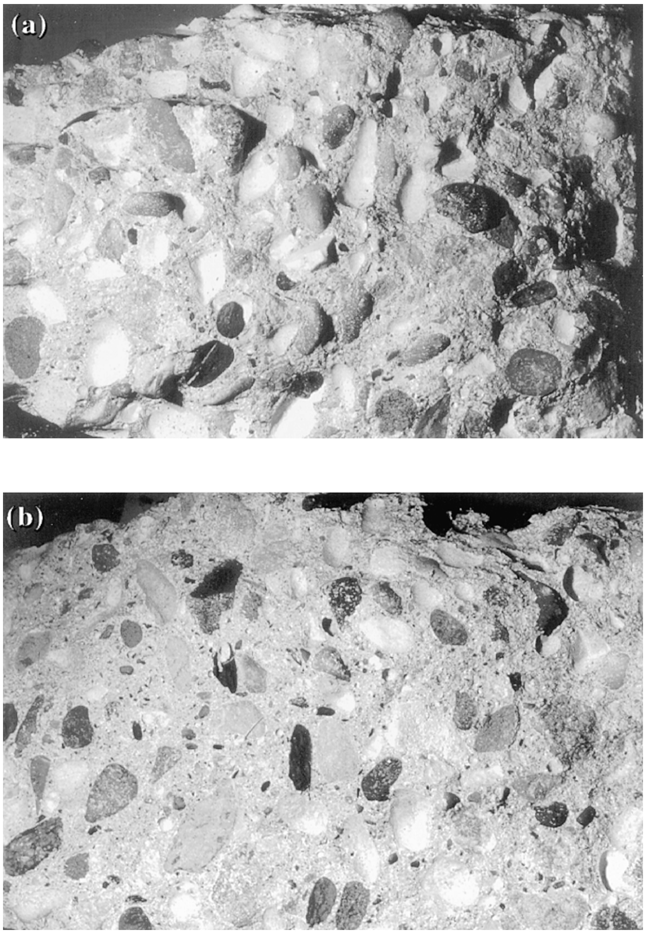

Fig. 8. Macrophotographs of the fracture surfaces of concretes. (*a*) Without PVA, (*b*) with 2 wt% PVA (based on cement). Hydration time, 28 days; w/c ratio, 0.5.

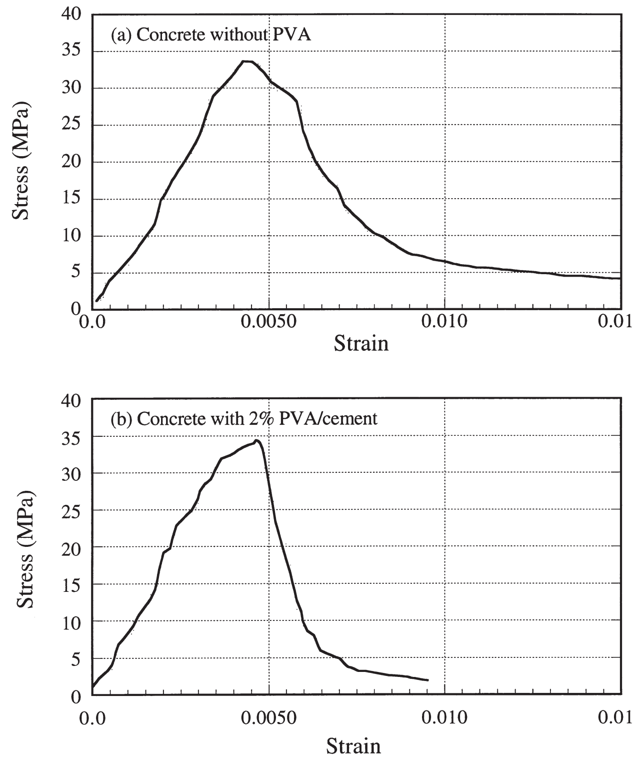

Fig. 9. Typical stress-strain curves of concretes from compression test. (*a*) Concrete without PVA, (*b*) concrete with 2 wt% PVA (based on cement). Hydration time, 28 days; w/c ratio, 0.5.

face, in the cavities left by the stones. This deposit is thought to be calcium hydroxide ($Ca(OH)_2$) crystals [6].

