

MMA계 라텍스를 혼입한 폴리머 시멘트 모르타르의 인장강도 및 부착강도

형원길[†] · 이찬태 · 박성무

영남대학교 건축학부

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Tensile Strength and Tensile Adhesive Strengths of Polymer-Modified Mortar with Methyl Methacrylate-Based Latexes

Wongil Hyung[†], Chantae Lee, and Sungmoo Park

School of Architecture, Yeungnam University,

Gyeongsan City, Gyeongbuk 712–749, Korea

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초록: 본 연구에서는 시멘트 복합체의 단점을 보완하기 위해 유기화합물인 폴리머를 시멘트 모르타르에 혼입하여 폴리머 시멘트 모르타르를 제작하고 이에 대한 인장력과 부착특성을 개선시키고자 하였다. 또한, 폴리머 시멘트 모르타르 내에서 형성되는 폴리머 필름의 인장강도와 유리전이온도가 폴리머 시멘트 모르타르의 인장강도와 부착특성에 미치는 영향을 파악하였다. 본 연구 결과 폴리머 시멘트 모르타르는 보통 시멘트 모르타르에 비해 인장강도의 경우 최대 2배 정도 증진효과를 나타내고 있었으며 부착특성에 있어서도 약 4배 정도의 증진효과가 나타났다.

Abstract: This paper investigates the effects of the monomer ratios on the typical properties of polymer-modified mortars that contain methyl methacrylate-based latexes. Basic data are also obtained to develop appropriate latexes for cement modifiers. Polymer-modified mortars that contain methyl methacrylate latexes copolymerized with butyl acrylate or ethyl acrylate are prepared for different polymer-cement ratios. They are then tested to obtain the tensile and tensile adhesive strengthes of polymer-modified mortar with methyl methacrylate-based latexes. From the test results, the tensile strength of MB7 polymer-modified mortar was higher than normal cement mortar by a maximum of 94% with a 20% polymer-cement ratio, which was almost twice higher than normal. The tensile adhesive strength of the MB polymer-modified mortar was higher for higher MMA monomer contents and polymer-cement ratios, and increased up to four times than that of normal cement mortar. The basic properties of the polymer-modified mortars are more affected by the polymer-cement ratio than by the monomer ratio, and are improved over unmodified mortar.

Keywords: polymer-modified mortar, tensile strength, tensile adhesive strength.

Introduction

Polymer-modified mortar or concrete is effective in improving tensile strength, flexural strength, tensile adhesive strength, chemical resistance, and density. It is being re-searched for diverse applications since it is not only a more durable and stable structural material but it also supplements the disadvantages of the existing cement concrete.¹

The reinforcement of polymer-modified mortar can be explained by the formation of a co-matrix phase wherein the hydration product and the polymer film are unified. The hydration reaction occurs in the polymer-modified mortar

after it is mixed, and thus, the polymer film fills the spaces between its surfaces and in minute cracks, as well as the spaces between the cement and its aggregates. The polymer film is improved in terms of durability since spaces are densely formed in the mortar and because it has a high tensile strength and a high tensile adhesive strength compared with normal cement mortar. The tensile strength or tensile adhesive strength of polymer-modified mortar varies according to the type of polymer, but it usually increases as the polymer-cement ratio increases.²⁻⁴

In this study, MMA (methyl methacrylate) with BA (butyl acrylate) and MMA with EA (ethyl acrylate) were used as monomers for polymerization, and polymer-modified mortar was manufactured with synthesized polymer to measure

[†]To whom correspondence should be addressed.

