

Properties of Polymer-Modified Mortars Based on Methyl Methacrylic Latexes with Emulsifier Contents and Various Monomer Ratios

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ABSTRACT: This study investigates the effects of the emulsifier content and monomer ratio on the typical properties of the polymer-modified mortars with methyl-methacrylate-butyl-acrylate (MMA/BA) and methyl-methacrylate-ethyl-acrylate (MMA/EA) latexes and obtains basic data necessary to develop appropriate latexes for cement modifiers. The polymer-modified mortars using the MMA/BA and MMA/EA latexes polymerized with emulsifier contents and at various monomer ratios are prepared for different polymer-cement ratios, and tested to obtain the particle size of the polymer latexes, the glass transition temperature of the polymer film, air contents, water-cement ratios, flexural and compressive strengths, water absorption, and chlo-

ride ion penetration. From the test results, the polymer-modified mortars using MMA/BA and MMA/EA latexes with the mix proportions of synthesis having emulsifier contents of 5–6% and monomer ratios of 50 : 50 to 60 : 40 for the appropriate mix proportions can be recommended for practical applications. The basic properties of the polymer-modified mortars are more affected by the polymer-cement ratio rather than the monomer ratio and emulsifier content, and are improved over unmodified mortar. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3010–3018, 2007

Key words: polymer-modified mortars; emulsifier contents; monomer ratios

INTRODUCTION

Polymer-modified mortars have been largely used as paving materials, floorings, waterproofing materials, adhesives, anticorrosive linings, deck coverings, and various other materials.^{1–3} The characteristics of polymer-modified mortar that is mixed with polymer latexes are largely affected by the type and properties of the mixed polymer. Consequently, its application purposes also vary according to these properties. Polymer is classified as either a natural polymer or a chemically synthesized polymer. Chemically synthesized polymers are usually applied in the construction field because the production of natural polymers is limited. The characteristics of chemically synthesized polymer present various differences, according to synthesis methods and mixture conditions, such as the kinds or amount of added monomer, emulsifier, or initiator.^{1,4–7} The purpose of this study was to investigate the effects of various synthetic conditions, such as the kind of monomer [MMA/BA, methyl-methacrylate-butyl acrylate; MMA/EA, methyl-methacrylate-ethyl-acrylate], monomer ratios, and amounts

of the added emulsifier, on the properties of polymer-modified mortars, and to obtain basic data that can be used in the development of appropriate polymers for cement modifiers.

In this article, the polymer-modified mortars using MMA/BA and MMA/EA latexes polymerized with emulsifier contents and at various monomer ratios are prepared for various polymer-cement ratios, and tested to obtain the particle size of polymer latexes, the glass transition temperature of polymer film, air contents, strengths, water absorption, and chloride ion penetration. From the test results, the effects of the type of monomer, monomer ratio, amount of emulsifier, and polymer-cement ratio on the properties of polymer-modified mortars are discussed.

EXPERIMENTAL

Emulsion polymerization of MMA/BA and MMA/EA

Two kinds of polymer latexes were synthesized by emulsion polymerization using different monomers of MMA : BA and MMA : EA. The ratios of the MMA : BA monomer selected were 60 : 40, 70 : 30, and 80 : 20. The ratios of the MMA : EA were 50 : 50, 60 : 40, and 70 : 30. The addition ratios of the emulsifier were applied with the ratios of 5 and 6% for the entire amount of monomer. First, the reactor was charged with the desired

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TABLE I
Mix Proportions of Synthesis

Type of polymer	Monomer ratio (MMA/BA,EA), by weight	Initiators/monomer (%)	Emulsifiers/monomer (%)	Solid content (%)
MB5	50 : 50	0.7	5 and 6	48
MB6	60 : 40	0.7	5 and 6	48
MB7	70 : 30	0.7	5 and 6	48
MB8	80 : 20	0.7	5 and 6	48
ME4	40 : 60	0.7	5 and 6	48
ME5	50 : 50	0.7	5 and 6	48
ME6	60 : 40	0.7	5 and 6	48
ME7	70 : 30	0.7	5 and 6	48

amounts of monomer, emulsifier, deionized and distilled water, and small portion of the deionized and distilled water was set 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 nitrogen gas and stored in a dropping funnel, into the reaction mixture for 12–24 h. In all experiments, reaction temperature was kept within 80°C. The mix proportion of synthesis and basic properties of synthesized polymer are shown in Tables I and II.

