Pergamon

Available online at www.sciencedirect.com
SCIENCE DIRECT

Cement and Concrete Research 33 (2003) 1655–1658

CEMENT AND CONCRETE RESEARCH

Research on increasing effect of solution polymerization for cement-based composite

Wang Zhihong[a,*], Han Yucui[a], Hua Yuan[b]

[a] *Beijing University of Technology, Pingleyuan 100, Beijing, 100022, PR China*
[b] *Shijiazhuang Railway Institute, Shijiazhuang, 050043, PR China*

Received 5 May 2000; accepted 7 April 2003

Abstract

Cement-based materials are brittle and low in flexural strength, which can be greatly improved by adding organic monomers to cement-based matrixes due to the polymerization effect of added the organics. The solution polymerization behaviors of organic monomer in cement paste and its effect on cement properties have been studied in this paper. The results show that the organic monomers used in the experiment can well polymerize themselves in cement pastes by solution polymerization effect under common conditions. As results, the cement composites have a flexural strength between 17.8 and 33.4 MPa, greatly dependent on the amount of organic monomers added and is stable when it is immersed in water, acid, alkali and salt solutions. Besides, the setting time of the composites can be controlled and regulated.

Keywords: Bending strength; Hydration products; Composite; Cement; Polymers

1. Introduction

There are three types of cohesive bonds in cement hydrates. The ionic bond is much stronger than the van der Waal and the H bond [1], but its fraction is small, so the flexural strength and the tensile strength of hardened cement is low. Polymer modification is a method for decreasing the brittleness of cement [2–5], but there has been no big breakthrough in polymer-modified cement for a long time. Under dry condition, MDF cements can attain 70–150 MPa in flexural strength [3,4], however, it will have a big strength loss when it comes in contact with water. For this reason and the complexity in its production, there have been no commercially available MDF cement products in the world up to now [5]. Recently, a new class of MDF cement with high strength and good durability has been developed, in which an anhydrous and alcohol soluble resin serves as precursor and high alumina cement is used instead of Portland cement [6]. This modified MDF cements have similar high flexural strength and very high water resistance compared to conventional MDF cement [1,5,6], but the technology of the modified MDF cement is very difficult and not practical under normal service conditions. The use of EVA (ethylene vinyl acetate copolymers) and others is a common method for improving toughness of cement, but it enhances the coherence and deteriorate the flowability of cement paste, problems also exist in its practical application [2,5].

To modify the properties of hardened cement paste, we began to research the application of solution polymerization in cement. Solution polymerization means that the water-dispersion monomer polymerizes with the cross-linking agent and initiating of the initiator [7–9], and the free-radical polymerizes into lattices. At the same time, the carboxyl ionic of the organic can chelate Ca^{2+} ionic into chelate compound [10,11]. Therefore, the polymer lattice and inorganic lattices (hardened cement paste) overlap together, which enhances the toughness of the composites [11].

2. Experimentation

Cement pastes were prepared by mixing ordinary Portland cement 525R (Jidong Cement Plant, Tangshan, Hebei),

* Corresponding author. Tel.: +86-10-67392498; fax: +86-10-67391536.
E-mail address: wzhhwbj@sohu.com (Z. Wang).

0008-8846/03/$ – see front matter
doi:10.1016/S0008-8846(03)00140-6

Table 1
Mix proportions of AAM-modified cement

Materials	Parts by weight (%)
Cement (OPC or sulphoaluminate cement)	100.0
Slag	36.23
Water	27.5
AAM	2–12
Modifier	0.13–0.17

sulphoaluminate cement (Tangshan Polar Bear Special Cement, Luan County, Hebei), slag (Capital Iron and Steel, Beijing), water solution of the monomer (AAM: Dongfang Chemical Plant, Beijing) and other additives. The mix proportions are given in Table 1.

The mixture was made into 4 × 4 × 16 cm. specimens after mixed for about 5 min.

The initial setting time of the pastes is between 7 and 22 min, and the final one is about 12 to 120 min, which is dependent on the content of the catalyst, monomer and the modifier. Any compaction or heat curing is not required for these pastes. The setting time, flexural strength and compressive strength are measured according to standards that are used in China.

3. Results and discussion

3.1. Properties

The properties of AAM-modified cements are given in Tables 2 and 3.

Table 2
Properties of AAM-modified ordinary Portland cement 525R (cement: slag = 11:4)

Am/c (%)	Flexural strength (MPa)			Compressive strength (MPa)		
	3 days	7 days	28 days	3 days	7 days	28 days
0	8.08	8.27	9.02	56.8	84.4	99.2
4	12.56	13.69	20.12	49.8	65.3	96.0
5.45	11.75	16.63	25.37	37.2	61.0	94.7
12	9.22	19.53	33.37	27.4	55.1	88.6

Curing condition: 3 days moisture, 25 days dry; Am: AAM.

