Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement & Concrete Composites 27 (2005) 920–925

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

Study of cement mortars modified by emulsifier-free latexes

Wang Jingang [a,b], Zhang Shuxiang [a], Yu Haiqin [a], Kong Xiangzheng [a,*], Wang Xikui [a], Gu Zhongmao [b]

[a] *College of Chemistry and Chemical Engineering, Jinan University, Jinan, Shandong 250022, China*
[b] *China Institute of Atomic Energy, P.O. Box 275 (26), Beijing 102413, China*

Received 17 October 2003; accepted 19 May 2005

Abstract

Cationic copolymer latex of vinyl acetate (VA) with methacryloxyethyl trimethylammonium chloride (MTC) and anionic copolymer latex of VA with sodium acrylate (SA) were prepared via emulsifier-free emulsion copolymerization. Modifications of cement mortars by these copolymer latexes were studied, and the results were compared with mortars modified by homopolymer of VA (PVA) as well as with blank mortars. The experimental results showed that flow of the mortars modified by PVA homopolymer and P(VA–MTC) copolymer latexes were increased compared with the blank, whereas a decrease was observed for that modified by P(VA–SA) anionic copolymer latex; a volume expansion was detected in polymer modified mortars by PVA and P(VA–MTC), while no volume expansion was observed in the anionic P(VA–SA) modified mortars; the flexural strength of mortars modified by P(VA–MTC) increased by 79.5% compared to unmodified mortars after 5 day water curing plus 21 day air curing. This value reached 95% when the curing process was followed by a supplementary 24 h vacuum curing. These polymer modified mortars were then subjected to hydration analysis through X-Ray diffraction (XRD). Mechanisms of the mortar modification are discussed based on the characterization results.

Keywords: Emulsifier-free latex; Polymer-modified mortar; Performance; XRD

1. Introduction

Polymer-modified mortars became well known in the 1970s and are actually used for repair [1,2], thin overlays for floors and bridges, and for precast components thanks to their excellent performances such as high flexural strength, corrosion resistance and good adhesion [3–5]. The mortar modification by polymers can be done either by adding polymer powder into cement or blending polymer latex with cement. Modification by latexes is more interesting owing to the great amount and variety of manufactured polymer latexes and their direct application without necessity to separate polymers out from their production media.

At present, most of latexes used in mortar modification are generally commercially manufactured with presence of up to 5% surfactants for latex particle stabilization. However, it is well known [6] that performing substances in latexes are polymers and emulsifiers usually bring about adverse influence to the performance of modified mortars. Emulsifier-free emulsion polymerization is one of the hotspot in emulsion polymerization in recent years [7]. Knowing that most emulsifier molecules are water absorbent, absence of surfactant molecules in polymer modified mortars is expected to enhance water resistance of the mortars. And on the other hand, surfactant molecules are not chemically attached to the polymer backbones, they will eventually migrate with time and thus leaving voids in the

---

[*] Corresponding author. Tel.: +86 531 85175202; fax: +86 531 87161600.
E-mail address: xzkong@ujn.edu.cn (X. Kong).

0958-9465/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2005.05.005

polymer-containing construction materials, or cause surface soiling of the construction element.

This paper deals with an emulsifier-free cationic copolymer latex based on vinyl acetate (VA) and methacryloxyethyl trimethylammonium chloride (MTC, the copolymer being shortened as P(VA–MTC)) and an emulsifier-free anionic copolymer latex of VA and sodium acrylate (SA) (P(VA–SA)) used for mortar modification. The results are compared with those from mortars modified by homopolymer latex of PVA as well as those from blank mortars without polymer latex modification.

2. Experimental

2.1. Materials

Portland cement type 42.5R was used according to GB/T17671 issued April 1 2001 by Chinese General Bureau of Building Materials. The composition and properties of the cement are summarized in Table 1. The sand sample used in the test is of ISO standard, SiO_2 content $\geqslant 98\%$, moisture $\leqslant 0.2\%$ after 2 h baking at 110 °C, granular size over 2 mm $\leqslant 5\%$. All chemicals for latex preparation (monomers, initiator, surfactant etc) were used as received.