Materials and mix proportions

An ordinary Portland cement specified in KS (Korea Standard)-L5201 was used in all the mixes. Siliceous sand (sizes, 0.25–0.6 mm) specified in KS-L5100 was used as the fine aggregate. The mortar mix proportions used in this investigation were as follows: a cement–sand ratio of 1 : 3 (by weight); polymer–cement ratios of 0, 5, 10, 15, and 20% (calculated on the basis of the total amount of solids of emulsions). The degree of flow for the mortars was maintained within 170 ± 5 mm by controlling the water–cement ratio. Antifoaming agent (0.7%) was added for prevention of air entrainment.

Experimental methods

The particles of polymer latexes were measured by using the microtac ultrafine particle analyzer and the glass transition temperature (T_g) was tested by differential scanning calorimetry (DSC). Mortars were mixed according to KS-F2476 (making method of test sample of polymer-modified mortar in the laboratory), with the mix proportions given in Table III, and their flows were adjusted to be constant at 170 ± 5 mm. Mortar beam specimens ($40 \times 40 \times 160$ mm³) were molded, and then subjected to a 2-day exposure to moisture at 20°C and 80% relative humidity, 5-day immersion in water at 20°C, and a 21-day curing at 20°C, and 50% relative dry humidity. The degree of flow and the air content were tested according to KS-L5105 and KS-F2409 respectively. The flexural and compressive strengths were tested according to KS-F2477, and water absorption was tested according to JIS-A6203. The chloride ion penetration depth was tested according to JCI.

RESULTS AND DISCUSSION

Particle size distribution and glass transition temperature of MMA/BA and MMA/EA latexes

Figure 1 shows the distribution of the particle size of MMA/BA polymer latexes. The average size and the

TABLE II
Properties of Synthetic Polymer Latexes

Type of polymer	Monomer ratio (MMA/BA,EA), by weight	Amount of emulsifier (%)	Specific gravity (20 °C)	pH (20 °C)	Total solids (%)
5MB5	50 : 50	5	1.03	7.0	40
5MB6	60 : 40	5	1.03	7.0	40
5MB7	70 : 30	5	1.03	7.0	40
5MB8	80 : 20	5	1.03	7.0	40
6MB7	70 : 30	6	1.03	7.0	50
6MB8	80 : 20	6	1.03	7.0	50
5ME4	40 : 60	5	1.03	7.0	48
5ME5	50 : 50	5	1.03	7.0	48
5ME6	60 : 40	5	1.03	7.0	48
6ME5	50 : 50	6	1.03	7.0	50
6ME6	60 : 40	6	1.03	7.0	58
6ME7	70 : 30	6	1.03	7.0	50

TABLE III
Mix Proportions of Polymer-Modified Mortars

Type of mortar	Cement : sand	Emulsifier content (%)	P/C (%)	W/C (%)	Air content (%)	Flow (mm)
Un-modified	1 : 3	–	0	67	3.6	167
5MB5-modified	1 : 3	5	5	54	13.2	167
			10	49	11.5	167
			15	45	9.2	171
			20	41	8.1	175
5MB6-modified			5	57	11.7	172
			10	53	10.1	173
			15	49	8.7	169
			20	46	7.2	171
5MB7-modified			5	58	10.2	165
			10	55	8.2	171
			15	52	6.9	168
			20	48	6.1	166
5MB8-modified			5	62	14.8	180
			10	57	13.8	173
			15	54	11.9	169
			20	53	12.0	172
6MB7-modified	1 : 3	6	5	55	13.7	167
			10	52	11.9	166
			15	49	11.5	168
			20	46	11.2	166
6MB8-modified			5	55	11.2	171
			10	52	8.7	166
			15	50	8.1	166
			20	47	7.8	165
5ME4-modified	1 : 3	5	5	58	15.2	172
			10	52	14.1	168
			15	49	10.8	170
			20	46	9.3	166
5ME5-modified			5	56	14.1	165
			10	51	12.8	169
			15	45	10.1	174
			20	42	8.0	171
5ME6-modified			5	53	13.8	173
			10	48	11.2	171
			15	43	9.0	166
			20	40	7.9	176
6ME5-modified	1 : 3	6	5	53	12.6	165
			10	48	12.2	175
			15	43	11.7	173
			20	40	11.1	170
6ME6-modified			5	52	15.9	170
			10	47	14.8	171
			15	43	13.7	178
			20	40	12.4	169
6ME7-modified			5	51	15.4	180
			10	48	13.8	168
			15	43	14.8	166
			20	42	16.9	168

distribution range of polymer particles of the MMA/BA polymer latexes increase with the increase in the bound MMA contents. Among the MMA/BA polymer latexes, the MB6 polymer latex has the smallest particle size. The average particle size and distribution range of the MB6 polymer latex are 0.17 and 0.85 μm respectively.