Table 3
Properties of AAM-modified sulphoaluminate cement 525

Am/c (%)	Flexural strength (MPa)				Compressive strength (MPa)			
	1 day	3 days	7 days	28 days	1 day	3 days	7 days	28 days
0	7.43	8.21	8.39	7.98	51.4	55.6	67.0	68.0
2	8.94	10.76	12.05	14.35	44.6	54.6	65.8	67.5
4	9.78	11.24	12.54	20.90	46.3	64.8	76.9	95.2
5.45	10.36	12.29	14.39	21.10	34.8	56.2	76.0	97.2
8	11.92	14.48	15.84	21.94	34.4	58.4	76.6	95.2

Idem.

Table 4
Effect of different organic matter on strength of sulphoaluminate cement 525

Type of matter	Water/solid	Flexural strength (MPa)			Compressive strength (MPa)		
		3 days	7 days	28 days	3 days	7 days	28 days
Unmodified	0.247	8.20	8.40	7.98	54.6	67.0	68.0
EVA powder	0.247	6.18	6.67	8.74	38.4	48.6	55.2
VAE emulsion	0.247	5.23	5.82	8.59	40.0	44.0	56.0
AAM	0.247	10.45	12.23	17.89	58.4	76.6	95.6

Idem.
EVA: Wacker, Germany; VAE: Beijing Organic Chemical Plant.

Table 2 shows that the addition of AAM worsens the compressive strength of cement paste at 3 and 7 days, but has no evident influence on the strength at 28 days. The decrease in compressive strength at early ages is attributed to the retardation of cement hydration due to the incorporation of AAM. The higher the AAM/C ratios, the greater the retardation of hydration at the early stages [11]. But the flexural strength of cement paste increased with AAM/C ratio. When AAM/C = 5.45%, the flexural strength increased by 1.7 times at 28 days and by 2.7 times when AAM/C = 12%.

AAM addition also has the same influence on the strength of sulphoaluminate cement (Table 3), but it only decreases its compressive strength at 1 day. For both cement, the optimum AAM/C ratio was about 5% to 8%.

The influence of organic matter on the strength of cement paste is varied with the kind of the organics used. Table 4 shows that with the same addition of 5.45%, AAM, among

Table 5
The relationship between the catalyst-to-water ratio and the setting time (sulphoaluminate cement 525)

Catalyst/water (ml/ml)	Initial set (min)	Final set (min)
0.016	7.25	9.25
0.012	7.67	10.50
0.008	7.80	10.83
0.004	10.03	14.17
0	22.00	120
Unmodified	>45	< 720

W/C = 0.247, Am/C = 0.0545.

Table 6
The relationship between the concentration of the catalyst and 28-day strength of the composite (idem)

Catalyst/water (ml/ml)	Flexural strength (MPa)			Compressive strength (MPa)		
	1 day	3 days	7 days	1 day	3 days	7 days
0.016	10.36	12.29	20.48	54.4	73.4	81.2
0.012	9.96	12.24	21.63	57.2	71.9	76.2
0.008	10.12	12.18	21.47	58.4	71.5	79.4
0.004	10.16	12.00	21.48	57.8	73.1	77.0
0	7.30	12.41	19.08	54.6	72.3	77.1

Idem.

Table 7
The relationship between the solution and the strength of the AAM-modified composite (OP525)

Condition	Flexural strength (MPa)	Compressive strength (MPa)
Drying curing	32.67	89.6
Water	24.65	90.0
Sulfuric acid	25.89	86.4
Sodium chloride	25.27	92.4
Sodium hydroxide	31.64	86.6

Idem.

the three organic compounds used, has the best strength increasing effect.

3.2. Setting time

The setting time of AAM-modified cement paste can be regulated by controlling the concentration of the catalyst in the composite. The initial and final setting time of unmodified cement paste was >45 min and < 720 min, respectively. With use of catalyst, the initial setting time can be reduced to 7 to 22 min, and the final set can be reduced to 10 to 120 min. The relationship between the setting time and catalyst-to-water ratios are given in Table 5. It seems that from 0.008 to 0.016 of catalyst-to-water ratio, the setting time of paste changes little, but from 0 to 0.008 the catalyst-to-water ratio does have evident influence on setting time and with increase of it the setting time of cement paste is decreased. According to the results of this study, the optimum catalyst-to-water ratio is ≤ 0.004.

Table 6 shows that the addition of catalyst does not worsen the strength of cement paste.

3.3. Resistance to chemical attack

After demoulding, the specimens were soaked in water, saturated sodium chloride solution, sodium hydroxide solution (10% by weight) and sulfuric acid solution (pH2) for 4 months. Then their strengths were tested. The results are shown in Table 7, which shows that when the AAM-modified composites were soaked in water and the three solutions for 4 months, the compressive strength of the composites kept at the same strength level of the composite under dry curing condition, but the flexural strengths were lowered a little. The decrease in flexural strength maybe due to fact that the formed PAM (polyacrylamide) absorbs water, leading to the weakening of the connection of the hydrate particles.

