

Effect of the Monomer Ratio on the Properties of Poly(methyl methacrylate butyl acrylate) Latex-Modified Mortars

Meishan Pei,^{1,2} Yue Wu,¹ Wanki Kim,² Wongil Hyung,² Yangseob Soh²

¹College of Chemistry and Chemical Engineering, Jinan University, Jinan, Shandong 250022, People's Republic of China

²Department of Architecture, College of Engineering, Chonbuk National University, Chonju, 561-756, South Korea

Received 24 October 2003; accepted 22 March 2004

DOI 10.1002/app.20744

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article deals with the effect of the monomer ratio on the typical properties of polymer-modified mortars with poly(methyl methacrylate butyl acrylate) latices. Polymer-modified mortars, with methyl methacrylate/butyl acrylate copolymer latices of various methyl methacrylate/butyl acrylate ratios, were prepared with different polymer/cement ratios and were tested for their workability, air content, compressive strength, flexural strength, and

water absorption. On the basis of the test results, the effects of the monomer ratio and polymer/cement ratio on the typical properties were examined. The properties of the latex-modified mortars were affected to a great extent by both the monomer ratio and polymer/cement ratio. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2403–2409, 2004

Key words: latices; emulsion polymerization; monomers

INTRODUCTION

Polymer-modified mortars are widely used in the construction industry because of their properties, characteristics, and superior performance. In the production of polymer-modified mortars, polymer latices are used as cement modifiers to improve the properties of the mortars. Recent studies^{1–10} have shown that the properties of any latex have a key influence on the performance of latex-modified mortars. Polymer latex is characterized by different properties. The most relevant factors for use in mortars are the type of monomer, the monomer ratio, the emulsifier used in the polymerization process, the pH value, and the content of solid parts. The polymer latices used in modifying mortars are copolymers of various monomers. The effect of the monomer ratio on the properties of polymer-modified mortars with copolymer latices, such as styrene/butadiene latex,⁸ ethyl/vinyl acetate latex,⁹ and styrene/butyl acrylate (BA) latex,¹⁰ has already been reported, but the same effect, with respect to polymer-modified mortars with methyl methacrylate (MMA)/BA latex, now a popular cement modifier, has

hardly been examined. The purpose of this study was to clarify the effect of the monomer ratio on the typical properties of polymer-modified mortars with MMA/BA latices and to obtain the basic data necessary to develop appropriate latices for cement modifiers.

EXPERIMENTAL

Emulsion polymerization of MMA and BA

Recently, poly(methyl methacrylate butyl acrylate) (MMA-co-BA) latices have become popular cement modifiers. For the purpose of optimizing the properties of MMA-co-BA latices, they were synthesized by emulsion polymerization with different MMA/BA ratios. Batch emulsion polymerizations were carried out. First, a four-necked flask was charged with the desired amounts of the monomer, the emulsifier (dodecyl benzene sulfate), and deionized and distilled water. A small portion of the water was put aside for the preparation of an initiator (potassium persulfate) solution. Dissolved oxygen was later purged via the bubbling of nitrogen gas through the reaction mixture. The polymerization was begun by the pouring of the initiator solution, which had been deoxygenated with nitrogen gas and stored in a dropping funnel, into the reaction mixture. In all the experiments, the reaction temperature was kept at 80°C. The copolymer latices were synthesized with the same recipe and reaction conditions, except for the MMA/BA ratio. The solid content

Correspondence to: M. Pei (peims2000@hotmail.com).

Contract grant sponsor: Natural Science Foundation of China; contract grant number: 50373017.

Contract grant sponsor: Natural Science Foundation of Shandong Province; contract grant number: Y2003F03.

TABLE I
Properties of the MMA-co-BA Latices

Type of latex	Monomer ratio by weight (MMA/BA)	T_g (°C)	MFT (°C)
MMA-20	20/80	-36.2	-17.8
MMA-40	40/60	-10.8	10.5
MMA-50	50/50	2.6	25.4
MMA-60	60/40	17.4	38.8
MMA-70	70/30	33.5	61.6
MMA-80	80/20	49.8	77.4

of the obtained polymer latices was 45%. The properties of the MMA-co-BA latices are shown in Table I.