Figure 2 shows the distribution of the particle size of MMA/EA polymer latexes. The average particle

size of polymer particles of the MMA/EA polymer latexes decreases with the increase in the bound MMA contents. However, the distribution range of the particle size is almost the same regardless of the bound MMA contents. Among the MMA/EA polymer latexes, the MB7 polymer latex has the smallest particle size and distribution. The average particle size and range of the ME7 polymer latex are 0.23 and 1.01 μm respectively. The average size and the distri-

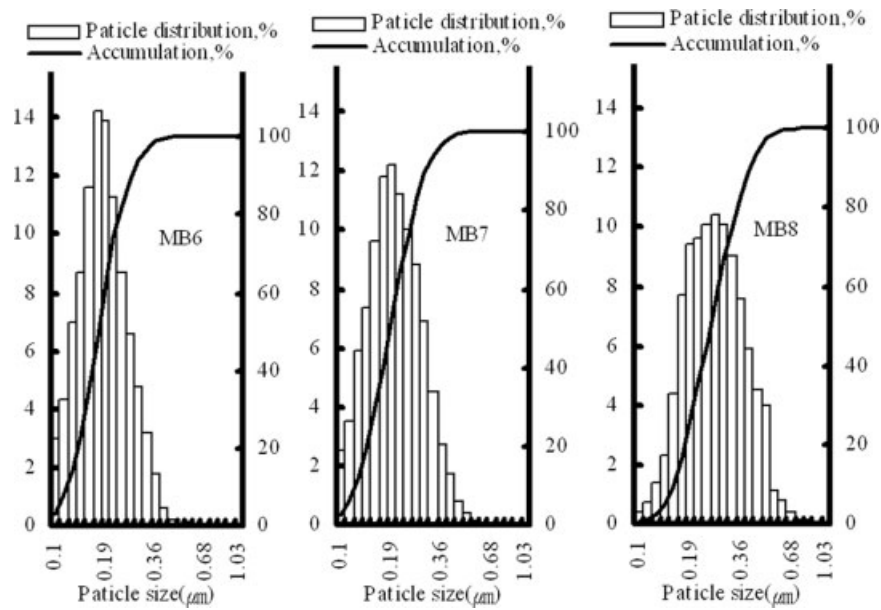


Figure 1 Particle size distributions of the MMA/BA polymer latexes.

bution range of polymer particles of the MMA/BA polymer latexes are fairly smaller than those of MMA/EA polymer latexes at respective bound MMA contents.

T_g is a temperature or temperature range in which polymeric materials change from a rigid, glasslike state to an elastomeric-like state. At this temperature, the behavior of the polymeric materials changes and they become softer, more workable, and exhibit plastic flow in the case of thermoplastics and a rubberlike behavior in the case of elastomeric polymers. In the case of amorphous polymers, the statistic structures from the fluid phase are frozen to form a glasslike structure. This thermodynamic unstable structure is

formed at temperatures lower than T_g because of their very slow and limited molecular rearrangements during cooling of the fluid. In this zone, high elasticity modulus is obtained and the material becomes rigid and hard. Therefore, T_g is a very important factor of the strength of polymer-modified mortar.^{8,9}

Figure 3 shows the glass transition temperature of a polymer film of MMA/BA and MMA/EA polymer latexes. The glass transition temperature increases remarkably with the increase in the bound MMA content regardless of the monomer types, and shows a slightly higher value when the emulsifier content is 6% than when it is 5% at the respective bound MMA contents. By contrast, the T_g of the MMA/EA polymer is

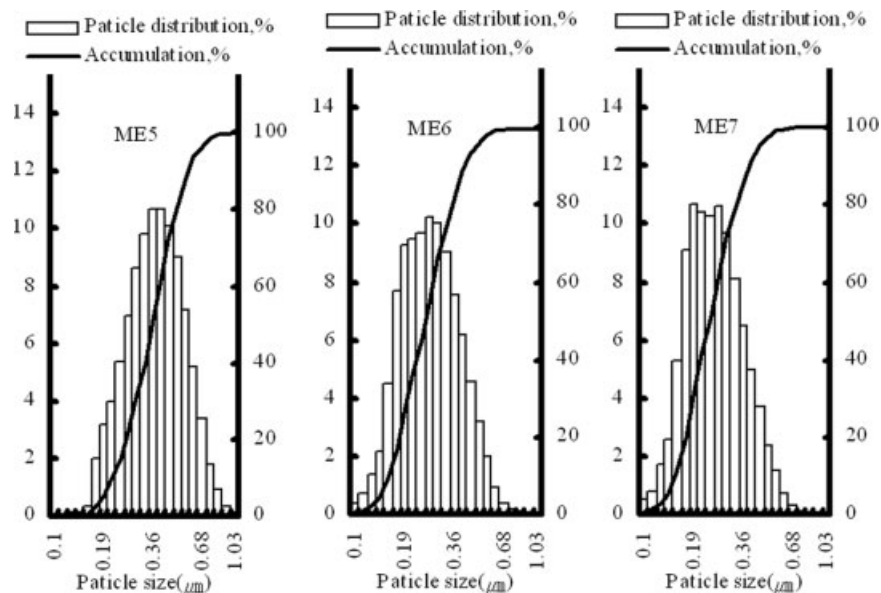


Figure 2 Particle size distributions of the MMA/EA polymer latexes.