With PVA-modified concrete (Fig. 8b), the fracture plane tended to propagate more often through the stones instead of around them, leaving a fracture surface that was macroscopically smoother. Also, the surfaces of the stones that did debond showed much less white deposit on their surfaces than did those from concrete without PVA.

2.2.4. Compression tests

Compression testing was performed with the cured cylindrical concrete specimens 102 mm (4 in) in diameter and 203 mm (8 in) high. Typical stress-strain curves for concrete without and with PVA are shown in Fig. 9. The initial slopes of the curves (moduli) and maximum stresses attained (ultimate compressive strengths) by the unmodified and PVA-modified concretes were similar, but the postpeak stress of the PVA-modified concrete dropped faster than that of the unmodified concrete, resulting in a smaller postpeak area under the curve with PVA.

The effects of PVA on the ultimate compressive strength of concretes with w/c ratios of 0.50 and 0.45 are shown in Fig. 10 and Fig. 11, respectively. The filled symbols connected by the solid lines are the measured strengths. The open symbols connected by the dashed lines show the effect of air voids and will be described later. After 28 days of hydration, the concrete strength was relatively unaffected by the presence of PVA, although there may have been a statistically significant decrease in strength with 1% PVA and an increase in strength with 2% PVA. After only seven days of hydration, the strength of the concrete made with w/c = 0.5 decreased with increasing PVA concentration, although the concrete made with w/c = 0.45 was relatively unaffected, behaving in the same manner after 28 days of hydration.

The effect of PVA on the ultimate strength of concrete with the density held fixed, obtained by vacuum-casting, is shown in Fig. 12. The unmodified concretes were prepared in the regular way without vacuum treatment, but the PVA-modified concretes were vacuum-cast to remove the extra air void content that typically develops with PVA. These respective procedures produced the same concrete density. With the same concrete density, the ultimate compressive strength increased about 15% with 2% PVA/cement. The increase was the same with both w/c = 0.45 and 0.50. Without vacuum-casting, the density of PVA-modified concrete was lower than that of unmodified concrete (2.5% lower with 2% PVA), but the strength was similar (this is indicated in Fig. 12 for 2% PVA and w/c = 0.45 by the open

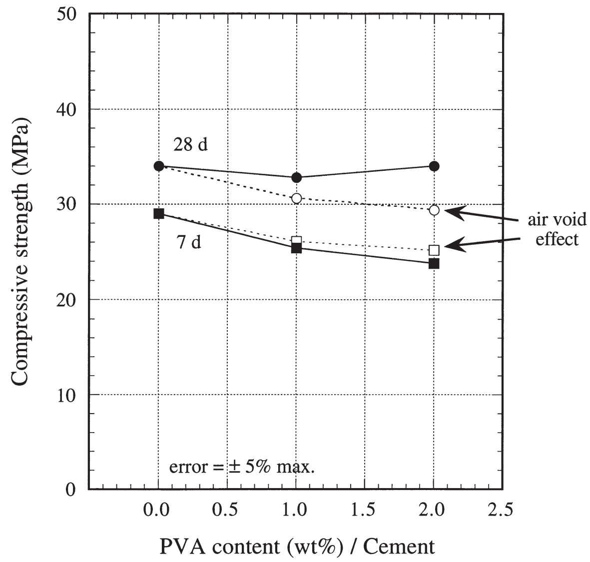

Fig. 10. Effect of PVA and hydration time on the compressive strength of concrete made with river sand and pea gravel. w/c ratio = 0.50. (The strengths expected from normal mixing, resulting in high air void content, are also shown.)