Materials and mix proportions of the polymer-modified mortars

The cement was ordinary Portland cement, as specified in ASTM C150. The fine aggregate was siliceous sand, with a maximum grain diameter not greater than 1.2 mm. The mix proportions of the polymer-modified mortars were as follows: the sand/cement ratio was 2.45 (by mass), and the polymer/cement (P/C) ratio was 0.05, 0.10, 0.15, or 0.20. The flow of the polymer-modified mortars was maintained at 170 ± 5 mm through the control of the water/cement (W/C) ratio. Table II shows the mix proportions of the polymer-modified mortars. To accurately compare the effect of the monomer ratios on the properties of the polymer-modified mortars, no antifoaming agent was added to the latices.

Experimental methods

Polymer-modified mortars with the mix proportions listed in Table II were prepared and tested according

to ASTM C 1439. The flow of the polymer-modified mortars was tested according to ASTM C 230. The air content of the polymer-modified mortars was tested according to ASTM C 185. For the testing of the compressive strength, flexural strength, and water absorption, prism specimens (40 mm \times 40 mm \times 160 mm) were molded. All the specimens were covered with polyethylene sheets, demolded after 48 h, and then subjected to the following regimen: a 2-day moist cure at 20°C and 80% relative humidity, a 5-day water cure at 20°C, and a 21-day dry cure at 20°C and 50% relative humidity. The compressive and flexural strengths were tested according to ASTM C 109, and the water absorption was tested according to ASTM C 1403.

RESULTS AND DISCUSSIONS

Effect of the monomer ratios on the properties of the polymer latex

The type of monomer, the monomer ratio, and the emulsifier used in the polymerization process affect the properties of polymer latices.¹¹ The monomer ratio plays a key role in the minimum film-forming temperature (MFT) and glass-transition temperature (T_g) of polymer latices. MFT indicates the temperature at which polymer particles have sufficient mobility and flexibility to flow together and form a continuous film. MFT is also an indication of the strength of a polymer. A high MFT corresponds to a high strength and a harder polymer. T_g indicates the temperature at which the polymer is transformed from an elastic form to a rigid, glasslike form. T_g is lower than MFT. The effect of the monomer ratios on the properties of MMA-co-BA latices is shown in Table I. To illustrate the film formability of various synthesized polymer latices

TABLE II
Mix Proportions of the Polymer-Modified Mortars

Mix	Cement/sand ratio (by mass)	P/C ratio (%)	W/C ratio (%)	Air content (%)	Flow (mm)
Plain		0	62	4.7	168
		5	54	13.6	167
MMA-50	1:2.45	10	49	12.4	167
		15	45	10.3	171
		20	41	9.8	175
		5	54	12.7	185
		10	49	9.9	181
MMA-60	1:2.45	15	45	8.7	189
		20	41	7.4	186
		5	54	11.4	188
MMA-70	1:2.45	10	49	8.2	184
		15	45	7.1	184
		20	41	6.8	180
		5	54	14.8	198
MMA-80	1:2.45	10	49	13.8	193
		15	45	11.9	196
		20	41	11.4	187