2.2. Emulsifier-free polymer latex preparation

All latexes were prepared in a 2 L glass reactor. There were no surfactants used in the cationic and anionic latex preparation, where a functional monomer (MTC or SA) served as surfactant upon polymerization in view of latex stabilization. However, polyvinyl alcohol and OP-10 (oxyethylated octyl phenol), have to be used as surfactants in VA homopolymerization in order to get stable PVA latex. All polymerizations were conducted at 70 °C using a semi-continuous process [8]. In the two copolymer latexes, the monomer ratios were 6:1 (VA/MTC for cationic latex and VA/SA for anionic latex). The solids in all the three latexes were about 30% in order to keep a same polymer–cement ratio in the mortar formulation. The average particles sizes, determined by dynamic light scattering, are 195 nm, 600 nm and 200 nm for P(VA–MTC) latex, P(VA–SA) latex and PVA homopolymer latex, respectively.

2.3. Mortar sample preparation and tests

Mortar specimens were prepared with water/cement/sands weight ratio at 0.45/1.0/2.5 with varying polymer amounts. It is to note that water amount included one part from the latex and another part added if required when mortars were prepared. The specimens were cured under different curing conditions given below. Specimen dimension for mechanical tests was of 40 × 40 × 160 mm.

Once mixed and prepared, mortar specimens were cured according to GB177-85 of China and Japanese Industrial Standard JISA1171. Three different curing processes were used for different samples. These curing processes are referred as curing conditions 1, 2 and 3 hereafter. Under curing condition 1, specimen was demolded after 48 h followed by water curing of 26 days at 20 °C; in curing condition 2, specimen was demolded after 48 h followed by 5 day water curing and 21 days air curing at 20 °C and 50% relative humidity (RH); in curing condition 3 the same curing process as curing condition 2 was followed, except the specimen was subjected to a subsequent final drying of 24 h under vacuum at 50 °C.

Flow of fresh mortars was tested according to method GB2419-81, compressive and flexural strengths were determined according to GB177-85, both standard methods of China. A D/max-rA X-ray instrument was used for X-ray analysis.

3. Results and discussion

3.1. Effects of latexes on flow of fresh polymer-modified mortars

Flow values of fresh polymer-modified mortars with different latexes and at different *P*/*C* (polymer/cement) ratios are presented in Table 2. It is seen that the flow of mortars modified by PVA or P(VA–MTC) increased,

Table 1
Properties of portland cement grade 42.5R

Chemical composition (wt%) of portland cement grade 42.5R						
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Total
22.02	4.80	3.54	65.48	2.51	0.42	98.99
C_3S	C_2S	C_3A	C_4AF			
56.32	20.64	6.74	10.76			94.46
Physical properties of the cement						
Ignition loss	Specific surface	Density	Granules $\geqslant 80$ μm			
0.22%	2782.6 cm^2/g	3.125 g/cm^3	$\leqslant 10\%$			

and this increase was more pronounced with higher polymer level; As to mortars modified by P(VA–SA), a slight decrease was observed at low polymer level, and it reached the flow of the blank at *P*/*C* ratio of 0.5. Knowing that cement particles are usually positively charged, there must be a strong ionic interaction between the negatively charged P(VA–SA) latex particles with positively charged cement granules, which would contribute to keep the latex particles and cement granules tightened up, and therefore to slow down the flow of the mortar. As to the PVA latex and anionic P(VA–MTC) latexes, their particle surfaces are negatively charged, and the same ionic interaction does not occur. Instead there must be a static repulsion between the latex particles and the cement granules, which might have contributed to the increase in the mortar flow. It is further seen that this flow increase becomes more significant at higher *P*/*C* ratios for PVA and P(VA–MTC) modified mortars. For P(VA–SA) modified mortars, their flows were relatively constant regardless of the continuous augmentation in *P*/*C* ratios. Further studies are needed for a thorough understanding of the observations.

Volume expansion of fresh mortars was also determined by comparing the filled height in a cylindrical container of the blank mortar with that of those prepared with polymer latex. Results are displayed in Table 3. It is clearly seen that this volume expansion is in accordance with the flow variation in Table 2, i.e. the PVA and P(VA–MTC) modified mortars, which showed distinguished flow increases, demonstrate high volume expansion; and for P(VA–SA) modified mortars, whose flow was relatively unchanged in comparison with the blank and with polymer level, no perceptible volume expansion is detected. In general, volume expansion is expected in fresh prepared polymer modified mortars due to a so-called ball-bearing action of polymer particles and the lubrication of entrained air [6,9]. The results from negatively charged PVA and P(VA–MTC) latex modified mortars are in agreement with this expectation; while the mortar modified with P(VA–SA) emulsifier-free latex shows no volume expansion.