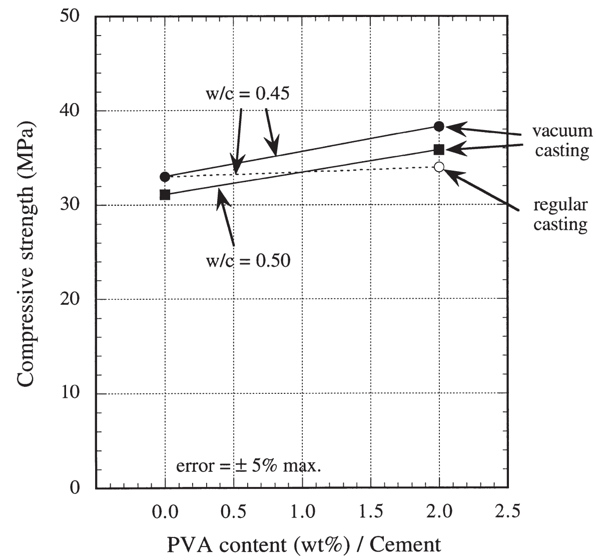

Fig. 12. Effect of PVA and w/c ratio on the compressive strength of vacuum-cast concrete made with silica sand and pea gravel. Hydration time, 28 days. The strength obtained from the (regular) prewetting mixing technique is also shown.

circle that is connected to the unmodified strength by the dashed line). The compressive strengths of the concretes mixed with silica sand (Fig. 12) were somewhat lower than those mixed with river sand (Figs. 10 and 11), probably because of the higher air contents (lower densities) with the finer silica sand.

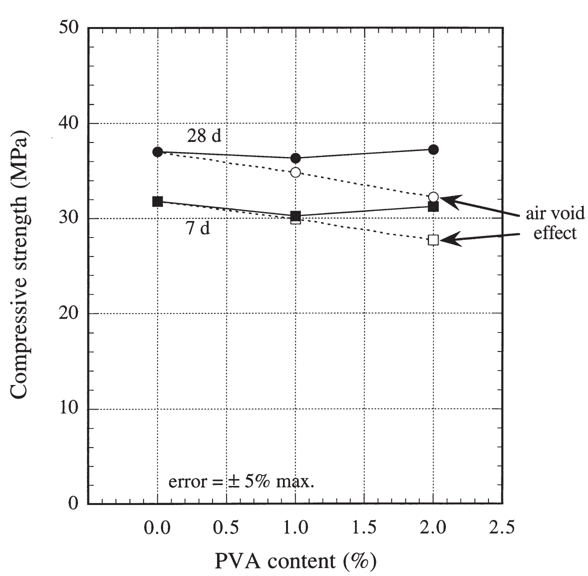

Fig. 11. Effect of PVA and hydration time on the compressive strength of concrete made with river sand and pea gravel. w/c ratio = 0.45. (The strengths expected from normal mixing, resulting in high air void content, are also shown.)

3. Discussion

The addition of PVA caused several changes in the microstructure and properties of mortar and concretes. The air void contents were increased, which decreased the mass density. The apparent viscosity and the bleeding of fresh mixtures were reduced. The porous interfacial transition zones around sand grains and coarse aggregate were reduced in size and number, and the unhydrated cement particles were distributed more uniformly in the cement paste phase, without significant depletion near aggregate surfaces in both mortars and concretes. For mortars, the compressive strength was decreased moderately, but the flexural strength was unchanged. For concretes, the compressive strengths after 28 days of hydration were relatively unchanged, even with their lower densities. However, the postpeak area under the compression stress-strain curve was reduced. The failure behavior had changed from a debonding of the coarse aggregate from the matrix to a cohesive fracture of the coarse aggregate. The compressive strength was modestly increased by PVA for a concrete having the same density as one without PVA.

Some of the changes in behavior of mortar and concrete induced by PVA are related to those found for a model aggregate-paste bond system reported previously [6].

3.1. Fresh mortar and concrete

The increased slump of concrete (and mortar) with the addition of PVA suggests an increase in fluidity or a decrease in viscosity. The behavior probably arises from the adsorption of PVA molecules on the cement particle surfaces, sterically stabilizing the particles [6]. By way of sterically stabilizing the particles, a water layer (containing dissolved polymer) is maintained between the particles. By reducing the tendency for the particles to flocculate or aggregate, the interparticle water effectively lowers the viscosity. The reduced bleeding of water in mortar and concrete seem to arise from the same behavior. Water is held around the particles, preventing the separation by gravity of water and particles to give bleeding and particle settling [6].

