

CEMENT_{AND} CONCRETE RESEARCH

Cement and Concrete Research 32 (2002) 837-841

Effects of emulsifiers on properties of poly(styrene-butyl acrylate) latex-modified mortars

Meishan Pei^{a,b,*}, Wanki Kim^a, Wongil Hyung^a, Aaron Joseph Ango^a, Yangseob Soh^a

^aDepartment of Architecture, College of Engineering, Chonbuk National University, Chonju, 561-756, South Korea ^bCollege of Chemical Engineering, Jinan University, Jinan, Shandong 250022, PR China

Received 7 March 2001; accepted 6 November 2001

Abstract

Two styrene—butyl acrylate copolymer latices having the same chemical components but different emulsifiers were synthesized under the same reaction conditions, and their effects on such properties as workability, air content, compressive strength, flexural strength and water absorption of fresh and hardened polymer-modified mortars were assessed and discussed. From the tested properties of the polymer-modified mortars, it is concluded that a polymeric emulsifier provides a much more positive effect on the properties of the polymer-modified mortars than a low-molecular emulsifier. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Emulsifier; Polymer-modified mortar; Water absorption

1. Introduction

Over 50 years, polymer-modified mortars have been used in the construction industry because of their properties, characteristics and superior performance. They are valued and widely utilized as finishing materials for flooring, paving, adhesives, integral waterproofing, decorative coatings, repair materials and protective coatings. In the production of polymer-modified mortars, polymer latices with various properties and characteristics are employed as cement modifiers in order to vary the properties of the mortars. Recent studies [1-10] have shown that the properties of any polymer latices have a major influence on the performance of polymer-modified mortars.

Polymer latex is a colloidal dispersion of small polymer particles in water, which is generally produced by the emulsion polymerization of monomers with emulsifiers. The properties of the polymer latex are mainly affected by the chemical components that are present in the polymer latex and the emulsifiers used in the polymerization process. Though polymer latices may have the same chemical components, it has been known that their properties depend on the type of emulsifier. Conventional emulsifiers used in emulsion

polymerization are low-molecular surfactants such as sodium dodecylsulfate and sodium dodecylbenzenesulfonate. The polymeric surfactants as emulsifiers for emulsion polymerization have been examined recently [11-21], and the reports have highlighted two advantages of polymeric emulsifiers: (a) polymeric surfactants provide high density of charges and (b) polymeric surfactants exhibit an efficient steric hindrance. Thus, the polymeric surfactants will be important emulsifiers in the field of emulsion polymerization.

The effect of a chemical component on the properties of polymer-modified mortars has already been reported [8–10], but the effects of emulsifiers on the properties of the polymer-modified mortars have not been examined. The purpose of this study is to investigate the effects of the emulsifiers on the properties of the polymer-modified mortars and to obtain basic data necessary to develop appropriate polymer latices for cement modifiers.

2. Experimental program

2.1. Synthesis of polymeric emulsifier, poly(methyl methacrylate (MMA)-methacrylic acid (MAA))

It is well known that polymeric emulsifiers such as amphiphilic polymers are often used in emulsion polymer-

^{*} Corresponding author. College of Chemical Engineering, Jinan University, Jinan, Shandong 250022, PR China. Tel.: +86-531-276-5675; fax: +86-531-276-7830.

ization to obtain functional properties of polymer latex. In this study, a surface-active polyelectrolyte made from MMA and MAA-poly(MMA-MAA) with a composition of MMA/MAA=75.0:25.0 was synthesized and used as an emulsifier in the synthesis of poly(styrene-butyl acrylate) latex.

The poly(MMA-MAA) was synthesized at 85 °C by using a semibatch emulsion polymerization process, and the molecular weight of the copolymer was controlled by adjusting the amount of a chain-transfer agent, *n*-dodecyl mercaptan, added. An aqueous solution of an initiator, potassium persulfate, using deionized and distilled water was first charged into a reaction vessel and then a mixture of MMA, MAA and the chain-transfer agent was continuously fed into the reaction vessel for 120 min. The reaction vessel was maintained at 85 °C for another 240 min in order to complete the polymerization. An appropriate amount of sodium hydrogensulfite was added to decompose the residual initiator completely. Finally, an aqueous solution of sodium hydroxide was added to dissolve the copolymer latex produced.

