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Experimental study on properties of polymer-modified cement mortars with silica fume

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Abstract

This paper discussed the flexural and the compressive strengths of polyacrylic ester (PAE) emulsion and silica fume (SF)-modified mortar. The chloride ion permeability in cement mortar and the interfacial microhardness between aggregates and matrix were measured. The chemical reactions between polymer and cement-hydrated product were investigated by the infrared spectral technology. The results show that the decrease of porosity and increase of density of cement mortars can be achieved by the pozzolanic effect of SF, the water-reducing and -filling effect of polymer. Lower porosity and higher density can give cement mortars such properties as higher flexural and compressive strength, higher microhardness value in interfacial zone and lower effective diffusion coefficient of chloride ion in matrix.

Keywords: Polymer; Silica fume; Flexural strength; Effective diffusion coefficient; Microhardness

1. Introduction

Polymer-modified cement mortars possess higher flexural and ductility, impermeability and higher adhesion with steel compared with normal cement mortars. So polymer-modified cement mortars have been used widely in all kinds of antiseptic projects and as repairing materials for concrete structure and pavement [1]. In recent years, more research has focused on properties of polymer-modified cement mortars such as strength, durability and fine pore structure [2], but there is little research on polymer-modified cement mortars with silica fume (SF). In this paper, we studied the properties of polymer-modified cement mortars with SF. The flexural and compressive strength, interfacial microhardness (H_v) and permeability of chloride ion were measured. The infrared spectral technology was introduced to study the chemical reaction between the polymer and cement-hydrated products, $Ca(OH)_2$ in particular. The results show that the decrease of porosity and increase of density can be achieved by the pozzolanic effect of SF, the water-reducing and -filling effect of polymer. Under the combined effects of polymer and SF, cement mortars get extra high flexural and compressive strength, microhardness in interfacial zone and lower effective diffused coefficient of chloride ion in matrix.

2. Experimental

2.1. Materials and mixing proportions

A Portland cement was used, with a Blaine surface area of 3560 cm^2/g and a density of 3.15 g/cm^3. Polymer used in this experiment was a polyacrylic ester (PAE) emulsion. SF with a N_2-absorbing surface area of 23.2 m^2/g was used. A naphthalene-based superplasticizer was used. Aggregate used for the preparation of all mortar specimens was standard sand specified by Chinese standard GB178-77. The physical properties and chemical compositions of cement and SF are listed in Table 1. The mixing proportions of polymer-modified cement mortars are shown in Table 2. Cement mortars with different proportions were provided

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Table 1
The physical properties and chemical compositions of cement and SF

	Cement	SF
Physical properties		
Specific surface (m^2/g)	0.356	23.2
Density (g/cm^3)	3.15	2.24
Chemical compositions (%)		
SiO_2	22.06	90.7
Al_2O_3	5.13	1.29
Fe_2O_3	5.36	1.14
CaO	65.37	0.83
MgO	0.16	1.99
SO_3	2.03	0.66
Loss on ignition	–	3.6

Table 2
The mixing proportions of mortar specimens

Number	Water to binder	Sand to binder	PAE to cement (%)	SF to cement (%)
1	0.35	1.5	0	0, 5, 10, 15
2	0.28	1.5	5	0, 5, 10, 15
3	0.26	1.5	10	0, 5, 10, 15
4	0.24	1.5	15	0, 5, 10, 15

with the same flowing capacity through the adjustment of superplasticizer.

2.2. Test methods

First, cement and SF were premixed for 3 min. Second, water or water together with PAE and superplasticizer were added and mixed for 3 min. The specimens with 40_40_160 mm and Φ70×4 mm in size were made. All the specimens were demolded after curing in temperature 20 ± 3°C and humidity over 80% for 24 h. After demolding, the specimens without PAE should be cured in temperature 20 ± 3°C and humidity over 95% for 28 days. For the specimens mixed with PAE, firstly they should be cured in temperature 20 ± 3°C and humidity over 95% for 7 days, and then be kept in curing chamber with stable temperature of 20 and humidity 60% until the 28th day. The compressive strength and flexural strength were tested on 40×40×160 mm specimens. The permeability of chloride ion (effective diffusion coefficient of chloride ion) was measured on Φ70×4 mm specimens. Testing apparatus for the penetrability of chloride ion was showed as Fig. 1.

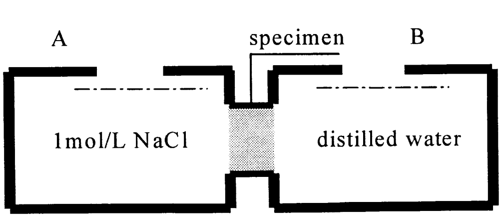

Fig. 1. Testing apparatus of the diffusion of chloride ion.