3.2. Interfacial transition zone in mortar and concrete

The reduction of the interfacial transition zone around sand grains and pea gravel in mortar and concrete with the addition of PVA (Figs. 1, 2, 6, and 7) also seems to have arisen from the tendency for PVA to retard flocculation of the cement particles. Steric stabilization can also increase the efficiency of deflocculation by shear and vibration. The formation of a water-rich layer around aggregate surfaces is thus minimized or avoided [6].

Although not quantitatively measured, the hardened and dried PVA-modified mortar showed much slower absorption of water than did unmodified mortar when several droplets of water were placed on their cut surfaces. Water on the surface of PVA-modified mortar spread much less and stayed much longer. The reduction of the interfacial transition zone in the PVA-modified mortar seems to have contributed to the slower absorption of water, which is an indication of low permeability. The interconnected porous interfacial transition zones around sand grains in unmodified mortar are known to act as continuous channels, causing a high permeability of mortar and concrete [9]. By reducing the occurrence and thickness of the zones with PVA, the porosity becomes discontinuous, resulting in low permeability. The swelling of the PVA by water that has been used by Ohama to explain the low water permeability of methyl cellulose-modified mortar [5] may also have contributed to the lower permeability of the PVA-modified mortar. Because high permeability is known to reduce the durability of mortar and concrete [10], the addition of even small amounts of PVA to mortar and concrete, as in the present work, may improve the durability of these materials.

3.3. Mechanical properties of mortar

Previous work has indicated that the addition of small amounts of PVA and other water-soluble polymers can cause substantial decreases in the compressive and flexural strengths of mortar [5]. For example, the addition of 1.12 wt% PVA (based on cement mass) caused the compressive strength of the mortar to drop by 55%, from 408 kg/cm^2 (40 MPa) to 185 kg/cm^2 (18 MPa), and the flexural strength to drop by 43% [5]. These are equivalent to an ~50% decrease in compressive strength and a 40% decrease in flexural strength per 1% addition of PVA. Therefore, the relatively small decrease of the compressive strength found in this work (~10% with 1 wt% PVA and ~20% decrease with 2 wt% PVA) and essentially no decrease of the flexural strength (Fig. 3) may be considered to be relative improvements in the strengths of the PVA-modified mortar.

The decrease in the compressive strength of mortar with PVA seems to have been caused by the concomitant increase in air content arising from the surface activity of PVA. The strength of concrete is known to decrease significantly with increasing air content [11]. The relatively small decrease in compressive strength of the mortar with PVA in this work seems to arise from the minimal air void content attending the use of low-foaming PVA and the prewetting technique [7]. The heating of the initial mixture of PVA in water to effect dissolution by providing a void-free PVA solution may also be considered to have contributed to the reduced void content. Since the flexural strength is known to be affected more by flaws (such as cracks) at the specimen surface than by small defects in the interior, the behavior suggests that the surface was relatively unaffected by the addition of PVA using the prewetting technique.

3.4. Aggregate-cement bond strength in concrete

The change in concrete behavior with the addition of PVA to mostly cohesive failure (Fig. 8) from mostly adhesive failure at the interface between the pea gravel and the matrix (mortar) suggests that the bond between the coarse aggregate and cement matrix was improved. The presence of broken aggregate in the strength testing of concrete is known to indicate good bonding between mortar and aggregate [12]. Increases in bond strength and the incidence of cohesive failure of either the aggregate or cement paste were also observed with PVA for aggregate-paste bonds [6]. The gain in bond strength is suggested to arise from a significant reduction in the thickness of the interfacial transition zones, a significant reduction or even elimination of the calcium hydroxide crystals that normally coat aggregate surfaces, and their possible replacement by calcium silicate hydrate (C–S–H). The reduction in calcium hydroxide on aggregate surfaces possibly arose from the inhibition of crystallization nucleation of calcium hydroxide by adsorbed PVA [6].