Table 2
Flow of mortars with different latexes at varying polymer/cement (*P*/*C*) ratios

P/*C*	Flow (mm) of mortars modified by			
	Blank	PVA	P(VA–MTC)	P(VA–SA)
0.005	124	166	176	118
0.01	124	203	217	118
0.02	124	>300	>300	122
0.05	124	>300	>300	124

Table 3
Flow and volume expansion in fresh mortars at *P*/*C* ratio 0.01 (1% polymer)

Modifying polymer	Volume expansion (%)	Flow of the mortars (mm)
Blank (unmodified)	0 (reference)	124
PVA	16	203
P(VA–MTC)	9	217
P(VA–SA)	~0	118

3.2. Influences of polymer latexes on hydration of modified cement

In order to investigate the influence of the polymer on the cement hydration in the polymer modified mortars, cured samples with and without polymer latex were subjected to XRD test, the spectra are displayed Fig. 1. The degree of cement hydration could be estimated by comparing the peaks corresponding to $Ca(OH)_2$ (at $2\theta = 18.0°$ or $d = 4.92$, numbered as peak 1 in Fig. 1) and C_3S (at $2\theta = 29.4°$or $d = 3.04$, numbered as peak 2). With more hydration, it is anticipated that the relative surface area of the peak due to $Ca(OH)_2$ will increase and that of C_3S will decrease. It is seen that the $Ca(OH)_2$ peaks for P(VA–MTC) and P(VA–SA) modified samples (spectra c and d) are of similar relative intensities in regard to the other peaks on a same spectrum. However, PVA modified sample displays the smallest $Ca(OH)_2$ peak accompanied by a largest C_3S peak amongst the four spectra. This indicates that a lesser hydration occurred in this sample in comparison with the blank and those modified by the two emulsifier-free copolymers.

It is conceivable that a long lasting close contact of water molecules with cement granules is required for the hydration to occur. In case of presence of surfactant molecules, they could be gathering around cement granules to form a surfactant layer, in which the hydrophobic ends of the surfactant molecules are in contact with the cement granule surface, and their hydrophilic heads orientate towards surrounding water molecules, similar to the picture of surfactant micelles and that of surfactant stabilized latex particles. The surfactant molecules in such a conceived orientation are surely less packed or less organized compared with the structure in a latex, nevertheless, it might well act as a barrier keeping part of water molecules away from cement granules' surface. This can serve to explain the lower hydration degree in PVA modified mortars, where abundant surfactant was present.

3.3. Effects of polymers on the compressive and flexural strength

At *P*/*C* ratio 0.02, the compressive and flexural strengths of latex modified mortars after 26 days of water curing (condition 1) are presented in Table 4. It is seen from the table that the strengths of PVA modified