E-mail: endue@ynu.ac.kr

Table 1. Mix Proportion of Polymerization Using MMA/BA and MMA/EA Monomers

Type of polymer	Monomer ratio (MMA:BA or EA), by weight	MAA (%)	Initiator/Monomer (%)		Emulsifier/Monomer (%)		Expected solid content (%)
			KPS	NaHCO ₃	TX100	SDS	
MB6	60:40	2.0	0.3	0.4	3.0	3.0	50
MB7	70:30	2.0	0.3	0.4	3.0	3.0	50
MB8	80:20	2.0	0.3	0.4	3.0	3.0	50
ME5	50:50	2.0	0.3	0.4	3.0	3.0	50
ME6	60:40	2.0	0.3	0.4	3.0	3.0	50
ME7	70:30	2.0	0.3	0.4	3.0	3.0	50

MAA=Methylacrylate acid. KPS=Potassium persulfate. TX-100=Octoxynol(made by Aldrich). SDS=Sodium dodecylbenzenesulfonate.

Table 2. Properties of Polymer Dispersions for Cement Modifier

Type of polymer	Monomer ratio (MMA/BA or EA), by weight	Viscosity (20 °C, Mp · s)	Density (20 °C)	pH (20 °C)	Total solids (%)
MB6	60 : 40	2354	1.03	7.0	50.4
MB7	70 : 30	1080	1.03	6.5	49.8
MB8	80 : 20	838	1.03	6.5	50.1
ME5	50 : 50	2134	1.03	6.5	50.2
ME6	60 : 40	1167	1.03	7.0	57.9
ME7	70 : 30	357	1.03	7.0	50.0

its tensile strength and its tensile adhesive strength according to the monomer mixing ratio and the polymer-cement ratio. In addition, to determine the effect of the polymer film formed in the polymer cement mortar, the glass transition temperature and the tensile strength of the polymer film were measured to find out the correlation between the polymer-modified mortar and the tensile adhesive strength.

Experimental

Emulsion Polymerization of MMA Latexes. The copolymer latexes were synthesized by emulsion polymerization using two monomer combinations of MMA and BA or MMA and EA. Weight ratios of MMA:BA monomers were selected 60:40, 70:30, and 80:20. Those of MMA:EA monomers were 50:50, 60:40, and 70:30. At first the reactor was charged with the desired amounts of monomer, emulsifier, de-ionized and distilled water. A small portion of the de-ionized and distilled water was put aside for preparing an initiator solution. Dissolved oxygen was removed by bubbling nitrogen gas through the reaction mixture. The process of polymerization began by pouring the initiator solution; which had been de-oxygenated with nitrogen gas and stored in a dropping funnel, into the reaction mixture for 12 to 24 hrs. In all experiments, reaction temperature was kept at 80 °C. The polymerization conditions for MMA-BA and MMA-EA copolymers and the basic properties of synthetic polymer dispersions for cement modifier are represented in Tables 1 and 2, respectively.

Table 3. Chemical Compositions of Ordinary Portland Cement (unit: wt%)

SiO ₂	Al ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Fe ₂ O ₃
21.09	4.84	63.85	3.32	3.09	1.13	0.29	2.39

Table 4. Physical Properties of Ordinary Portland Cement

Specific gravity (20 °C)	Blainess specific surface (cm ² /g)	Setting time		Compressive strength of mortar (kgf/cm ²)		
		Initial set (min)	Final set (h)	3days	7days	28days
3.15	3300	240	7:00	196	228	378

Table 5. The Properties of Fine Aggregate

Max. size (mm)	Unit weight (kg/L)	Specific gravity (20 °C)	Water absorption (%)	Solid volume percentage (%)
<1.2	1.5	2.62	0.40	58.1

Materials and Mix Proportions. An ordinary Portland cement specified in KS L 5201 standard was used in all the mixtures. Siliceous sand (sizes: 0.25~0.6 mm), as specified in KS L 5100 standard, was prepared as fine aggregate. Table 3 and Table 4 represent the chemical and physical properties of ordinary portland cement and Table 5 represents the properties of fine aggregate. The mortar compositions used in this investigation were given as follows: a cement-sand ratio of 1 : 3 (by weight); and polymer-cement ratios of 0, 5, 10, 15, and 20% (calculated on the basis of the total solids of emulsions). The degrees of flow for the mortars were maintained at 170±5 mm by controlling the water-cement ratio.