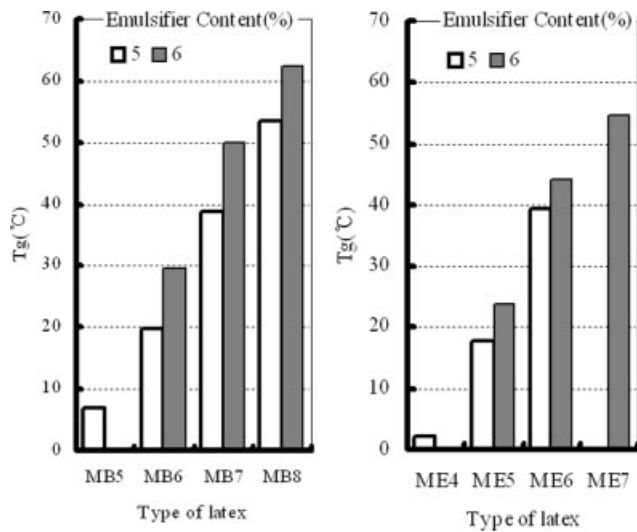


Figure 3 Glass transition temperatures of the polymer film.

slightly higher than that of the MMA/BA polymer film. These results reveal that the property of increasing hardness with increasing glass transition temperature affects the strength of polymer films significantly.^{8,10}

Properties of the fresh polymer-modified mortars using MMA/BA and MMA/EA latexes

Figure 4 represents the water–cement ratios of polymer-modified mortars using MMA/BA and MMA/EA latexes. The water–cement ratio of MMA/BA- and MMA/EA-modified mortars decreases markedly with increasing polymer–cement ratio, monomer ratio, and emulsifier content. This decrease is mainly interpreted in terms of improved consistency due to

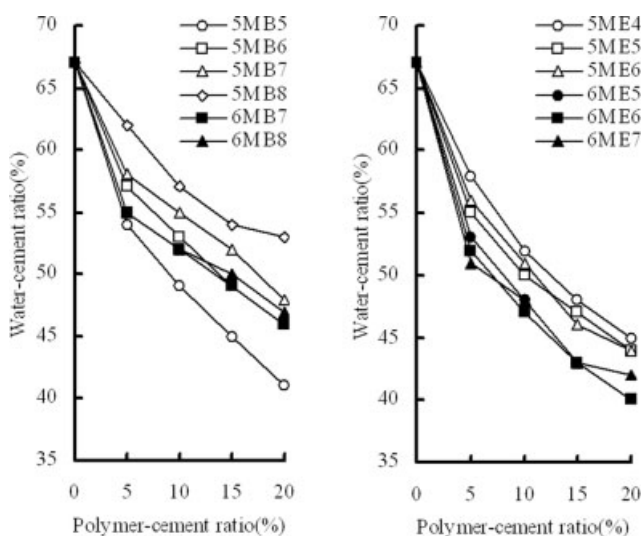


Figure 4 Polymer–cement ratio versus water–cement ratio of the MMA/BA- and MMA/EA-modified mortar.

the ball bearing action of polymer particles and entrained air and the dispersion effect of surfactants in the latexes. The reduction of the water–cement ratios of the MMA/BA-modified mortars tends to decrease according to the increase in the emulsifier content rather than the variation of monomer ratios. The water–cement ratios of MMA/BA-modified mortars with emulsifier content of 5% decrease considerably with the increase in the bound MMA content. And, it is considered that the improvement of the flowability of the 5MB5-modified mortars is due to the large content of butyl acrylate having high ductility, comparatively. On the other hand, in the MB5- and MB6-modified mortars with an emulsifier content of 6%, it is impossible to make a specimen because it is difficult to mix the mortars.