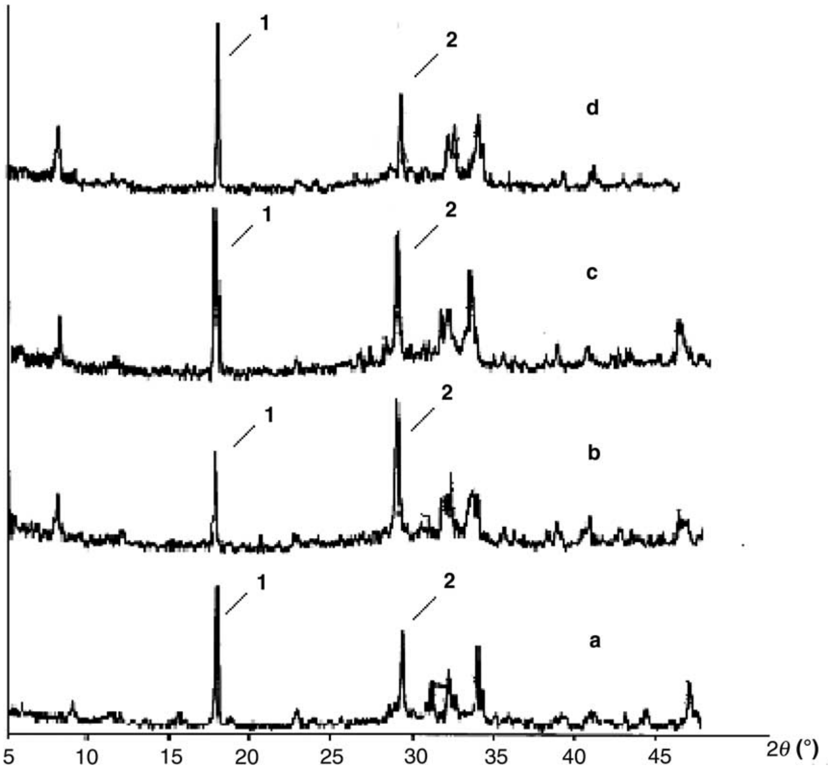

Fig. 1. XRD spectra of mortars with 26 day water curing after demolded: (a) blank; (b) 2% PVA; (c) 2% P(VA–MTC) and (d) 2% P(VA–SA).

Table 4
Compressive and flexural strength of mortars after 28 day water curing ($P/C = 0.02$)

Mortars[a] modified by	Compressive and flexural strengths (MPa)		Strength changes relative to blank (%)	
	Compressive	Flexural	Compressive	Flexural
Blank	48.2	8.9	0 (Reference)	0 (Reference)
PVA	39.8	7.4	−17.4	−16.9
P(VA–MTC)	47.7	8.6	−1.0	−3.4
P(VA–SA)	47.8	8.8	−0.8	−1.1

[a] Curing condition 1: demolded after 48 h at 20 °C, followed by 26 day water curing at 20 °C.

Table 5
Compressive and flexural strength of mortars prepared with P/C at 0.02

Mortars[a] modified by	Compressive and flexural strengths (MPa)		Strength changes relative to blank (%)	
	Compressive	Flexural	Compressive	Flexural
Blank	46.3	7.8	0 (Reference)	0 (Reference)
PVA	44.8	9.1	−3.2	16.6
P(VA–MTC)	48.4	10.2	4.5	30.8
P(VA–SA)	48.2	9.4	4.1	20.5

[a] Curing condition 2: demolded after 48 h at 20 °C, followed by 5 day water curing and 21 day air curing all at 20 °C and 50% RH in air curing.

mortar decreased by about 17%, namely from 48.2 to 39.8 MPa (a 17.4% decrease) for compressive strength and from 8.9 to 7.4 MPa (a 16.9% decrease) for flexural strength. In contrast, these strengths in both emulsifier-free copolymer latex modified mortars remained basically unchanged in comparison with the blank sample.

In Table 5 the results are gathered of compressive and flexural strength of the same mortars but air cured in a second step. The data clearly indicate that both compressive and flexural strengths are increased for the emulsifier-free latexes. Even for the sample with PVA where surfactants were used, the flexural strength showed a slight increase accompanied by a slight decrease in compressive strength. Compressive strength decrease in polymer modified mortars is a quite common observation [6], and has been widely accepted as a sacrifice because the materials are usually over-performing in other aspects such as water-resistance, acid resistance, anti-shocking or anti-impact properties. The unchanged or slightly improved compressive strength observed in emulsifier-free latex modified mortars is an extra-gain, which tells that mortar performance could be improved with no sacrifice in the mechanical strengths. This reveals a supplementary excellence of emulsifier-free latex in mortar modification. This could be attributed to the absence of the emulsifiers and eventually also to

Table 6
Compressive and flexural strength of mortars cured under different conditions ($P/C = 0.1$)

Mortars modified by		Blank	PVA	P(VA–MTC)	P(VA–SA)
Curing condition 2[a]	Compressive strength (MPa)	46.3	36.2	43.1	42.4
	Flexural strength (MPa)	7.8	9.8	14.0	11.2
	Flexural strength change (%)	0 (reference)	25.6	79.5	43.6
Curing condition 3[a]	Compressive strength (MPa)	N/A	36.7	43.6	42.7
	Flexural strength (MPa)	7.8	10.3	15.2	13.6
	Flexural strength change (%)	0 (reference)	32.1	94.9	74.4

[a] Curing condition 2: demolded after 48 h at 20 °C, followed by 5 day water curing and 21 day air curing at 20 °C and 50% RH in air curing; curing condition 3 same as condition 2 except air curing lasted 20 days, followed by 24 h curing under vacuum at 20 °C.

the monodispersity of the latex particles, characteristic of emulsifier-free emulsion polymerization. Comparing the results in Tables 4 and 5, it can be also seen that air cured polymer modified samples demonstrated better performance than water cured ones with a sole exception of the blank sample. It is assumed that water curing would reduce the effectiveness of polymers in the modified specimens, because polymer latex films could not be formed under water curing.