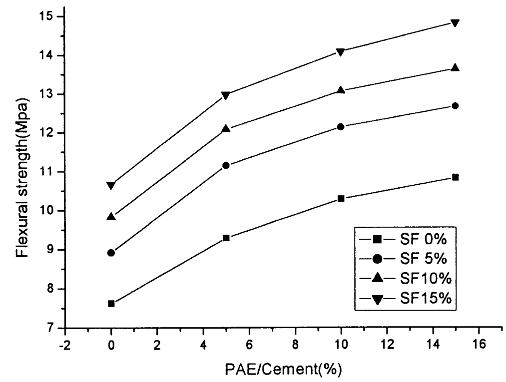

Fig. 2. Influence of PAE and SF on flexural strength.

During experiment, 50 ml of solution was withdrawn from container B every at interval and the electric current of solution was measured by a pH meter. After the measurement, the solution was fed back into container B, until the diffusion of chloride ion became stable. The diffusing quantity of chloride ion has linear relationship with time, so we can get the concentration of chloride ion via the standard curve between concentration and electric current. The measurement of interfacial microhardness and the infrared analysis are processed as in Ref. [3].

3. Results and discussion

3.1. The strength of polymer-modified mortar

The compressive strength and flexural strength are shown in Figs. 2 and 3. Figs. 2 and 3 show the flexural strength of polymer-modified mortars increasing with increase of SF content. Under the conditions of PAE/cement of 15% and SF content of 15%, the flexural strength can be achieved up to 14.8 MPa, which is double the strength of normal mortars. At various content amounts of SF, the flexural strength and the compressive strength increase with the increase of PAE content. The same relationship happens

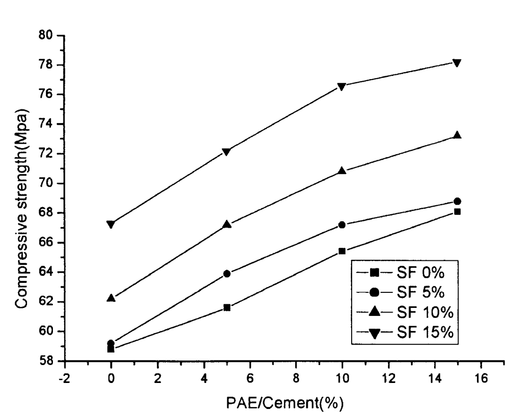

Fig. 3. Influence of PAE and SF on compressive strength.

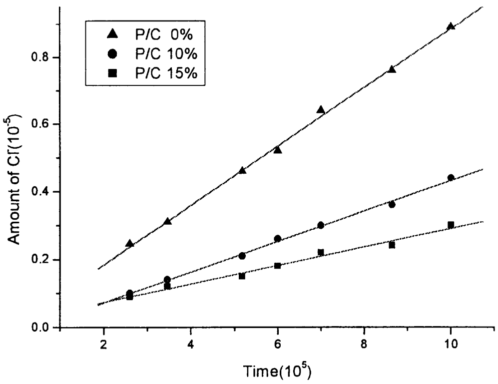

Fig. 4. The relationship between the amount of Cl^- and time.

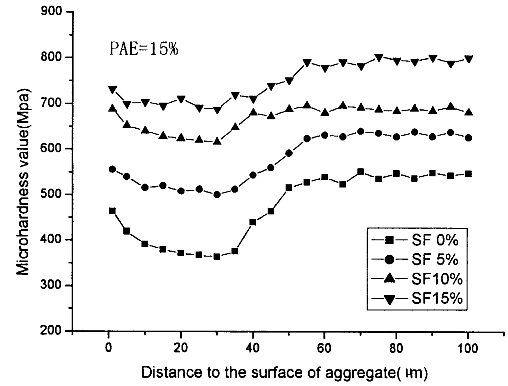

Fig. 6. Influence of SF on H_v of interface zone.

between the compressive strength and SF quantity. If PAE/cement equals to 15% and the weight percentage of SF is 15%, the compressive strength of polymer-modified cement mortars can be achieved up to 78 MPa, whereas the compressive strength of normal cement mortars without PAE and SF is only 58 MPa. Such conclusion, that the reinforcing effect of PAE and SF on compressive strength is lower than that on flexural strength, can be withdrawn.