Table 6. Mix Proportions of Polymer-Modified Mortars

Type of mortar	Cement : Sand	P/C (%)	W/C (%)	Air content (%)	Flow (mm)
Unmodified	1 : 3	0	67	3.6	167
MB6* -modified	1 : 3	5	53	9.6	173
		10	48	8.4	170
		15	43	7.0	170
MB7 -modified	1 : 3	20	40	6.0	170
		5	55	13.7	167
		10	52	11.9	166
MB8 -modified	1 : 3	15	49	11.5	168
		20	46	11.2	166
		5	55	11.2	171
ME5 -modified	1 : 3	10	52	8.7	166
		15	50	8.1	166
		20	47	7.8	165
ME6 -modified	1 : 3	5	53	12.6	165
		10	48	12.2	175
		15	43	11.7	173
ME7 -modified	1 : 3	20	40	11.1	170
		5	52	15.9	170
		10	47	14.8	171
ME8 -modified	1 : 3	15	43	13.7	178
		20	40	12.4	169
		5	51	15.4	180
ME9 -modified	1 : 3	10	48	13.8	168
		15	43	13.5	166
		20	42	12.7	168

*MMA : BA=60:40.

An antifoaming agent was added at a proportion of 0.7% in order to prevent air entrainment. Table 6 represents the compositions of copolymer-modified mortars.

Tensile Strength of the Polymer Film. To measure the tensile strength of the polymer film, a specimen was manufactured by drying polymer latex in a drying furnace at 40 °C for 48 hrs, and tests were performed according to KS F 2241 (Tensile Strength Test Method for Glass-fiber-reinforced Plastic).

Glass Transition Temperature. The glass transition temperatures (T_g) of copolymers were measured by differential scanning calorimetry (DSC).

Tensile Strength of Polymer-modified Mortar. The tensile strength of the polymer-modified mortar was measured with a test piece shown in Figure 1, according to KS L 5104 (Tensile Strength Test Method for Cement Mortar).

Tensile Adhesive Strength of Polymer-modified Mortar. The tensile adhesive strength of the polymer-modified mortar was measured after the adherend was attached, as shown in Figure 2, according to KS F 4716 (Cement Floor Coating Material). The curing condition for the adhesion test was

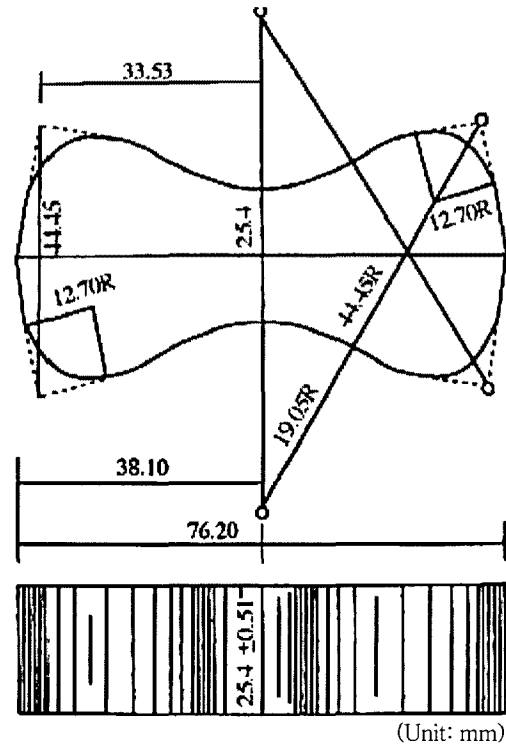


Figure 1. Mortar specimen for the tensile strength test.