The above synthesis procedures for the poly(MMA-MAA) have been confirmed by the previous study [18].

2.2. Emulsion polymerization of styrene and butyl acrylate by using different emulsifiers

Recently, poly(styrene-butyl acrylate) latex has become popular as a cement modifier. For the purpose of this study, two poly(styrene-butyl acrylate) copolymer latices were synthesized by emulsion polymerization using different emulsifiers. One of the copolymer latices (HL) was synthesized with the above synthesized polymeric emulsifier, poly(MMA-MAA), while the other (LL) was synthesized with a conventional low-molecular emulsifier, dodecyl benzenesulfate. In order to maintain a low film-forming temperature for the synthesized copolymer, a monomer ratio of 30:70 of styrene/butyl acrylate was selected.

Batch emulsion polymerizations were carried out. First of all, a reactor was charged with the desired amounts of monomer, emulsifier, deionized and distilled water. A small portion of the deionized and distilled water was put aside for preparing an initiator solution. Dissolved oxygen was later purged out by bubbling nitrogen gas through the reaction mixture. The process of polymerization began by pouring the initiator solution, which had been deoxygenated with the nitrogen gas and stored in a dropping funnel, into the reaction mixture. In all experiments, reaction temperature was kept within 80 °C. Two copolymer latices, HL and LL, were synthesized under the same recipe and reaction conditions except the emulsifier. The solid content of the obtained polymer latices was 45.0.

2.3. Materials and mix proportions for polymer-modified mortars

The cement used is ordinary Portland cement as specified in Korea Standard (KS)-L5201. The fine aggregate is 6#

Table 1
Mix proportions for polymer-modified mortars

Mix no.	Cement/sand ratio (by mass)	Polymer/cement ratio (%)	Water/cement ratio (%)	Air content (%)	Flow (mm)
Plain	1:2.45	0	60	3.1	168
HL-5		5	52	25.0	166
HL-10		10	48	28.9	168
HL-15		15	45	28.1	169
HL-20		20	43	30.2	167
LL-5		5	56	23.6	172
LL-10		10	50	25.1	172
LL-15		15	46	25.3	168
LL-20		20	44	25.6	166

siliceous sand as specified in KS-L5100. The mix proportions of polymer-modified mortars using two poly(styrene—butyl acrylate) latices are as follows: sand/cement ratio = 2.45 (by mass); polymer/cement ratio = 0.05, 0.10, 0.15 and 0.20. The flow of the polymer-modified mortars was maintained at 170 ± 5 mm by controlling the water/cement ratio. Table 1 shows the mix proportions for the polymer-modified mortars. The emulsifiers have the different foaming property, and in order to accurately compare the effects of emulsifiers on the properties of the polymer-modified mortars, no antifoaming agent was added to the latices.

2.4. Experimental methods

Polymer-modified mortars with the mix proportions given in Table 1 were prepared and tested according to the related KS and Japanese Industrial Standard (JIS). The flow and air content of the polymer-modified mortars were tested according to KS-L5105 and KS-F2409, respectively. For compressive strength, flexural strength and water absorption tests, prism specimens ($40 \times 40 \times 160$ mm) were molded. All the specimens were covered with polyethylene sheets, demolded after 48 h and then subjected to a 2-day, 20 °C, 80% RH moist plus 5-day, 20 °C water plus 21-day, 20 °C, 50% RH dry cure. The compressive and flexural strengths were tested according to KS-F2477, and the water absorption was tested according to JIS A 6203.