Polymer content in the mortars is also an important factor in controlling mortar properties. Strengths of polymer-modified mortars will change upon a variation in P/C ratio. Results given in Table 6 are obtained from mortars prepared with P/C at 0.1 (10% of polymer on cement by mass). It clearly shows that the flexural strength in this series of samples improved comparative to the data obtained at lower P/C ratio in Tables 4 and 5. On the same time, a very slight decrease in compressive strength is observed when compared with the blank sample as one would have expected. One can also see from Table 6 that air curing led to a higher performance in flexural strength than the corresponding water cured mortars, while the compressive strength was kept unchanged. This is easily understandable because polymer film cannot be well formed under water curing, so that the benefits of added latex polymer for mortar modification are not fully exploited under this curing process.

4. Conclusions

Based on the results presented in the paper, the following conclusions can be drawn:

1. Cationic copolymer latex, of vinyl acetate (VA) and methacryloxyethyl trimethyl ammonium chloride (MTC), and anionic copolymer latex of VA and SA (sodium acrylate) are successfully prepared via emulsifier-free emulsion polymerization process. Latex particles are monodisperse.
2. The above two emulsifier-free latexes were used to prepare polymer modified mortar samples, results were compared with unmodified and PVA latex modified mortar samples. It is revealed that flow of the modified mortars by PVA and P(VA–MTC) increased, and flow in the sample with P(VA–SA) remained relatively constant compared with the blank sample. Regardless of the polymer latexes, flow increased with increase in polymer amount. A volume expansion was observed in the polymer modified fresh mortars with exception for P(VA–SA), in which the volume expansion is close to null. It was found that a larger flow was related to a more important volume expansion in the fresh mortar samples. Tests on compressive and flexural strength of the samples showed that mortar samples modified by the emulsifier-free latexes had a better performance than the emulsifier-containing PVA latex.
3. XRD characterization of the samples showed that a higher degree of hydration was obtained in emulsifier-free latex modified samples. A film layer formation mechanism was suggested for the polymer modified samples in order to interpret the results.

Acknowledgements

This work is supported by Natural Science Foundation of China (grant no. 50173010).

References

[1] Cabrera JG, Al-Hasan AS. Performance properties of concrete repair materials. Construction Building Mater 1997;11(5–6): 283–90.

[2] Pinelle DJ. Curing stresses in polymer-modified repair mortars. Cem Concr Aggregates 1995;17(2):195–200.

[3] Fowler DW. Polymers in concrete: a vision for the 21st century. Cem Concr Compos 1999;21(5):449–52.

[4] Pindado MA, Aguado A. Fatigue behavior of polymer-modified porous concretes. Cem Concr Res 1999;29(7):1077–83.

[5] Justnes H. Protecting Concrete Against Chloride Ingress by Latex Addition. In: Polymers in Concrete Proceeding of 6th International Congress, Shanghai, China, 1990. p. 261–7.

[6] Pei M, Kim W, Hyung W, Ango AJ, Soh Y. Effects of emulsifiers on properties of poly(styrene-butyl acrylate) modified mortars. Cem Concr Res 2002;32:837–41.

[7] Fang SJ, Fujimoto K, Kondo S. Amphoteric initiators suitable for emulsifier-free emulsion polymerization and the properties of the resulting latexes. Colloid Poly Sci 2001;279(6):589–96.

[8] Kong XZ, Pichot C, Guillot J, Cavaille J. Studies on particle morphology in vinyl acetate–butyl acrylate emulsion copolymers. In: El-Aasser MS, Sudol D, editors. Polymer latexes: preparation, characterization and applications. Washington DC: American Chemical Society; 1992. p. 163–88.

[9] Liang NX. Cement and concrete modified by polymer. Beijing: Communication Press; 1995.