論 文

[1148] 湿潤セメントコンクリートに対するポリメタクリル酸メチルモルタルの接着性の改善

IMPROVEMENT IN ADHESION OF POLYMETHYL METHACRYLATE MORTAR TO WET ORDINARY CEMENT CONCRETE

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1. INTRODUCTION

Polymethyl methacrylate (PMMA) mortar has widely been used as finishing materials such as floorings, pavings, integral waterproofings, decorative coatings and repairing materials in the construction industry because of their superior performance. The most important aspect in the applications of PMMA mortar is the drying of concrete substrates. The drying process can be eliminated by developing new primers which can produce high adhesion or bond strength even for wet ordinary cement concrete surfaces. This will not only reduce the cost but also simplify the application process.

This paper deals with an improvement in the adhesion or bond strength of PMMA mortar to wet ordinary cement concrete by use of various primers. Substrates used are molded using an ordinary cement concrete with a slump of 10 cm. Specimens are prepared by jointing PMMA mortar to the wet and dry concrete substrates treated with methyl methacrylate-based primers with or without coupling agents, coupling agents and crosslinking agent-based primers with silane coupling agent. The effects of the primers on the adhesion in tension of PMMA mortar to the wet and dry concrete surfaces are discussed.

2. MATERIALS

2.1 MATERIALS FOR BINDER AND PRIMER SYSTEMS

The binder system used was based on methyl methacrylate (MMA) monomer, together with trimethylolpropane trimethacrylate (TMPTMA) as a crosslinking agent, unsaturated polyester resin (UP) and polyisobutyl methacrylate (PIBMA) as a material for shrinkage-reducing agent, benzoyl peroxide (BPO) as an initiator and N,N-dimethyl-p-toluidene (DMT) as a promoter. The primer systems used were prepared by using these materials and coupling agents such as γ-methacryloxypropyltrimethoxy silane(Silane), acetoalkoxyaluminium-di-iso propylate (Aluminate), tetra -n-butoxy zirconium(Zirconium), titanium acylate- and titanium phosphate-type coupling agent(Titanate).

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2.2 FILLER AND AGGERGATES FOR PMMA MORTAR

Commercially available ground calcium carbonate (size; 2.5 μm or finer) was used as a filler and silica sands (sizes; 0.6-1.2mm and 0.1-0.4mm) as aggregates. The water contents of the filler and aggregates were controlled to be less than 0.1%.

2.3 CONCRETE SUBSTRATES

Ordinary portland cement, river sand (size; 2.5mm or finer) and river gravel (size; 5-20mm) were used for the preparation of concrete substrates.

3. TESTING PROCEDURES

3.1 PREPARATION OF CONCRETE SUBSTRATES

Table 1 Mix Proportions of Concrete.

Water-Cement Ratio (%)	Sand-Aggregate Ratio (%)	Mix Proportion by Weight (kg/m³)				Slump (cm)	Air Content (%)
		Cement	Water	Sand	Gravel		
63.0	41.5	294	185	715	1045	10.0	4.0

According to JIS A 1138 (Method of Making Test Samples of Concrete in the Laboratory), concrete was mixed with the mix proportions as shown in Table 1. Concrete substrates 10x10x40cm were molded, and then subjected to a 1-day-20°C-80% R.H.-moist plus 6-day-20°C-water plus 7-day-20°C- 50% R.H.-dry cure. After curing, the concrete substrates for dry surface were stored at 20°C and 50% R.H. to a constant weight, and for wet surface were immersed in water at 20°C for 7 days. The surfaces of the concrete substrates were ground by using an electric grinder. After grinding, the dry surface of the concrete substrates was blown by pressurized air to remove all the free dust particles, and the wet surface was washed with pressurized water. The washed wet surfaces were covered with wet towels until primer treatment.