Figure 5 represents the air content of polymer-modified mortars using MMA/BA and MMA/EA latexes. In general, the air content of the MMA/BA- and MMA/EA-modified mortars decreases with the increase in the polymer–cement ratio regardless of the monomer ratios and the emulsifier contents. The air content of the MMA/BA- and MMA/EA-modified mortars with emulsifier content of 5% is slightly reduced than that of the polymer-modified mortars with emulsifier content of 6% at the respective bound of MMA contents. On the other hand, most MMA/BA- and MMA/EA-modified mortars represent a considerably larger air content than does the unmodified mortar because of air entrainment. In this study, the air content of the MMA/BA-modified mortars ranges from 6 to 15%, and that of the MMA/EA-modified mortars from 8 to 17%. Emulsifiers of 5 and 6% should not be used for the monomer ratios of 70 : 30 and 40 : 60, respectively, because of the coagulation of the mixture, as polymer for cement modifiers.

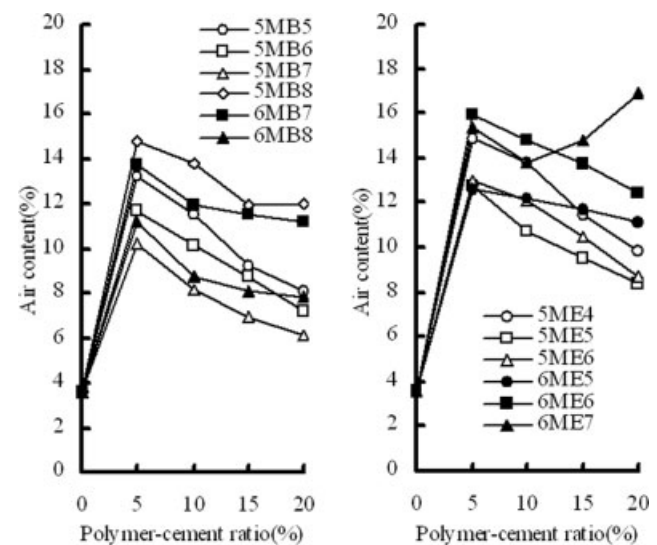


Figure 5 Polymer–cement ratio versus air content of the MMA/BA- and MMA/EA-modified mortar.

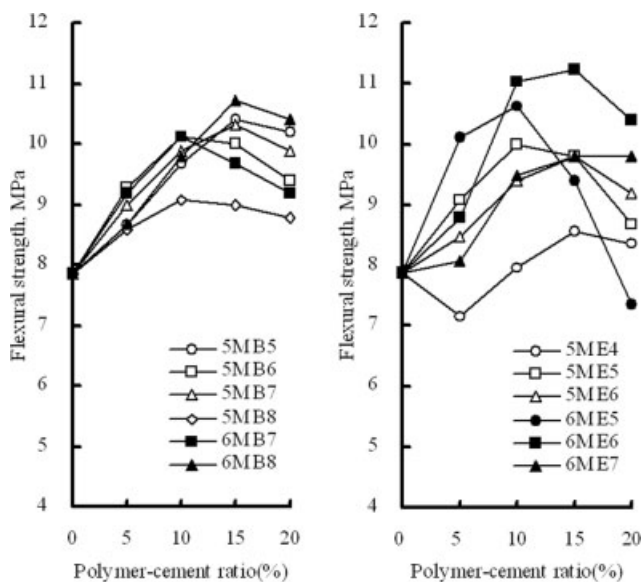


Figure 6 Polymer–cement ratio versus flexural strength of the MMA/BA- and MMA/EA-modified mortar.

Strength properties of polymer-modified mortars using MMA/BA and MMA/EA latexes

Figure 6 represents the flexural strength of polymer-modified mortars using MMA/BA and MMA/EA latexes. Except for the 5ME4-modified mortars, the flexural strength of the polymer-modified mortars is generally higher than that of the unmodified mortar. The flexural strength increases sharply at polymer–cement ratios up to 10%, and reaches the maximum at polymer–cement ratios of 10–15%. Generally, the flexural strength of the MMA/BA-modified mortars is similar to that of the MMA/EA-modified mortars. There is little difference in the flexural strength among the MMA/BA-modified mortars according to emulsifier content and monomer ratio, but there is noticeable difference among MMA/EA-modified mortars. The flexural strength of the MMA/BA- and MMA/EA-modified mortars with emulsifier content of 5% is slightly reduced than that of the polymer-modified mortars with emulsifier content of 6% at the respective bound MMA contents. The highest flexural strength of the MMA/BA- and MMA/EA-modified mortars are achieved by the 6MB8- and 6ME6-modified mortars, respectively. The flexural strength of the 6ME5-modified mortars is markedly decreased at polymer cement ratios of 15 and 20%. It is judged that a continuous polymer film is not properly formed with increasing polymer–cement ratio because of incomplete synthesis.