3.2. Penetrability of chloride ion

Considerable research on permeability of chloride ion has been presented in recent years [4,5]. Main result is that there is a relationship between the effective diffusion coefficient of chloride ion and the chemical component of raw materials, pore structure, density and interfacial structure between aggregates and cement matrix. But few researches discussed the chloride ions' diffusion in polymer- and SF-modified cement mortars. In the case of polymer and SF both being added in cement mortars, the relationship between the amount of chloride ions, which passed through cement specimens and arrived into chamber B, and time is shown in Fig. 4. It clearly demonstrates that the penetrated chloride ion increases linearly as time goes on, but the linear slope decreases by addition of PAE and SF. The effective diffusion coefficient of chloride ion can be calculated according to the slope. The calculation formula is as follows:

$$D = (K \times L)/(A \times \Delta C).$$

In this formula: L = thickness of specimens (cm), L = 0.4 in this research; A = saturated area (cm^2); K = slope of the line; ΔC = concentration difference between chambers A and B. $\Delta C = Cl_A^- - Cl_B^-$. Cl_B^- can be omitted because it is much smaller than Cl_A^-, so $\Delta C = Cl_A^-$.

The chloride ion's diffused coefficients of cement mortar with PAE and SF calculated by the above formula are showed in Fig. 5. Effective diffused coefficient of chloride ion decreases significantly by addition of SF and PAE in cement mortar. Such conclusion, that the effective diffused coefficient of chloride ion reduces as PAE/cement and SF contents increase, can be drawn.

3.3. Microhardness of interface

Interfacial adhesion between aggregates and cement paste has great effects on strength and impermeability of cement mortar. The test results on H_v of interface between aggregates and cement paste with PAE and SF were shown in Figs. 6 and 7. It shows that the interfacial H_v falls down

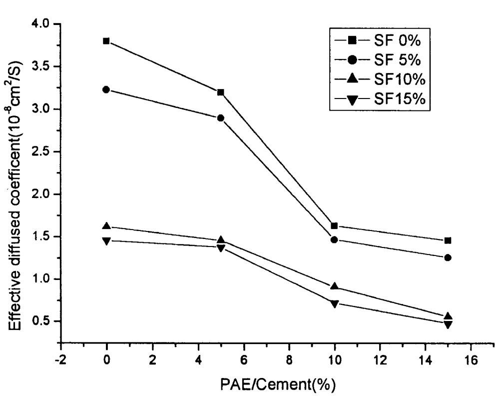

Fig. 5. Influence of SF and PAE/cement on effective diffused coefficient of Cl^-.

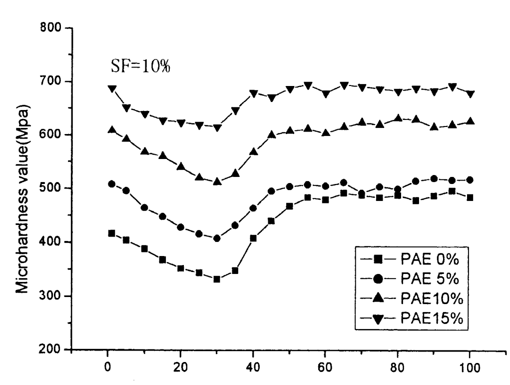

Fig. 7. Influence of PAE on H_v of interface zone.

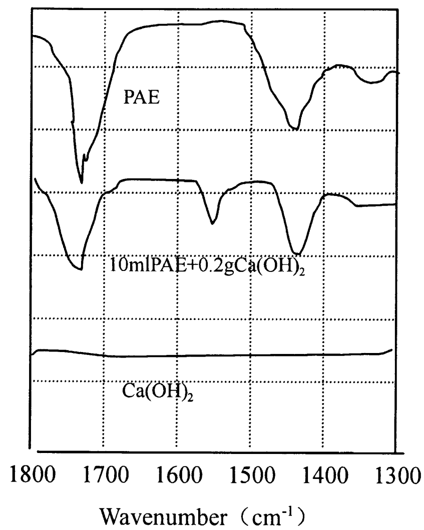

Fig. 8. The infrared spectrum of PAE, $Ca(OH)_2$ and their mixture.

to nadir gradually at the point of 30 μm away from aggregate surface, then it rises up slowly. Until the place 60 μm away from the surface, the interfacial H_v becomes stable. The distribution of interfacial H_v changes with the quantity of PAE and SF. The interfacial H_v increases by increasing quantity of PAE and SF. Out of the place 70 μm away from the surface, H_v is not affected by interface. The difference of H_v between the weakest point in interfacial zone (0–70 μm) and cement matrix (> 70 μm) decreases due to addition of PAE and SF.