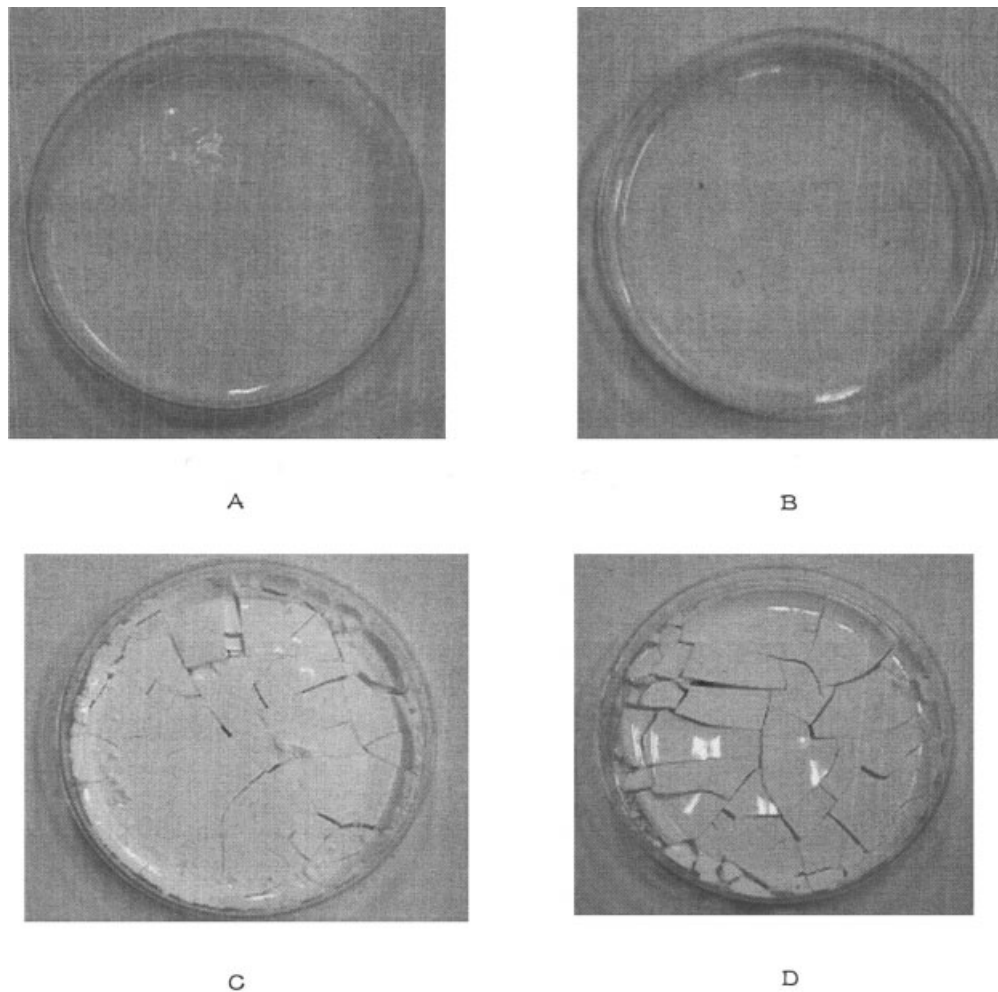


Figure 1 Effects of the monomer ratios on the film formability of the synthesized polymer latices: (A) 50/50 MMA/BA, (B) 60/40 MMA/BA, (C) 70/30 MMA/BA, and (D) 80/20 MMA/BA.

with different monomer ratios, we poured the polymer latices onto a watch glass and cured them at 40°C for several hours. The result is shown in Figure 1. When MFT of the polymer latices was lower than the curing temperature, a continuous film was formed with elastic properties [Fig. 1(A,B)]. When MFT of the polymer latices was higher than the curing temperature, no continuous film was formed [Fig. 1(C,D)].

Effect of the monomer ratios on the properties of the fresh polymer-modified mortars

The properties of fresh polymer-modified mortars with various mix proportions are listed in Table II. The air content of the polymer-modified mortars is much higher than that of the plain mortar. This is attributed to the ability of the polymer latices to entrain air and the foaming property of the emulsifiers. Regardless of the MMA content in the polymer latices, the W/C ratio for the polymer-modified mortars is lower than that of the plain mortar, and

the air content and W/C ratio decrease as the P/C ratio increases at the same flow. The reduction of the W/C ratio can be attributed to the presence of the emulsifier in the polymer latices, the ball-bearing action of the polymer particles, and the entrained air. This result is consistent with the findings of some other researchers, such as Afridi et al.⁷ and Ohama et al.¹⁰ At the same P/C and W/C ratios, the flow of the polymer-modified mortars decreases with a decreasing MMA content, and the setting speed of the mortars modified with MMA-20 and MMA-40 is too fast for an exact determination of the flow. The reason is the lower MFT of the polymer latices with an MMA content lower than 40%. The higher film-forming speed restricts the flow of the polymer-modified mortars. The mortar modified by MMA-20 has the maximum flow at the same P/C and W/C ratios because it has the highest MFT. The film formability of the polymer latex with the highest MFT is inferior to that of other latices.