Figure 7 represents the compressive strength of polymer-modified mortars using MMA/BA and MMA/EA latexes. Except for the 5MB8-, 5ME4-, and 6ME5-modified mortars, the compressive strength of the MMA/BA- and MMA/EA-modified mortars are generally

higher than that of the unmodified mortar. The flexural strength increases sharply at polymer–cement ratios up to 20%, becomes constant, or reaches the maximum at polymer–cement ratios of 10–20%. The compressive strength of the MMA/BA-modified mortars is higher than that of the MMA/EA-modified mortars. There is no specific trend in the compressive strength of the MMA/BA-modified mortars according to the emulsifier contents and the monomer ratios. The highest compressive strengths of the MMA/BA- and MMA/EA-modified mortars are achieved in the 5MB7- and 6ME6-modified mortars, respectively. The compressive strengths of the 5MB8- and 6ME5-modified mortars are markedly decreased at polymer cement ratios of 15 and 20%. Like the flexural strength of the MMA/BA- and MMA/EA-modified mortars, a continuous polymer film is not properly formed with increasing polymer–cement ratio because of incomplete synthesis. Moreover, it is considered that an increase in the compressive strength according to the increase in the MMA content affects the compressive strength because of the high glass transition temperature of the MMA, which increased the hardness when a film is formed under a normal temperature.^{8,10}

Water absorption and chloride ion penetration of the polymer-modified mortars using MMA/BA and MMA/EA latexes

Figure 8 shows the 48-h water absorption of the polymer-modified mortars using MMA/BA and MMA/EA latexes. The water absorption of the MMA/BA- and MMA/EA-modified mortars is less than that of the unmodified mortar, and tends to decrease considerably with increasing polymer–cement ratio rather than with increasing monomer ratio and emulsifier content. This

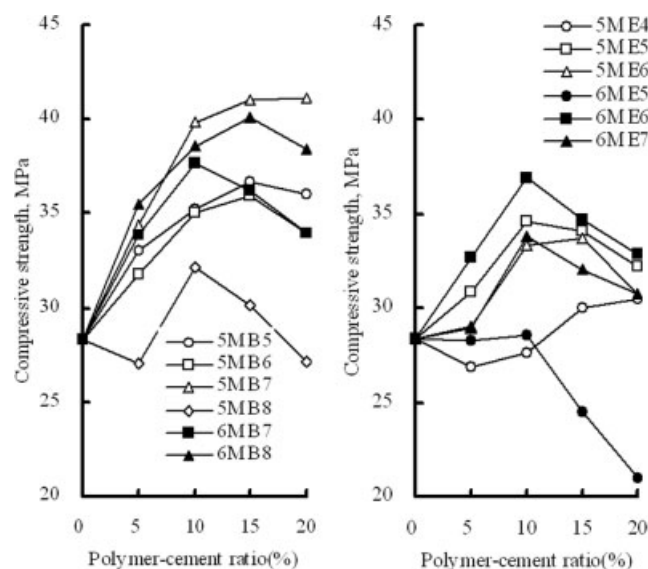


Figure 7 Polymer–cement ratio versus compressive strength of the MMA/BA- and MMA/EA-modified mortar.

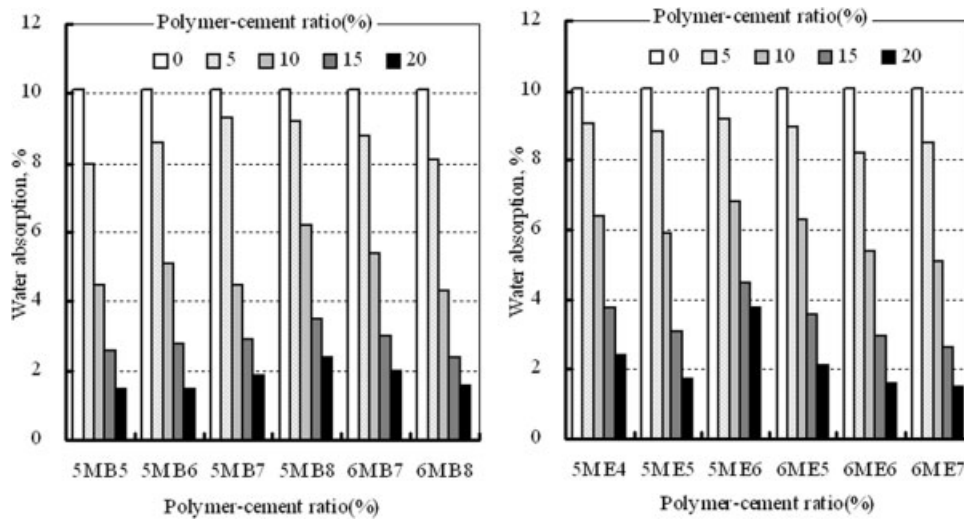


Figure 8 Polymer-cement ratio versus water absorption of the MMA/BA- and MMA/EA-modified mortar.

trend reveals that the water absorption of polymer-modified mortar is generally affected by the polymer-cement ratio.¹¹ The water absorption of the MMA/BA-modified mortars is slightly less than that of the MMA/EA-modified mortars at respective bound MMA contents. MMA/BA- and MMA/EA-modified mortars are completely waterproof in the 6MB8 and 6ME7-modified mortars, respectively.