3.4. Infrared analysis

In order to study reactivity between PAE and hydrates of cement ($Ca(OH)_2$), infrared analysis method was introduced in this research. The infrared spectrum of PAE, $Ca(OH)_2$ and their combination is shown in Fig. 8. The peak point of COO^- in PAE occurs at 1740 and at 1550 cm^{-1} for the products of PAE and $Ca(OH)_2$. This result demonstrates clearly that PAE can react with hydrates of cement.

4. Discussion

The mechanical properties can be improved significantly due to addition of polymer and SF. The reasons are as follows.

(1) *Water-reducing effect of polymer:* Surfactant existing in polymer modifier can disperse the flocculent structure of cement particles. Free water will be released out to enhance the mixing effect. For this reason, water-to-cement ratio of cement mortar at the same flowability can be reduced remarkably. The porosity of hardened mortar decreases greatly for the same reason.

(2) *Filling effect of polymer:* During the hardening of cement, polymer can fill into microcracks, pores and cracks in transition zone and film in these places, so that the density and impermeabilty can be improved very well.

(3) *Pozzolanic effect:* Hydrates of cement, such as $Ca(OH)_2$, react with active SiO_2 in SF. The reaction not only decreases the quantity of $Ca(OH)_2$, but also decreases the volume of large pores, and increases small pores, and then reduces continuous pores in cement paste. The directional distribution of $Ca(OH)_2$ decreases around the aggregates and interfacial, which results in the increase of H_v.

(4) *Filling effect of fine particle:* The specific surface area of SF is 23.2 m^2/g and cement's specific surface is 3560 m^2/g. Such fine particles of SF can fill between cement particles with good grading, and further, this effect reduces water quantity at standard consistency. At the same time, the filling effect of SF results in the increase of the density, the decrease of water filling in interspaces of cement particles and the increase of the flowability of cement mortar.

(5) *Reaction between PAE and hydrates of cement $Ca(OH)_2$:* PAE includes a large amount of COO^-. It can react with Ca^{2+}, as the following formula shows, because ester hydrolyzes in alkali circumstance:

$$RC\underset{\underset{O}{\|}}{-}O\!-\!R + OH^- \rightarrow RCOO^- + R(OH)$$

$$2RCOO^- + Ca^{2+} \rightarrow [RCOO]^- Ca^{2+} [OOCR]^-.$$

According to above-mentioned reaction, $[RCOO]^- Ca^{2+}[OOCR]^-$ was formed on surface of C–S–H gel or $Ca(OH)_2$ crystal; the interweaved net structure consists of ion-bonded large molecular system which bridged by means of Ca^{2+}.

For the above-mentioned reasons, the following advantages can be achieved:

1. The compressive and flexural strength of cement mortar increase.
2. Interfacial H_v of transition zone increases.
3. The effective diffused coefficient of chloride ion in mortar decreases.

5. Conclusions

(1) The compressive and flexural strength of cement mortar can be improved due to addition of SF and polymer.

(2) Because of the water-reducing effect of polymer and pozzolanic reactions of SF, the porosity and the effective diffused coefficient of chloride ions decrease and the density increases after adding polymer and SF in cement paste.

(3) The interfacial H_v increases by increasing the quantity of SF and PAE/cement ratio. The difference of H_v between the weakest point of interfacial zone (0–70 μm) and cement matrix (>70 μm) decreases.

(4) Infrared analysis results show that COO^- in polymer can react with hydrates of cement such as $Ca(OH)_2$. The reaction can compact the organic structure of polymer-modified mortar and improve the impermeability and chemical resistibility.

(5) In order to use this kind of mortar as repairing materials, the shrinkage properties and the adhesion capacity with various materials need to be studied in the future.

Acknowledgments

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References

[1] Z. Chen, M. Tan, Progress of polymer concrete composite, Proceedings of the First East Asia Symposium Polymers in Concrete, Korea, May 2–3, 1994, pp. 25–40.

[2] U.M.K. Afridi, Z.U. Chaudhary, Y. Ohama, K. Demura, M.Z. Iqbal, Elastic properties of powders and aqueous polymer modified mortars, Cem. Concr. Res. 24 (1994) 1199–1213.

[3] W. Sun, J.M. Gao, Study of the bond strength of steel fiber reinforced concrete, Proceedings of 2nd International Symposium on Cement and Concrete, Beijing, China 2 (1985).

[4] H.G. Midgley, J.M. Illston, The penetration of Cl^- into hardened cement plaster, Cem. Concr. Res. 14 (1984) 546–558.

[5] K.A. Macdonald, D.O. Northwood, Experimental measurements of chloride ion diffusion rates using a two-compartment diffusion cell, Cem. Concr. Res. 25 (1995) 1407–1416.