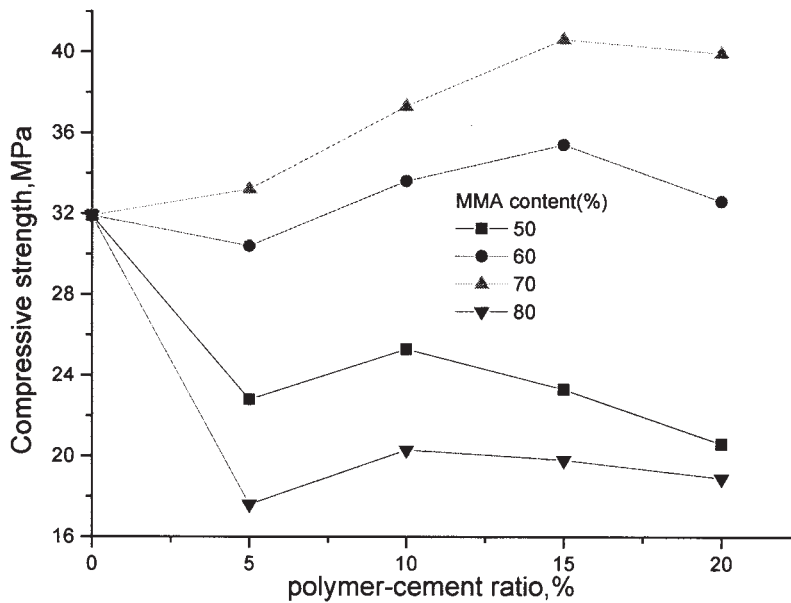
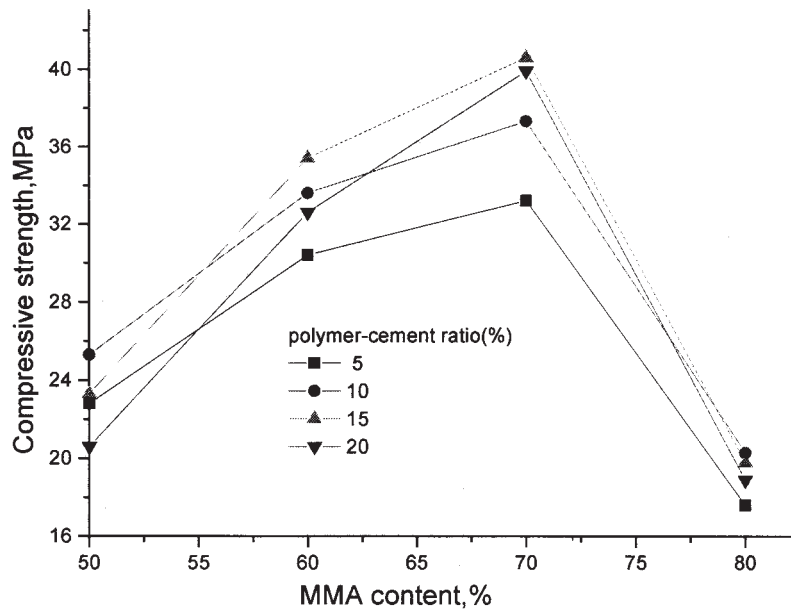


Figure 2 Effects of the MMA content and P/C ratio on the compressive strength of the polymer-modified mortars with MMA-co-BA latices.

Effect of the monomer ratios on the compressive strength of the polymer-modified mortars

Figure 2 illustrates the effects of the MMA content and P/C ratio on the compressive strength of polymer-modified mortars with MMA-co-BA latices. Regardless of the P/C ratio, the compressive strength of the polymer-modified mortars increases with increasing MMA content and attains its maximum at MMA-70.