Figure 9 exhibits the chloride ion penetration depth of the polymer-modified mortars using MMA/BA and MMA/EA latexes. The chloride ion penetration depth of the MMA/BA- and MMA/EA-modified mortars is less than that of the unmodified mortar, and tends to decrease with increasing value of the polymer-cement ratio.

The chloride ion penetration depth of the MMA/BA-modified mortars is slightly less than that of the MMA/EA-modified mortars at respective bound MMA contents. This tendency is linked with the re-

sults of the above-mentioned water absorption. The MMA/BA-modified mortars present the highest chloride ion penetration depth of the 5MB8-modified mortars, which have low water-cement ratio, air content, and strength. However, resistance to the chloride ion penetration is generally improved. In particular, resistance is improved by an exceptional 8–1.6 times at the maximum and minimum levels, relatively, compared with that in unmodified mortar. In addition, the resistance varies greatly with the polymer-cement ratio, rather than with the addition of emulsifier content or monomer ratio, similar to the case of the water absorption. The MMA/EA-modified mortar shows a large difference of the polymer-cement ratio, rather than with the effects of the bound MMA content and emulsifier content. The 6ME5-modified mortars, which show similar negative results as do the MMA/BA-modified mortars, pre-

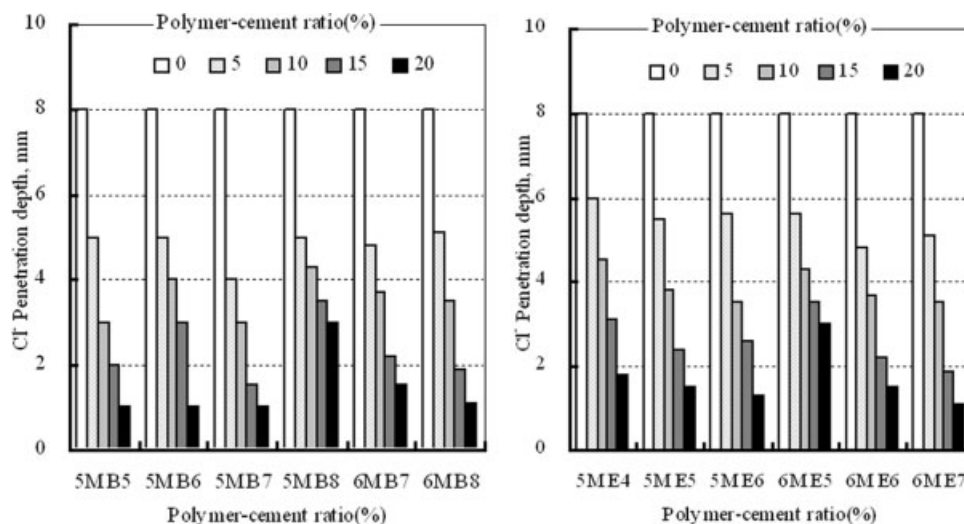


Figure 9 Polymer-cement ratio versus chloride ion penetration depth of the MMA/BA- and MMA/EA-modified mortar.