3.4. Mechanism of hardening

A possible mechanism [10,11] of the cement solidification is shown in Fig. 1.

The formed organic lattice and the inorganic lattice (cement formed) overlaps, which improves the strength and the toughness of the composite.

4. Conclusions

1. AAM/C ratio has an effect of the strength of AAM-modified cement. Generally, the flexural strength of AAM-modified cement increases with the increase of AAM/C. However, there is an optimum AAM/C ratio, about 5% to 8%. Higher AAM/C ratios will retard the hydration of cement and decrease the compressive strength at later stages.
2. The concentration of catalyst has an effect on the setting time. By regulating the catalyst-to-water ratio, the setting time of cement can be controlled. The optimum catalyst-to-water ratio is about ≤ 0.004 (ml/ml).
3. The influence degree of organic compounds on the flexural strength of cement is varied with the kind of the compounds. In comparison to EVA- and VAE-modified cement, AAM-modified cement has the biggest strength at the same polymer-to-cement ratio (5.45%).
4. AAM-modified cement can well resist attacks by the chemicals and is stable in water.

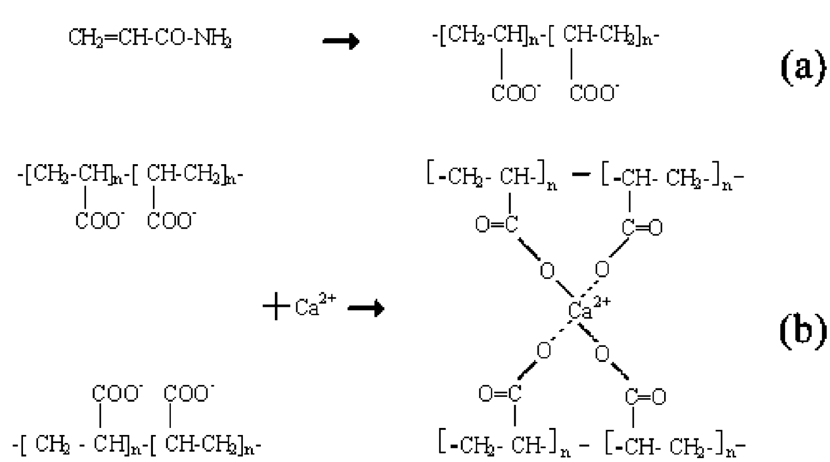

Fig. 1. Mechanism of the composite solidification.

5. Organic and inorganic lattices overlap in AAM-modified cement paste, which improve the flexural strength and the toughness of the cement-based composite.

References

[1] M. Hasegawa, A new class of high strength, water and heat resistant polymer-cement composite solidified by an essentially anhydrous phenol resin precursor, Cem. Concr. Res. 25 (6) (1995) 1191–1198.
[2] M. Shufang, Polymer Composite and Its Application (in Chinese), Science and Technology Press, Beijing, 1996.
[3] J.D. Birchall, A.J. Howard, K. Kendale, Flexural strength and porosity of cements, Nature 259 (5796) (1981) 388–389.
[4] S. Goto, E. Koyata, S. Kimura, Hardened cement paste with high bending strength (in Japanese), Semento Gijutsu Nenpo 37 (1983 Dec.) 101–111.
[5] Y. Ohama, Development of sustainable concrete composite materials in Japan, Proceedings of the 4th Beijing International Symposium on Cement and Concrete, vol. 3, International Academic Publishers, Beijing, 1998, pp. 97–108.
[6] G.K. Dinilprem Pushpalal, T. Kobayashi, T. Kawano, N. Maeda, The processing, properties, and applications of calcium aluminate–phenol resin composite, Cem. Concr. Res. 29 (1) (1999) 121–132.
[7] H. Jinquan, G. Tongyu, Emulsion Polymerization (in Chinese) Chemical Industry Press, Beijing, 1982.
[8] A.C. Young, O.O. Omatete, M.A. Janney, P.A. Mechhofer, Gelcasting of alumina, J. Am. Ceram. Soc. 74 (3) (1991) 612–618.
[9] O.O. Omatete, M.A. Janney, R.A. Strehlow, Gelcasting—A new ceramic farming process, Ceram. Bull. 70 (10) (1991) 1641–1649.
[10] S.A. Rodger, S.A. Brooks, W. Sinclair, G.W. Groves, D.D. Double, High strength cement pastes: Part 2. Reaction during setting, J. Mater. Sci. 20 (1985) 2853–2860.
[11] H. Yucui, Research on Powder Organic Compound Modified Cement-based Composites Master's thesis, Beijing University of Technology, Beijing, 2000. In Chinese.