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論 文

[1210] Strength Properties of Polymethyl Methacrylate Mortars Placed and Bonded Underwater

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1. INTRODUCTION

Recently, polymethyl methacrylate (PMMA) mortars have been developed, and widely used as construction materials throughout the world because of their good workability, low-temperature curability, high-early-strength development, watertightness, chemical resistance and abrasion resistance. The possibilities of the underwater applications of PMMA mortars have already examined [1]. In general, reinforced concrete structures such as offshore platforms, breakwaters, jetties, harbor walls, harbor and coastal buildings and other structures in or adjacent to seawater are always subjected to severe marine environment, and are apt to suffer chloride-induced damage. Therefore, the effective materials which can use in seawater are required to protect such concrete structures and to repair such damage. PMMA mortars can be considered as such effective protective and repair materials.

In this paper, PMMA mortars with the silane coupling agent added to their binders or the sands treated with it are prepared, placed or bonded to PMMA mortar substrates in artificial seawater, tap water and air, and tested for strength and adhesion. Developments in their compressive strength, flexural strength and adhesion in flexure are examined underwater.

2. MATERIALS

2.1 MATERIALS FOR BINDER SYSTEMS

Binder systems were based on methyl methacrylate (MMA) monomer, together with trimethylolpropane trimethacrylate (TMPTMA) as a crosslinking agent, unsaturated polyester resin (UP) and polyisobutyl methacrylate (PIBMA) as shrinkage-reducing agents, benzoyl peroxide (BPO) as an initiator, N,N-dimethyl-p-toluidine (DMT) as a promoter. γ - methacryloxypropyltrimethoxy silane (Silane) as a coupling agent was used for the binder systems and the treatment of sands.

2.2 FILLER AND FINE AGGREGATES

Commercially available ground calcium carbonate (size; 2.5μm or finer) sands was used as a filler, and silica sands (sizes; 0.70-1.17mm and 0.05-0.21mm) were done as fine aggregates. The water contents of the filler and silica were

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controlled to be less than 0.1% by heat drying. Silane-treated sands were prepared by treating the dried silica sands with Silane-based solution at 20°C. Silane-based solution was prepared by mixing Silane with methanol and water at a weight ratio of water to methanol to Silane 1:9:0.09.

3. TESTING PROCEDURES

3.1 PREPARATION OF ARTIFICIAL SEAWATER

Artificial seawater (Seawater) for the curing of PMMA mortar substrates and specimens was prepared according to JIS A 6205 (Corrosion Inhibitor for Reinforced Steel in Concrete), Appendix 1 Method of Salt Water Immersion Test for Reinforcing Steel. Table 1 gives the chemicals for the preparation of the Seawater and its compositions.

Table 1 Chemicals for Preparation of Artificial Seawater and Its Compositions.

Type of Chemicals	Weight (g) of Chemicals Contained in 1ℓ of Artificial Seawater
Sodium Chloride (NaCl)	24.5
Magnesium Chloride ($MgCl_2.6H_2O$)	11.1
Sodium Sulfate (Na_2SO_4)	4.1
Calcium Chloride ($CaCl_2$)	1.2
Potassium Chloride (KCl)	0.7

3.2 WORKING LIVES OF PMMA BINDERS AND MORTARS

The working lives of PMMA binders and mortars with the formulations and mix proportions given in Tables 2 and 3 were measured in Seawater, tap water and air according to JIS K 6833 (General Testing Methods for Adhesives) and the Finger-Touching Method specified in JIS A 1186 (Measuring Method for Working Life of Polyester Resin Concrete) respectively.

Table 2 Formulations of Binders for PMMA Mortars.

Formulations by Weight (%)				(phr*)	
MMA	TMPTMA	UP	PIBMA	BPO	DMT
67.40	1.80	23.10	7.70	1.00	0.50
				1.50	0.50
				2.00	0.25
					0.50
					0.75
					1.00

Note, *:Parts per hundred parts of resin (MMA+TMPTMA+UP+PIBMA).

Table 3 Mix Proportions of PMMA Mortars.

Mix Proportions by Weight				
Binder	Filler	Silica Sand or Silane-Treated Sand		Binder-Filler Ratio, B/F
		No. 4	No. 7	
15.00	15.00	35.00	35.00	1.00