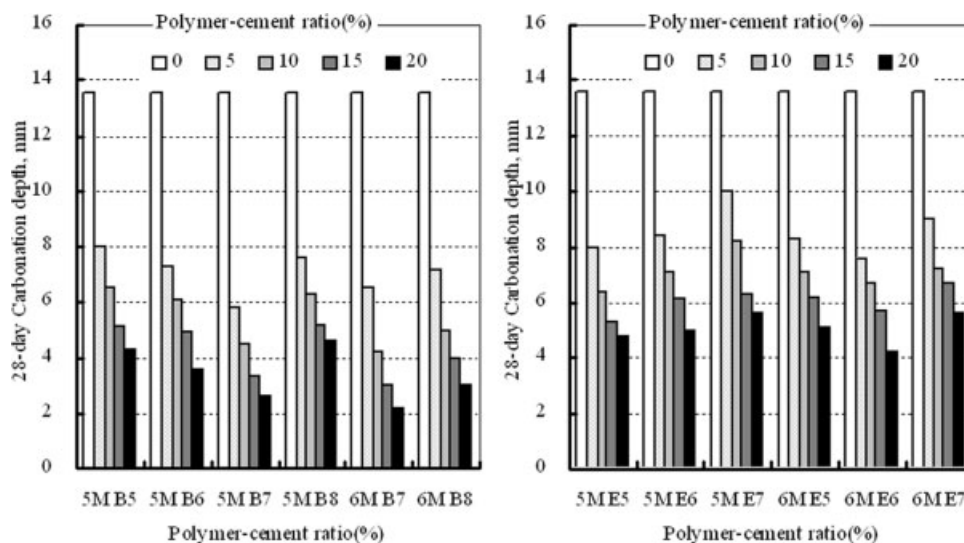


Figure 10 Polymer–cement ratio versus carbonation depth of the MMA/BA- and MMA/EA-modified mortar.

sented the lowest chloride ion penetration rate for the polymer–cement ratios of 15 and 20%. This reveals that the resistance to the chloride ion penetration rate in the polymer-modified mortar is largely affected by the polymer–cement ratio.

Carbonation of the polymer-modified mortars using MMA/BA and MMA/EA latexes

Figure 10 presents the carbonation depth of the polymer-modified mortars using MMA/BA and MMA/EA latexes. The carbonation depth of the polymer-modified mortars using MMA/BA and MMA/EA latexes is smaller than that of the unmodified mortar, and tends to decrease with increasing polymer–cement ratio and bound MMA content. Like the characteristics of waterproof and resistance to the chloride ion penetration, resistance to carbonation of polymer-modified mortars using MMA/BA and MMA/EA latexes varies greatly with the polymer–cement ratio rather than with the addition of an emulsifier content. It tends to behave similarly to water absorption and chloride ion penetration of polymer-modified mortars using MMA/BA and MMA/EA latexes.

CONCLUSIONS

The conclusions obtained from the test results of polymer-modified mortars using two synthetic polymer latexes are summarized as follows:

1. The water–cement ratio of MMA/BA- and MMA/EA-modified mortars were markedly reduced with increasing polymer–cement ratio, monomer ratio, and emulsifier content, and this reduction was mainly interpreted in terms of improved con-

sistency due to the ball bearing action of polymer particles and entrained air and the dispersion effect of surfactants in the latexes.

2. In general, the MMA/BA- and MMA/EA-modified mortars represent a considerably larger air content than does the unmodified mortar because of the air entrainment. The air content of the MMA/BA-modified mortars ranges from 6 to 15%, and that of the MMA/EA-modified mortars from 8 to 17%.
3. The flexural and compressive strengths of MMA/BA- and MMA/EA-modified mortars were generally higher than those of the unmodified mortar, and the extent of the strength improvement was higher in the MMA/BA-modified mortars than in the MMA/EA-modified mortars.
4. The water absorption, chloride ion penetration, and carbonation of polymer-modified mortars were greatly affected by the polymer–cement ratio than by the monomer ratio and emulsifier content, and were higher than those of the unmodified mortar.
5. In this study, the polymer-modified mortars using MMA/BA and MMA/EA latexes presented large differences in the workability, depending on the emulsifier content. This difference affected the properties of the polymer-modified mortars depending on the monomer ratio.
6. Consequently, it is concluded that MMA/BA- and MMA/EA-modified mortars can be used in the same manner as ordinary polymer-dispersion-modified mortars in practical applications.

References

1. Ohama, Y.; Demura, K.; Hamatsu, M.; Kakegawa, M. *ACI Mater J* 1991, 88, 56.

2. ACI Committee 548. Guide for the Use of Polymers in Concrete; American Concrete Institute: Detroit, 1992.
3. Ohama, Y. Handbook of Polymer-Modified Concrete and Mortar: Properties and Process Technology; Noyes Publications: New Jersey, USA, 1995.
4. Pei, M.; Kim, W.; Hyung, W.; Ango, A. J.; Soh, Y. Cement Concr Res 2002, 32, 837.
5. Ohama, Y. Study on properties and mix proportioning of polymer-modified mortars for building, Report No. 65. The Building Research Institute: Tsukuba, Japan, 1973; pp 74, 100–104, (in Japanese).
6. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953; Chapter 1.
7. Concrete Society. Polymer Concrete; London, 1987; pp 119.
8. Karasz, F. J Macromol Sci Rev Macromol Chem Phys 1979, 17, 37.
9. Zhao, S. Doctoral thesis, Delft University of Technology: The Netherlands, 1995, p 174.
10. Allcock, H. R.; Lampe, F. W. Contemporary Polymer Chemistry; Prentice Hall: New Jersey, 1992; p 425.