3.2 PREPARATION OF PMMA MORTAR

According to JIS A 1181 (Method of Making Polyester Resin Concrete Specimens), PMMA mortar was mixed with the binder formulations and mix proportions as shown in Tables 2 and 3 respectively.

Table 2 Formulations of Binder.

MMA	TMPTMA	UP	PIBMA	DMT	BPO
73	2	25	8.3	0.5	2

Table 3 Mix Proportions of PMMA Mortar.

Binder	Filler	Silica Sand	
		Size, 0.6~1.2mm	Size, 0.1~0.4mm
15.0	15.0	35.0	35.0

3.3 APPLICATION OF PRIMERS AND PREPARATION OF SPECIMENS

MMA-based primers which are the PMMA mortar binders with coupling agent contents of 0, 1, 3, 5 and 10 phr [parts per hundred parts of resin (binder for PMMA mortar)] and TMPTMA-based primers with Silane, filler, initiator and

Table 4 Formulations of TMPTMA-Based Primers (by Weight).

Material	Type of Primer (Identification)				
	TS10	TS10C	TS20C	TFS10C	TFS20C
TMPTMA(T)	100.0	100.0	100.0	100.0	100.0
Silane(S)	10.0	10.0	20.0	10.0	20.0
Filler $CaCO_3$(F)	–	–	–	50.0	50.0
BPO(C)	–	1.0	1.0	1.0	1.0
DMT	0.5	0.5	0.5	0.5	0.5

promoter as shown in Table 4 were formulated. The initiator was mixed immediately before the application of the primers. The primers and the coupling agents used as primers were applied on the dry and wet surfaces of concrete substrates at coverage rates of 400 and 100 g/m^2 respectively. The coupling agents except Silane were diluted with MMA monomer at a ratio of agents:MMA monomer=1 : 2 (by weight) to improve their applicability. PMMA mortar was cast immediately after the application of the primers, and cured at 20°C and 50% R.H. for 2 days.

3.4 ADHESION TEST

The cured specimens were tested for adhesion in tension in accordance with JIS A 6915 (Wall Coatings for Thick Textured Finishes) as shown in Fig.1, by using manually operated direct pull-gage machine. After adhesion test, the specimens were observed for failure modes, which were classified into the following three types(1):

A: Adhesive failure (failure in interface)
P: Cohesive failure in PMMA mortar
S: Cohesive failure in substrate (ordinary cement concrete)

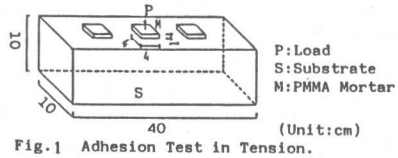

Fig.1 Adhesion Test in Tension.

The respective approximate rates of A, P and S areas in the total area of 10 on the failed crosssections were expressed as suffixes for A, P and S.

4. TEST RESULTS AND DISCUSSSION

Table 5 shows the adhesion in tension and failure modes of PMMA mortar to the wet and dry concrete sufaces treated with various primers. The coefficient of variation for the adhesion in tesion in this test is 0.15 or less. Fig. 2 represents the effects of coupling agents as primers and TMPTMA-based primers on the adhesion in tension of PMMA mortar to the wet and dry concrete surfaces. In the case of no primer and MMA-based primer (without coupling agents) treatments, the adhesion in tension of PMMA mortar to the wet surface is about one third of that to the dry surface, and is much lower than that of other primer-treated ones except a few cases. The reason for this phenomenon can be explained as follows; the moisture present on the wet surface forms a barrier to the binder of PMMA mortar and MMA-

Table 5 Adhesion in Tension and Failure Mode of PMMA Mortar to Wet and Dry Concrete Surfaces.