3. Test results and discussion

3.1. The effects of emulsifiers on the properties of fresh polymer-modified mortars

The properties of fresh polymer-modified mortars with various mix proportions are presented in Table 1. The air content of the polymer-modified mortars is much higher than that of plain mortar. This is attributed to the ability of the polymer latices to entrain air and the foaming property of emulsifiers. The air content of HL-modified mortars is

higher than that of LL-modified mortars at the same polymer/cement ratio because of the stronger foaming property of the polymeric emulsifier. At the same flow, the water/cement ratio for the polymer-modified mortars is lower than that of plain mortar because of the ball bearing action of polymer particles, the entrained air and the dispersing effect of the emulsifiers in the latices. From the experiment, the water/cement ratio decreases with increasing polymer/cement ratio even when the flow remains constant. This result is consistent with the findings of some researchers like Afridi et al. [7] and Ohama et al. [10]. Although the different latices have the same polymer/ cement ratio and flow, the water/cement ratio of HLmodified mortars is lower than that of LL-modified mortars. The reason for this is that the polymeric emulsifiers have better plasticizing effect and foaming property than the low-molecular emulsifier. It is found that the polymeric emulsifier is more effective against the workability of fresh cement mortar than the low-molecular emulsifier with regard to the polymer latices having the same chemical components.

3.2. The effects of emulsifiers on the compressive strength of polymer-modified mortars

Fig. 1 shows the compressive strength of polymer-modified mortars using two synthesized polymer latices. The polymer-modified mortars have a much lower compressive strength than plain mortar. The reasons for this are their much high air content and low elastic modulus of the polymer films formed in the polymer-modified mortars. The compressive strength of the polymer-modified mortars increases with increasing elastic modulus of the polymer films [5,10]. In this experiment, the synthesized polymer latices have a lower elastic modulus because of the lower styrene content. As a result of the decreased water/cement ratio with increasing polymer/cement ratio,

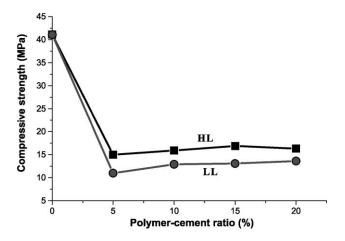


Fig. 1. Polymer/cement ratio vs. compressive strength of polymer-modified mortars.

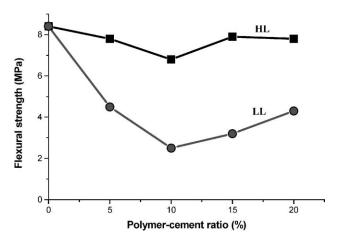


Fig. 2. Polymer/cement ratio vs. flexural strength of polymer-modified mortars.

the compressive strength of the polymer-modified mortars increases with increasing polymer/cement ratio except an HL-modified mortar with a polymer/cement ratio of 20%. In spite of the lowest water/cement ratio, the compressive strength of an HL-modified mortar with a polymer/cement ratio of 20% is impaired by the highest air content of it. The compressive strength of HL-modified mortars is higher than that of LL-modified mortars at the same polymer/cement ratio. This is attributed to the more water reduction effect of polymeric emulsifier compared with that of the low-molecular emulsifier. Accordingly, the polymeric emulsifier is more effective against the compressive strength of cement mortar than the low-molecular emulsifier as to the polymer latices with the same chemical components.

3.3. The effects of emulsifiers on the flexural strength of polymer-modified mortars

Fig. 2 represents the flexural strength of polymer-modified mortars using two synthesized polymer latices. Of all the mortars, plain mortar has the highest flexural strength because of the lowest air content of it. As explained earlier, the lower elastic modulus of synthesized polymers is another reason for all the polymer-modified mortars having a lower flexural strength than the plain mortar. As for the polymer-modified mortars, their flexural strength has a tendency different from their compressive strength. Regardless of the type of copolymer latex, the flexural strength decreases with increasing polymer/cement ratio and reaches a minimum at a polymer/cement ratio of 10%. The polymer-modified mortars with a polymer/cement ratio of 5% have the highest flexural strength among the polymermodified mortars because of its lower air content. Like its compressive strength, the flexural strength of an HL-modified mortar with a polymer/cement ratio of 20% is impaired by the highest air content of it. Even at the same polymer/ cement ratio, HL-modified mortars provide a much higher