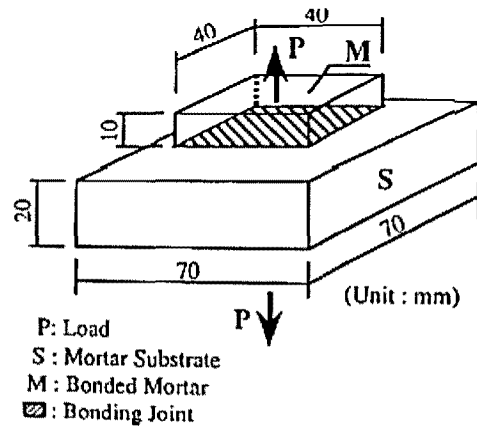


Figure 2. Mortar specimen for the tensile adhesive strength test.

identical to that for the curing of the polymer-modified mortar.

Results and Discussion

Tensile Strength of the Polymer Film. Figure 3 shows the tensile strength of the polymer film. The tensile strength decreased with the increase of the elongation of the polymer.

Glass Transition Temperature. It is known that the glass transition temperature has an effect on the strength of polymer cement mortar. That is, a high glass transition temperature leads to a high strength.⁵

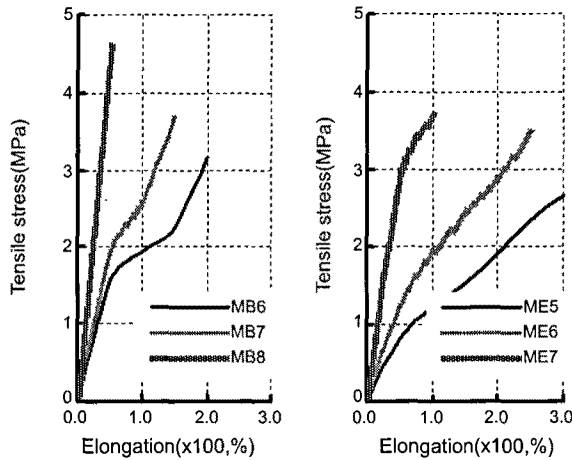


Figure 3. Tensile stress of polymer film.

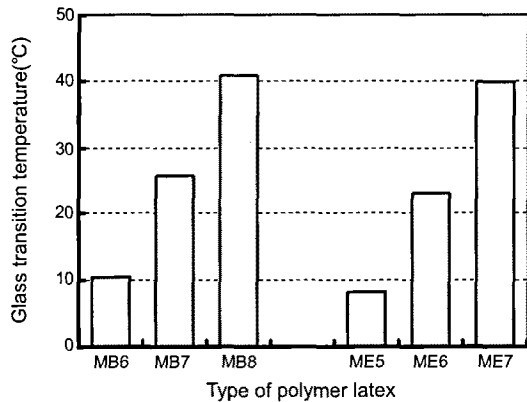


Figure 4. Glass transition temperature of polymer film.

Figure 4 shows the glass transition temperature of the copolymer film. The glass transition temperature was higher than the room temperature when both the monomer ratio of MMA:BA was 80:20 and the monomer ratio of MMA:EA was 70:30. These copolymers showed that a solid-state film with a low elongation and a high tensile strength was formed when the latex was dried. It was found that both the elongation and the tensile strength of the polymer film had a high correlation with the glass transition temperature. That is, a high glass transition temperature led to a low elongation and a high tensile strength. The compressive strength of the copolymer-modified mortar was not significantly improved due to the soft copolymer film, but an improvement in strength was expected with the copolymer with a high glass transition temperature.

Correlation between the Glass Transition Temperature and the Tensile Strength of the Polymer Film. The tensile strength of the polymer film is usually inversely proportional to the elongation. That is, a high elongation leads to high film ductility, and a high tensile strength leads to high film rigidity.⁵ Besides, a high tensile strength and a high glass transition temperature