Type of Primer			To Wet Surface		To Dry Surface	
			Adhesion in Tension (kgf/cm^2)	Failure Mode	Adhesion in Tension (kgf/cm^2)	Failure Mode
No Primer			6	A10	19	A1:S9
MMA-Based Primer*			6	A10	21	A2:S8
Coupling Agent*	Silane		17	A5:S5	23	S10
	Aluminate		6	A10	9	S10
	Zirconium		19	A5:S5	13	A10
	Titanate-A		10	A10	20	A9:S1
	Titanate-B		14	A10	21	A3:S7
	Titanate-C		2	A10	2	A1:S9
	Titanate-D		11	A10	13	A10
TMPTMA-Based Primer*	TS10		12	A10	27	S10
	TS10C		12	A7:S3	27	S10
	TS20C		15	A5:S5	30	S10
	TFS10C		22	A2:S8	34	S10
	TFS20C		18	A5:S5	27	S10
MMA-Based Primer with Coupling Agent	MMA-Silane	1**	16	S10	26	S10
		3	19	S10	27	S10
		5	18	A6:S4	23	S10
		10	18	A5:S5	23	S10
	MMA-Aluminate	1	19	A4:S6	20	A4:S6
		3	21	A3:S7	22	A3:S7
		5	19	A4:S6	19	A2:S8
	MMA-Zirconium	1	16	A1:S9	21	A1:S9
		3	24	S10	26	A2:S8
		5	20	A1:S9	22	A2:S8
	MMA-Titanate-A	1	18	A5:S5	26	A1:S9
		3	23	A3:S7	25	S10
		5	19	A4:S6	21	A1:S9
	Titanate-B	1	17	A4:S6	23	A1:S9
		3	20	A3:S7	25	A1:S9
		5	19	A4:S6	21	A1:S9
	MMA-Titanate-C	1	15	A4:S6	27	S10
		3	20	A3:S7	25	A2:S8
		5	20	A1:S9	18	A1:S9
	MMA-Titanate-D	1	15	A4:S6	22	S10
		3	20	A2:S8	27	S10
		5	25	A3:S7	27	S10

Notes, *: Without coupling agents
**: Coupling agent content of MMA-based primer(phr).

based primer, and hinders the penetration of the binder and the primer into the concrete to form a strong bond(2).On the other hand, no difference in the adhesion in tension of PMMA mortar between untreated and MMA-based primer-treated dry surfaces is observed because the binder of PMMA mortar may provide a good bond to the dry surface due to its effective penetration. Except Aluminate and Titanate-C, treatment for the wet surface with coupling agents gives 2 to 3 times adhesion in tension than no primer and MMA-based primer treatments. Especially the adhesion in tension of PMMA mortar to the wet surface treated with the Zirconium is almost the same as that to the untreated dry surface. Effectiveness of the treatment of the of the dry surface with the coupling agents as primers is hardly recognized as compared to the wet surface treatment. In the case of TMPTMA-based primer treatments, adequate adhesion in tension is obtained for the wet and dry surfaces. The adhesion in tension of PMMA mortar to the wet surface treated with TMPTMA-based primers which contain Silane is almost the same as or much higher than that of Silane-treated one. The excellent adhesion of PMMA mortar to the dry surface is produced by TMPTMA-based primers. TFS10C which is prepared by using TMPTMA, Silane and filler gives the highest adhesion in tension to the dry surface as compared to other primers. It is considered that TMPTMA in the primer improves the coupling reaction of Silane to the organic group of PMMA and the filler fills the rough concrete surface.

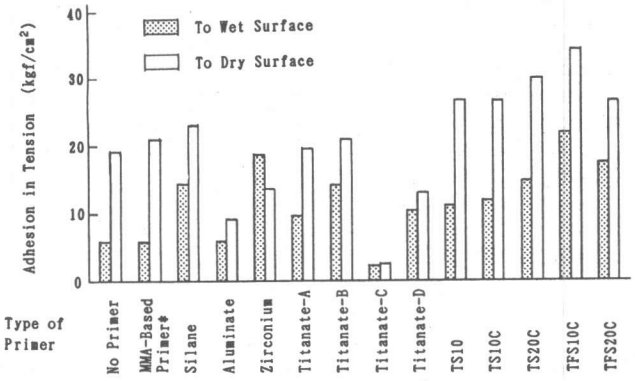

Fig. 2 Effects of Primers on Adhesion in Tension of PMMA Mortar to Wet and Dry Concrete Surfaces.
Note, #; Without coupling agents.