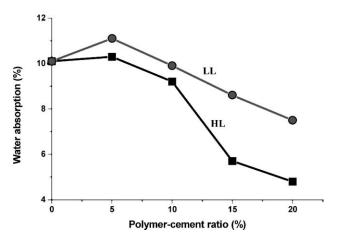


Fig. 3. Polymer/cement ratio vs. water absorption of polymer-modified mortars.

flexural strength than LL-modified mortars. This is attributed not only to the more water reduction effect of the polymeric emulsifier compared with that of the low-molecular emulsifier but also to the advantage of polymeric emulsifier as a polymeric component to the film formation and film characteristics [20]. The test results also show that the polymeric emulsifier has a more positive effect on the flexural strength of cement mortar compared with the low-molecular emulsifier (i.e., for polymer latices with the same chemical components).

3.4. The effects of emulsifiers on the water absorption of polymer-modified mortars

Fig. 3 illustrates the water absorption of polymer-modified mortars using two synthesized polymer latices. The water absorption of the polymer-modified mortars decreases with increasing polymer/cement ratio. This is due to the large pores in the polymer-modified mortars that are filled with polymer particles or sealed with continuous polymer films [6]. Comparing with the different latices, the water absorption of HL-modified mortars is lower than that of LL-modified mortars at the same polymer/cement ratio. This is attributed not only to the more water reduction effect of the polymeric emulsifier compared with that of the low-molecular emulsifier but also to the advantage of the polymeric emulsifier as a polymeric component to the film formation and film characteristics [20].

Fig. 3 indicates that the water absorption of both HL and LL polymer-modified mortars with a polymer/cement ratio of 5% are higher than that of plain mortar. Perhaps this is due to the low amount of polymer that is not enough to form continuous films, and the much larger air content than the plain mortar. For copolymer latices with the same chemical components, the polymeric emulsifier has a more positive effect on the water absorption of cement mortar, while the low-molecular emulsifier has a lesser effect.

4. Conclusions

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

- 1. The compressive and flexural strengths of polymermodified mortars using two synthesized polymer latices with different emulsifiers are lower than those of plain mortar when no antifoaming agent is added to the polymer latices.
- The compressive and flexural strengths of polymer-modified mortars using two synthesized polymer latices with different emulsifiers tend to decrease with increasing polymer/cement ratio and to attain minimums at polymer/cement ratios of 5% and 10%, respectively.
- 3. Regardless of the type of polymer latex, the water absorption of polymer-modified mortars tends to reach a maximum at a polymer/cement ratio of 5%.
- 4. As for the properties of polymer-modified mortars using the polymer latices synthesized with the same chemical components and different emulsifiers, the polymeric emulsifier is more effective than the lowmolecular emulsifier.