The compressive strength of the polymer-modified mortars with MMA-60 and MMA-70 reaches its maximum at a P/C ratio of 15 and then tends to decrease slightly with an increasing P/C ratio. The compressive strength of the polymer-modified mortars with MMA-50 and MMA-80 attains its maximum at a P/C ratio of 10 and then decreases with an increasing P/C ratio. The compressive strength of the polymer-mod-

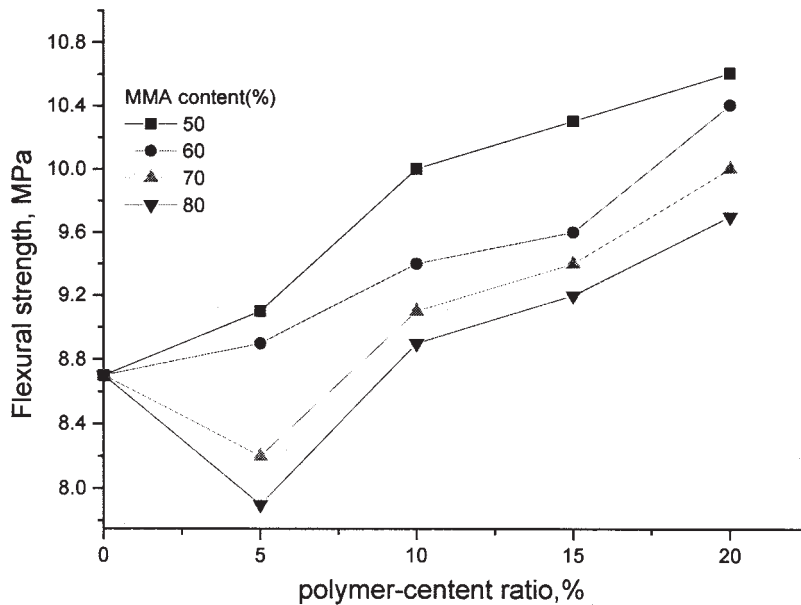
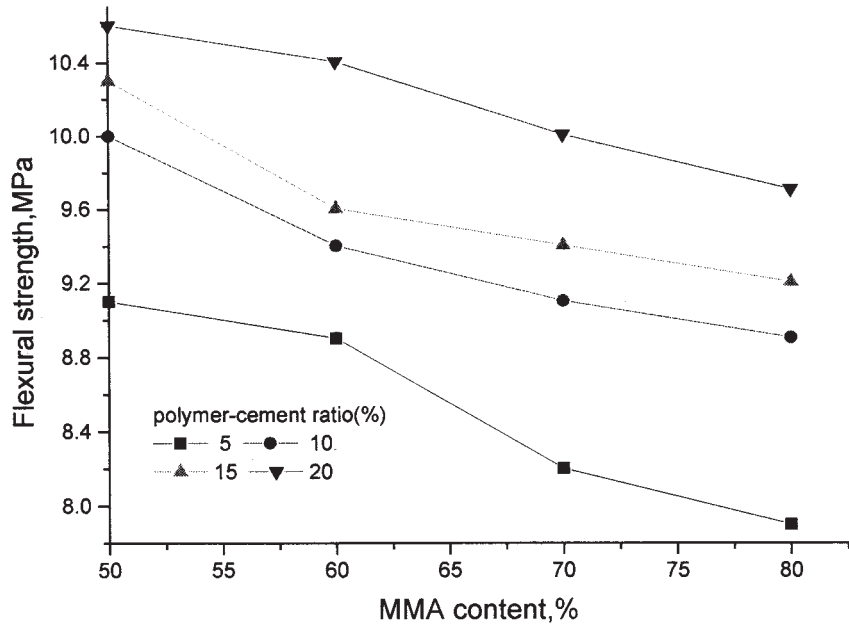


Figure 3 Effects of the MMA content and P/C ratio on the flexural strength of the polymer-modified mortars with MMA-co-BA latices.

ified mortars is affected by the W/C ratio, air content, and elastic modulus of the polymer films formed in the polymer-modified mortars. The polymer-modified mortars with MMA-50 and MMA-80 have a much lower compressive strength than the plain mortar because of their much higher air contents. The polymer-modified mortars with MMA-80 have the lowest compressive strength because they have the highest air content of all the mortars. At the same P/C ratio, the compressive strength of the polymer-modified mor-

tars with MMA-50 and MMA-70 increases with increasing MMA content in the polymer latex because of the increasing elastic modulus of the polymer films.^{5,10}

Effect of the monomer ratios on the flexural strength of the polymer-modified mortars