Fig. 3 represents the adhesion in tension of PMMA mortar vs. coupling agent content of MMA-based primers. In general, the adhesion in tension of PMMA mortar to the dry or wet concrete surface treated with MMA-based primers containing coupling agents increases with raising coupling agent content, and reaches its maximum at coupling agent contents of 1 to 3 phr. The adhesion to the dry surface is higher than that to the wet surface,and an improvement in the adhesion due to the use of MMA-based primers containing the coupling agents is remarkable for the wet surface. The addition of a small amount of the coupling agents to MMA-based primer significantly improves its properties, particularly for application to the wet surface. The dual organic-inorganic functionality of the coupling agents permits an improvement in the bond between inorganic concrete substrate and organic PMMA binder in the mortar.

Figs. 4 and 5 exhibit the failure mode distribution in adhesion test in tension for PMMA mortar to the wet and dry concrete surfaces treated with various primers. Ratio of cohesive failure in substrate (ordinary cement concrete) is increased with an increase in the adhesion in tension of PMMA mortar to the wet and dry surfaces regardless of the primer types. PMMA mortar having an adhesion in tension of 15 kgf/cm^2 or less generally shows adhesive failure(A10).The adhesion in tension of PMMA mortar to adequate primer-treated wet and dry surfaces gives 15 to 34 kgf/cm^2 with

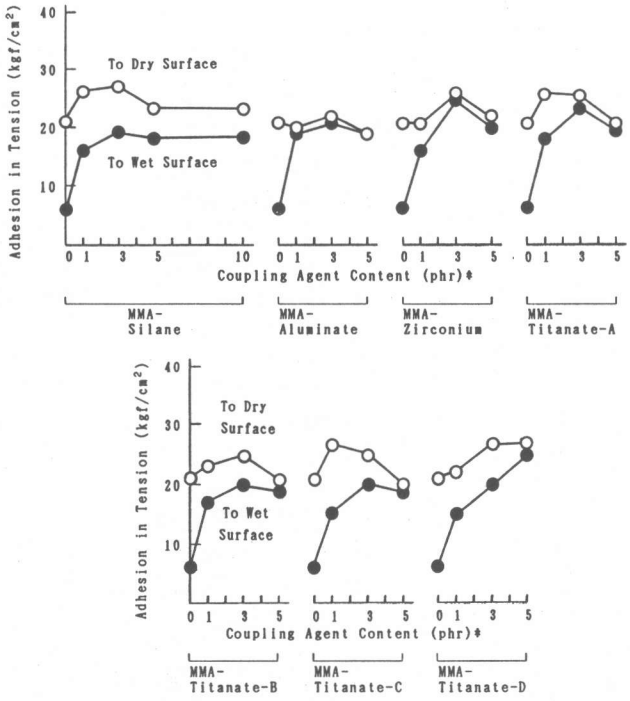

Fig. 3 Adhesion in Tension of PMMA Mortar vs. Coupling Agent Content of MMA-Based Primers.
Note, *;Parts per hundred parts of resin (MMA-based primer).