3.3 PREPARATION OF SPECIMENS

PMMA mortars using PMMA binders with Silane contents of 0 and 1.00 phr, untreated and Silane-treated sands were mixed with a binder content of 15.00% as shown in Tables 2 and 3. In the preparation of specimens for flexural and compressive strength tests, and of PMMA mortar substrates for adhesion in flexure, PMMA mortars were placed into molds 40x40x160mm and 40x40x80mm in Seawater and tap water at 20°C and in air at 20°C and 50% R.H., and then cured for 1 hour in the molds kept in Seawater, tap water and air till demolding. The bonding surfaces of PMMA mortar substrates were treated with the AA-150 abrasive papers specified in JIS R 6252 (Abrasive Papers), and the wet and dry surfaces of PMMA mortar substrates were washed with pressurized water and blown by pressurized air respectively to remove all the dust particles. In the preparation of specimens for adhesion test in flexure, PMMA mortars were bonded to PMMA mortar substrates 40x40x80mm in the molds 40x40x160mm in Seawater and tap water at 20°C and in air at 20°C and 50% R.H., and then cured for 1 hour in the molds kept in Seawater, tap water and air till demolding. After demolding, the specimens were cured in Seawater, tap water and air for 0, 2, 5, 11, 23, 167 and 671 hours for strength and adhesion developments.

3.4 STRENGTH AND ADHESION TESTS

According to JIS A 1172 (Method of Test for Strength of Polymer-Modified Mortar), the flexural strength test and adhesion test in flexure of cured specimens were conducted by use of the Amsler-type universal testing machine. After the flexural strength test, the broken portions were tested for compressive strength by using the same testing machine according to JIS A 1172. After the adhesion test, the failed crosssections of the specimens were observed for failure modes, which were classified into the following three types, A: Adhesive failure (failure at the interface), M: Cohesive failure in the bonded PMMA mortar, and S: Cohesive failure in PMMA mortar substrate. The total area of the bonded surfaces was supposed to be 10, and the respective approximate rates of A, M and S areas on the failed crosssections were expressed as suffixes for A, M and S. The relative flexural and compressive strengths, and relative adhesion in flexure of the specimens were calculated by the following equation:

$$\text{Relative strength (\%)} = (Fw/Fa) \times 100$$

where Fw and Fa are the strengths (kgf/cm^2) of the specimens placed or bonded underwater (in Seawater or tap water) and in air respectively.

4. TEST RESULTS AND DISCUSSION

Fig. 1 shows the effects of BPO and DMT contents on the working lives of PMMA binders and mortars placed in Seawater, tap water and air. The working lives of PMMA binders and mortars shorten rapidly with increasing BPO and DMT contents regardless of the placing conditions. A difference in the working life between PMMA binders and mortars becomes smaller with raising BPO and DMT contents. It can be said that there is no remarkedable difference in the working lives of PMMA binders and mortars placed in Seawater, tap water and air. In other words, the working lives of PMMA binders and mortars placed in Seawater are almost the same as those of the binders and mortars in tap water and air irrespective of BPO and DMT contents. It is concluded from these data that the working life of PMMA binders and mortars placed in Seawater and tap water can be controlled like those of the binders and mortars placed in air.

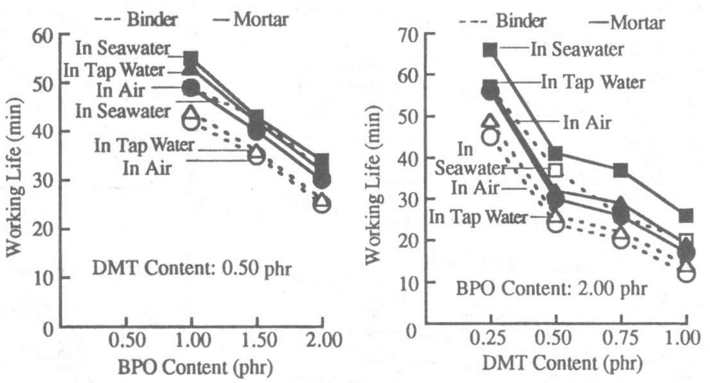

Fig. 1 Effects of BPO and DMT Contents on Working Lives of PMMA Binders and Mortars Placed in Seawater, Tap Water and Air.

Figs. 2 and 3 represent the curing period vs. flexural and compressive strengths of PMMA mortars placed in Seawater, tap water and air. Figs. 4 and 5 show the effects of Silane addition and the use of Silane-treated sands on 24-hour relative flexural and compressive strengths of PMMA mortars placed under such conditions. In general, the flexural and compressive strengths of PMMA mortars placed in Seawater, tap water and air increase sharply till a curing period of 3 hours, and become nearly constant at a curing period of 24 hours. PMMA mortars placed in Seawater, tap water and air develop 80% or higher of 672-hour (28-day) flexural and compressive strengths at a curing period of 3 hours because of the quick setting of their binders. The flexural and compressive strengths of PMMA mortars placed in Seawater and tap water develop 60 to 90% of those of PMMA mortars placed in air. However, the flexural and compressive strengths of PMMA mortars placed in Seawater are higher than those of PMMA mortars placed in tap water regardless of curing period. The relative flexural and compressive strengths of PMMA mortars placed in Seawater are larger than in tap water. The reasons for this may be explained to be due to a difference in