Figure 3 represents the effects of the MMA content and P/C ratio on the flexural strength of polymer-modified mortars with MMA-co-BA latices. As for the polymer-

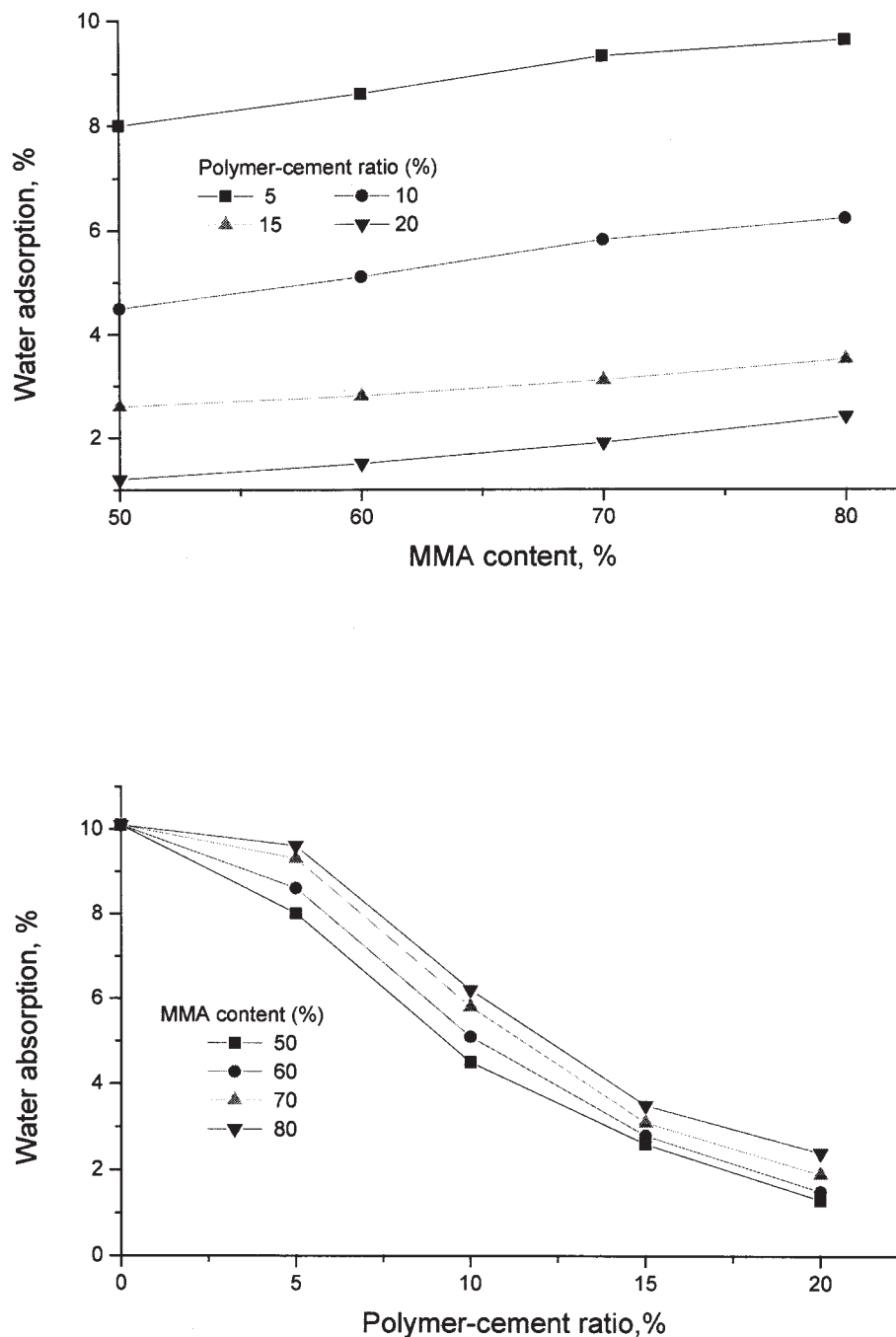


Figure 4 Effects of the MMA content and P/C ratio on the water absorption of the polymer-modified mortars with MMA-co-BA latices.