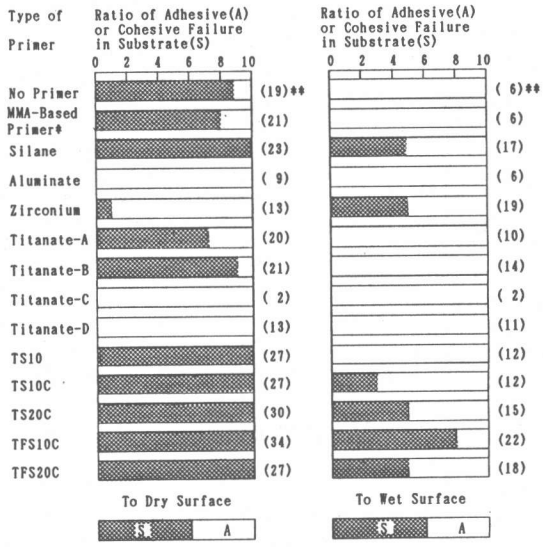

Fig. 4 Failure Mode Distribution and Adhesion in Tension of PMMA Mortar to Wet and Dry Concrete Surfaces Treated with Various Primers.
Notes, *; Without coupling agents.
**; Adhesion in tension (kgf/cm²).

cohesive failure in substrate(S10). Increasing adhesion in tension of PMMA mortar with cohesive failure may be performed by the strengthening of the substrate with the penetration of the primers.

5.CONCLUSIONS

(1) In no primer and MMA-based primer (without coupling agents) treatments, the adhesion in tension of PMMA mortar to wet concrete surface is about one third of that to dry concrete surface.
(2) The adhesion in tension of PMMA mortar to wet concrete surface is greatly affected by the types of primers used, hence primers which have a wide range of reactivity and can produce chemical bonds to the wet concrete surface are recommended for the wet surface tereatment of concrete. In particular, the use of TMPTMA- and MMA-based primers with Silane coupling agent is effective for this purpose.
(3) Treatments of wet concrete surface with suitable coupling agents, MMA- and TMPTMA- based primers containing the coupling agents provide a great increase in the adhesion in tension of PMMA mortar to the wet surface.

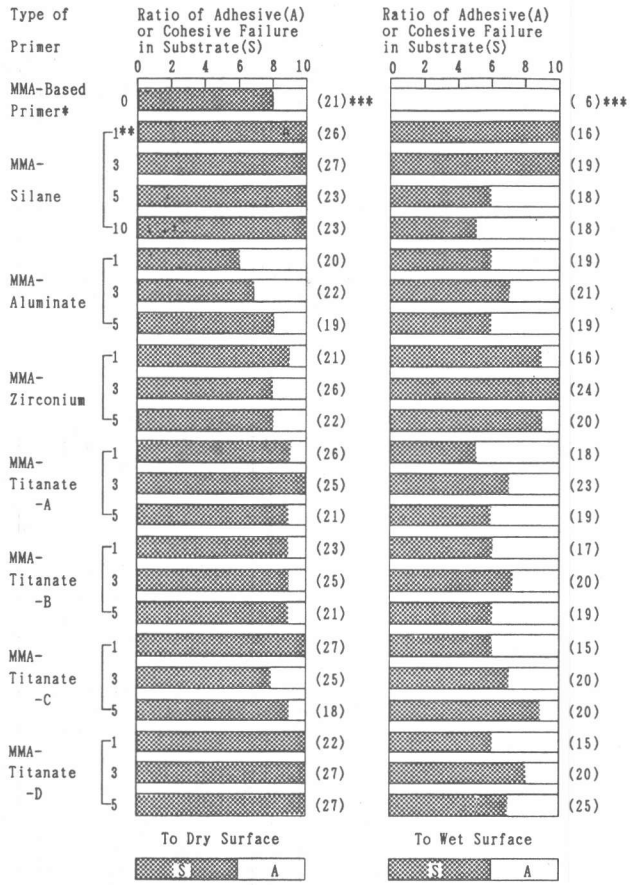

Fig. 5 Failure Mode Distribution and Adhesion in Tension of PMMA Mortar to Wet and Dry Concrete Surfaces Treated with MMA-Based Primers with Various Coupling Agent Contents.
Notes, *; Without coupling agents
**; Coupling agent content of MMA-based primer(phr).
***; Adhesion in tension (kgf/cm^2).

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