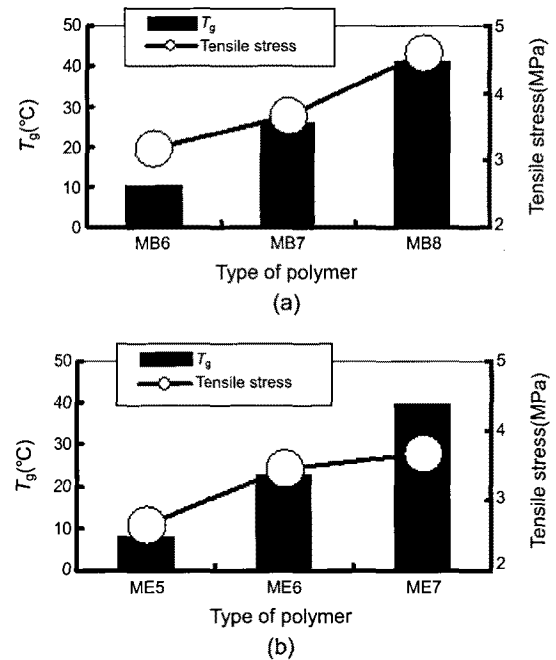


Figure 5. Glass transition temperature versus tensile stress of polymer film: (a) MMA-BA copolymer-modified mortar; (b) MMA-EA copolymer-modified mortar.

with respect to the polymer film leads to high film rigidity. The film formed in the polymer-modified mortar influences the strength improvement with its own strength.

Figure 5 shows the correlation between the glass transition temperature and the tensile strength of the polymer film, as seen in this study. The tensile strength of the polymer film increased as the glass transition temperature increased, whereas the elongation was inversely proportional to the tensile strength. The tensile strength was higher in the MMA-BA film than in the MMA-EA film. The tensile strength of the polymer film was higher for higher glass transition temperature. It was especially high for the glass transition temperature that was higher than the normal temperature, wherein the film was formed in a highly rigid glass phase instead of in a rubber phase. Also in this study, the tensile strength of the film was high when the glass transition temperature was high.

Tensile Strength of Polymer-modified Mortar. Figure 6 shows the tensile strength of the copolymer-modified mortar. The tensile strength increased as the polymer-cement ratio increased, and the tensile strength of the MMA-BA (MB) copolymer-modified mortar was highest, as in the cases with flexural strength and compressive strength. The tensile strength of the MMA-BA polymer-modified mortar greatly improved for higher MMA:BA monomer ratios, and also rose as the polymer-cement ratio increased. The tensile strengths of MB7 and MB8 copolymer modified mortars were

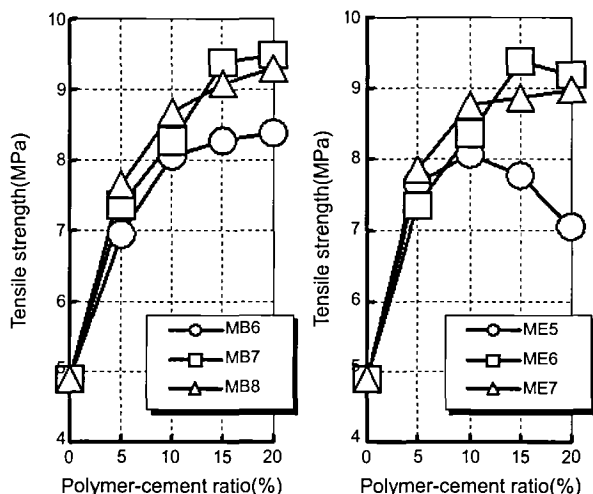


Figure 6. Tensile strength of polymer-modified mortar.