modified mortars, their flexural strength has a tendency different from that of their compressive strength. The flexural strength of the polymer-modified mortars is higher than that of the plain mortar, except for the mortars modified with MMA-70 and MMA-80 at a P/C ratio of 5. The main reason for the lower flexural strength of the mortars modified with MMA-70 and MMA-80 at a P/C ratio of 5 is their higher air content. Regardless of the P/C ratio, the flexural strength of the polymer-modified mortars decreases with increasing MMA content. This can be attributed to the film formability of the

polymer latex. The film formability of the polymer latex decreases with increasing MMA content, and the polymer latex with MMA-70 and MMA-80 cannot form a film at the casting and curing temperatures.

Effect of the monomer ratios on the water absorption of the polymer-modified mortars

Figure 4 indicates the effects of the MMA content and P/C ratio on the water absorption of polymer-modified mortars with MMA-co-BA latices. The polymer-

modified mortars have lower water absorption than the plain mortar. Because of the film formability of the polymer latex, the water absorption of the polymer-modified mortars increases with increasing MMA content, regardless of the P/C ratio. Moreover, the water absorption of the polymer-modified mortars decreases with an increasing P/C ratio, regardless of the MMA content. This is due to the existence of more pores in the polymer-modified mortars, which are filled with polymer particles or sealed with continuous polymer films, with an increasing P/C ratio.⁶

CONCLUSIONS

On the basis of the results presented in this article, the following conclusions can be drawn:

1. The air content of fresh polymer-modified mortars is much higher than that of a plain mortar. Regardless of the MMA content in the polymer latices, the W/C ratio for the polymer-modified mortars is lower than that of the plain mortar, and the W/C ratio decreases as the P/C ratio increases at the same flow. At the same P/C and W/C ratios, the flow of the polymer-modified mortars decreases with decreasing MMA content.
2. The compressive strength of polymer-modified mortars tends to decrease with increasing MMA content in the polymer latices at the same P/C ratio and attains its maximum at MMA-70. At the same MMA content, the compressive strength of the polymer-modified mortars tends to increase with an increasing P/C ratio, and it attains its

maximum at a P/C ratio of 10% for latices with MMA-50 and MMA-80 and at a P/C ratio of 15% for latices with MMA-60 and MMA-70.

3. The flexural strength of polymer-modified mortars decreases with increasing MMA content in the polymer latices at the same P/C ratio. At the same MMA content, the flexural strength of the polymer-modified mortars increases with an increasing P/C ratio.
4. Regardless of the P/C ratio, the water absorption of polymer-modified mortars increases with increasing MMA content in the polymer latices. At the same MMA content, the water absorption of the polymer-modified mortars decreases with an increasing P/C ratio.

References

1. Mandel, J. A.; Said, S. *ACI Mater J* 1990, 87, 54.
2. Lavelle, J. A. *ACI Mater J* 1988, 85, 41.
3. Folic, R. J.; Radonjanin, V. S. *ACI Mater J* 1998, 95, 463.
4. Schulze, J. *Cem Concr Res* 1999, 29, 909.
5. Walters, D. G. *ACI Mater J* 1990, 87, 374.
6. Banfill, P. F. G.; Bellagraa, L.; Benaggoun, L. *Adv Cem Res* 1993, 5, 103.
7. Afridi, M. U. K.; Chaudhardy, Z. U.; Ohama, Y.; Demura, K.; Iqbal, M. Z. *Cem Concr Res* 1994, 24, 1199.
8. Ohama, Y.; Ibe, H.; Mine, H.; Kato, K. *Rubber Chem Technol* 1964, 37, 758.
9. Ohama, Y. *Proceedings of the 13th Japan Congress on Materials Research*; Ohama, Y., Ed.; Society of Materials Science: Kyoto, Japan, 1970; p 212.
10. Ohama, Y.; Demura, K.; Hamatsu, M.; Kakegawa, M. *ACI Mater J* 1991, 88, 56.
11. Beeldens, A.; Monteny, J.; Vincke, E.; De Belie, N.; Van Gemert, D.; Taerw, L.; Vestraete, W. *Cem Concr Compos* 2000, 23, 47.