3.5. Mechanical properties of concrete

The changes with PVA in the shape of the stress-strain curve for the compression of concrete (Fig. 9) can be related to the failure behavior observed on the fracture surface (Fig. 8). With unmodified concrete, the stress decreased relatively slowly after the peak stress because cracks propagated around the aggregate surfaces, forming tortuous crack paths. In PVA-modified concrete, however, the stress dropped rapidly after the peak stress because cracks propagated through the aggregate, forming rather smooth fracture surfaces. Both the fracture surfaces and the stress-strain curves of concrete show that unmodified concrete became more brittle when PVA was added, probably because of the improved bond between aggregate and cement.

The unchanged compressive (peak) strength of concrete with the addition of PVA (Figs. 10 and 11) seems to result from two opposing effects. These are the increased air content with PVA addition that lowers the compressive strength and the improved aggregate-cement bond that raises the compressive strength. Glanville et al. [11] showed the high rate at which air voids reduced the strength of concrete: 5% air voids could reduce the strength by more than 30%, and 2.5% air voids reduced the strength by about 20%. Using the air void contents obtained from the measured densities and these reductions in strength with air void content, the expected compressive strengths in the absence of any other effect of the PVA were calculated. These are shown in the Figs. 10 and 11 as the open symbols connected by dashed lines. The measured strengths of the PVA-modified concretes are seen to be higher for both w/c ratios shown than are these calculated strengths, at least after 28 days of hydration: with 2 wt% PVA (based on cement mass), the measured strengths were 15–20% higher than those calculated based on air voids alone. This 15–20% difference seems to have been caused by the improved aggregate-paste bond strength with PVA.

To confirm this apparent improvement in strength, the air voids usually introduced with PVA were eliminated by vacuum-casting: the densities of the PVA-modified concretes were then about the same as those of unmodified concretes. The compressive strengths of PVA-modified concretes, as seen in Fig. 12, were higher than those without PVA by about 15% with 2% PVA. This 15% increase in compressive strength again seems to be attributable to the improved aggregate-paste bond strength with PVA.

The magnitude of the increase in bond strength is presumably greater than the 15% improvement in overall compressive strength. The contributions to the strength of concrete by paste strength and by aggregate-paste bond strength were studied by Alexander and Taplin [12]. They found that the contribution of the aggregate-paste bond strength to be rather modest compared to that of the paste strength. When the bond strength was changed from “no bond” to “perfect bond” the compressive strength increased approximtely 40% and when the bond strength was changed from “50% bond” to “perfect bond” the compressive strength increased by approximately 17%. Therefore, the 15% increase in compressive strength with 2% PVA and vacuum casting corresponds roughly to a change equivalent to that from a “50% bond” to a “perfect bond.”

Although the increase in concrete strength by increased aggregate-cement bond strength with PVA was found to be nullified by the decrease in strength arising from increased air voids, the extent of nullification was much reduced by the prewetting mixing technique for the concrete.

4. Conclusions

The addition of small amounts of PVA (up to 2 wt% PVA based on cement mass) caused several changes in the microstructure and properties of mortar and concretes. The air void contents were increased, which decreased the mass density. The apparent viscosity and bleeding of fresh mixtures were reduced. The porous interfacial transition zones around sand grains and coarse aggregate were significantly reduced in size and number, and the unhydrated cement particles were distributed more uniformly in the cement paste phase, without significant depletion near aggregate surfaces in both mortars and concretes. For mortars, the compressive strength was decreased moderately, but the flexural strength was unchanged. For concretes, the compressive strengths after 28 days of hydration were relatively unchanged, even with their lower densities, but the postpeak area of the compression stress-strain curve was reduced. The fracture behavior had changed from debonding to cohesive failure of the coarse aggregate. The essentially similar strengths for mortar and concrete with and without PVA were obtained mainly because air void formation with PVA was minimized by using a prewetting mixing technique. When the same density with PVA as without was obtained, the compressive strength was moderately increased.

Acknowledgments

This study was supported by the NSF Center for Science and Technology for Advanced Cement Based Materials (ACBM), NSF Grant No. DMR-8808432. The authors also would like to acknowledge the experimental helps from Drs. Yun-Mook Lim, Min Park, and Hong-Gyun Kim.

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