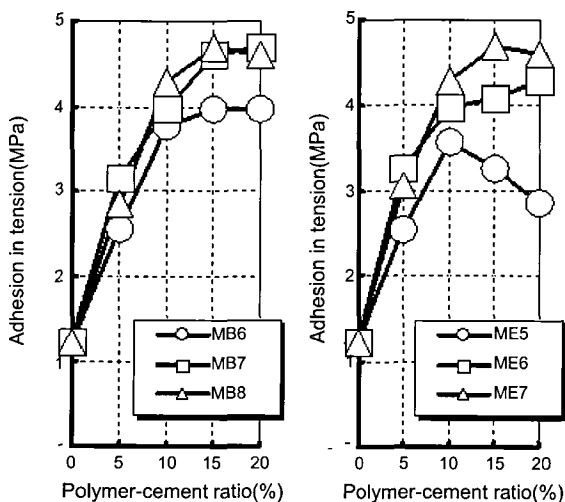


Figure 7. Tensile adhesive strength of polymer-modified mortar.

high. The tensile strength of MB7 polymer-modified mortar was higher than normal cement mortar by a maximum of 94% with a 20% polymer-cement ratio, which was almost twice higher than normal. The tensile strength change of the MMA-EA (ME) copolymer-modified mortar was similar to that of the MB polymer-modified mortar.

Tensile Adhesive Strength of the Polymer-modified Mortar. Figure 7 shows the tensile adhesive strength of the polymer-modified mortar. The tensile adhesive strength change of the copolymer-modified mortar was similar to the one shown in tensile strength of copolymer. The tensile adhesive strength of the MB polymer-modified mortar was higher for higher MMA monomer contents and polymer-cement ratios, and up to four times that of normal cement mortar. The tensile adhesive strength of the ME polymer-modified mortar was, as in the case of the MB polymer-modified mortar, higher

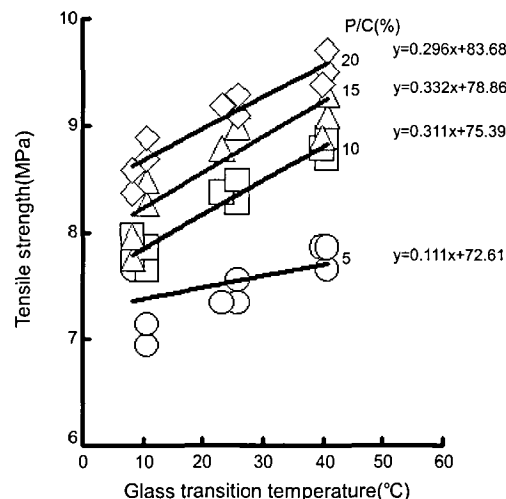


Figure 8. Glass transition temperature versus tensile strength.

for higher MMA/EA monomer ratios and polymer-cement ratios. The ME5 polymer-modified mortar showed significantly lower tensile adhesive strength as the polymer-cement ratio increased over 10%, and no improvement in tensile adhesive strength could be expected.

Correlation between the Glass Transition Temperature and the Tensile Strength of the Polymer-modified Mortar. Figure 8 shows the tensile strength of the copolymer-modified mortar mixed with MMA-based copolymer latex according to the glass transition temperature. The tensile strength of the polymer-modified mortar rose as the glass transition temperature increased, and was highest when the polymer-cement ratio was 20%. The tensile strength of the copolymer-modified mortar was directly correlated with the strength of the copolymer film, which acted as an adhesive to the cement mortar.⁷ Accordingly, the tensile strength of the polymer cement mortar mixed with the high glass transition temperature polymer was high at the polymer-cement ratio of 20%, which was the highest polymer content. If the glass transition temperature continued to increase, however, the film formation ratio would have decreased and the tensile strength would also have significantly decreased.

Conclusions

Both the tensile strength and the adhesion characteristic of the copolymer-modified mortar, wherein MMA-BA or MMA-EA copolymer was used as a modifier, were examined in this study. The tensile strength of copolymer-modified mortar was higher for the copolymer with a higher glass transition temperature; and a higher polymer content led to a higher tensile strength and better adhesion performance. The best copolymer-modified mortar has a tensile strength

about twice as high as that of normal cement mortar, and its tensile adhesive strength was four times higher than that of normal cement mortar. This indicates that the mixing of MMA-based copolymer into cement mortar can improve the quality of the cement mortar as a finishing material, a paving material, and a coating material.

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