References

- [1] A.M. James, S. Said, Effect of the addition of an acrylic polymer on the mechanical properties of mortar, ACI Mater. J. 87 (1) (1990) 54–61.
- [2] A.L. Joseph, Acrylic latex-modified Portland cement, ACI Mater. J. 85 (1) (1988) 41–48.
- [3] J.F. Radinir, S.R. Vlastimir, Experimental research on polymer modified concrete, ACI Mater. J. 95 (4) (1998) 463–469.
- [4] J. Schulze, Influence of water-cement ratio and cement content on the properties of polymer-modified mortars, Cem. Concr. Res. 29 (1999) 909-915.
- [5] D.G. Walters, Comparison of latex-modified Portland cement mortars, ACI Mater. J. 87 (4) (1990) 374–375.
- [6] P.F.G. Banfill, L. Bellagraa, L. Benaggoun, Properties of polymer-modified mortars made with blended cements, Adv. Cem. Res. 5 (19) (1993) 103–109.
- [7] M.U.K. Afridi, Z.U. Chaudhardy, Y. Ohama, K. Demura, M.Z. Iqbal, Strength and elastic properties of powdered and aqueous polymermodified mortars, Cem. Concr. Res. 24 (7) (1994) 1199–1213.
- [8] Y. Ohama, H. Ibe, H. Mine, K. Kato, Cement mortars modified by SB latex with variable bound styrene, Rubber Chem. Technol. 37 (3) (1964) 758-769.
- [9] Y. Ohama, Improvements in properties of vinyl acetate-type polymermodified mortars, Proceedings of the Thirteenth Japan Congress on Materials Research, The Society of Materials Science, Kyoto, Japan, 1970, pp. 212–215.
- [10] Y. Ohama, K. Demura, M. Hamatsu, M. Kakegawa, Properties of polymer-modified mortars using styrene-butyl acrylate latexes with various monomer ratios, ACI Mater. J. 88 (1) (1991) 56-61.
- [11] J.L. Mura, G. Riess, Polymeric surfactants in latex technology: Polystyrene-poly(ethylene oxide) block copolymers as stabilizers in emulsion polymerization, Polym. Adv. Technol. 6 (7) (1995) 497–508.
- [12] M. Berger, W. Richtering, R. Mülhaupt, Use of poly(styrene)-block—poly(ethylene oxide) as emulsifier in emulsion polymerization, Polym. Bull. 33 (5) (1994) 521–528.

- [13] I. Piirma, J.R. Lenzotti, Synthesis of poly(p-methylstyrene)-graft-poly(oxyethylene) and application as a polymeric surfactant in emulsion polymerization, Br. Polym. J. 21 (1) (1989) 45-51.
- [14] G.L. Jialanella, I. Piirma, Emulsion polymerization of methyl methacrylate using poly(methyl methacrylate-co-2-hydroxypropyl methacrylate)-graft-polyoxyethylene as the stabilizer, J. Appl. Polym. Sci. 42 (5) (1991) 1423-1431.
- [15] G.L. Jialanella, E.M. Firer, I. Piirma, Synthesis of polystyrene-block-polyoxyethylene for use as a stabilizer in the emulsion polymerization of styrene, J. Polym. Sci., Part A: Polym. Chem. 30 (1992) 1925-1933.
- [16] T. Cao, W.P. Yin, S.E. Webber, Poly(2-vinylnaphthalene-alt-maleic acid)-graft-polystyrene as a photoactive polymer micelle and stabilizer for polystyrene latexes, Macromolecules 27 (25) (1994) 7459-7464.
- [17] P.-L. Kuo, C.-J. Chen, Functional polymers for colloidal applications:

- V. Novel behavior of polymeric emulsifiers in emulsion polymerization, J. Polym. Sci., Part A: Polym. Chem. 31 (1993) 99-111.
- [18] S. Kato, K. Sato, D. Maeda, D. Maeda, M. Nomura, Synthesis and characterization of poly(methyl acrylate-acrylic acid), Preprint of the 9th Polymeric Microsphere Symposium, Japan, Tokyo, .
- [19] S. Kato, K. Sato, D. Maeda, D. Maeda, M. Nomura, A kinetic investigation of styrene emulsion polymerization with surface active polyelectrolytes as the emulsifier: II. Effects of molecular weight and the composition, Colloids Surf., A: Physicochem. Eng. Aspects 153 (1–3) (1999) 127–131.
- [20] G. Riess, Block copolymers as polymeric surfactants in latex and microlatex technology, Colloids Surf., A: Physicochem. Eng. Aspects 153 (1–3) (1999) 99–110.
- [21] D.Y. Lee, J.H. Kim, Emulsion polymerization of styrene using an alkali-soluble random copolymer as polymeric emulsifier, J. Polym. Sci., Part A: Polym. Chem. 36 (1998) 2865–2872.