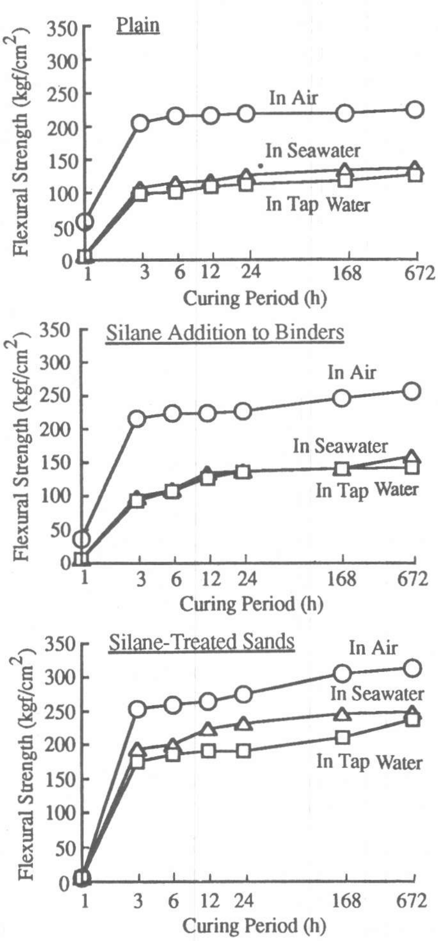

Fig.2 Curing Period vs. Flexural Strength of PMMA Mortars with Silane Coupling Agent or Silane-Treated Sands, Placed in Seawater, Tap Water and Air.

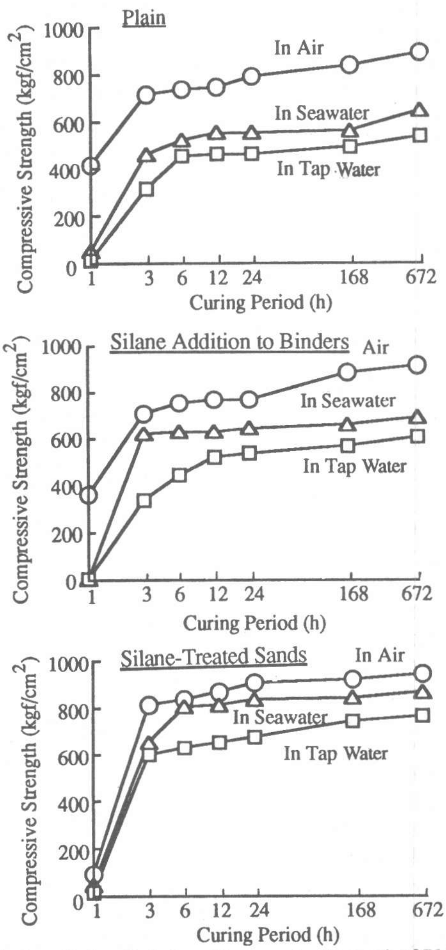

Fig.3 Curing Period vs. Compressive Strength of PMMA Mortars with Silane Coupling Agent or Silane-Treated Sands, Placed in Seawater, Tap Water and Air.

the osmotic pressure between Seawater and tap water [2] and the effects of inorganic salts in Seawater on the reactivity of MMA monomer in homo-polymerization [3]. The water absorption of PMMA mortar was 0.20% in tap water and 0.12% in Seawater at 672 hours after placing. In general, the flexural and compressive strengths or the relative flexural and compressive strengths seem to depend on Silane addition to the binders, the use of Silane-treated sands and the type of water.

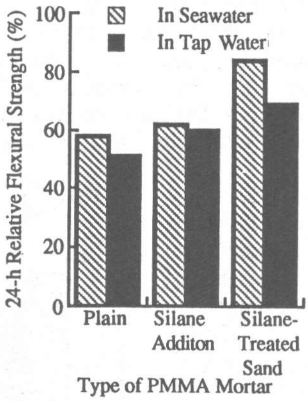

Fig. 4 24-h Relative Flexural Strength of PMMA Mortars Placed in Seawater and Tap Water.

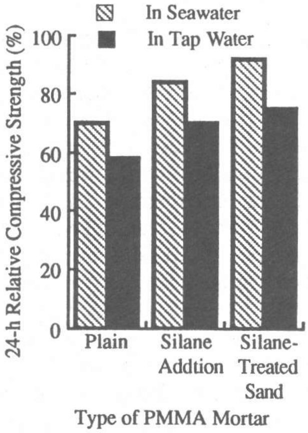

Fig. 5 24-h Relative Compressive Strength of PMMA Mortars Placed in Seawater and Tap Water.

Fig. 6 exhibits the curing period vs. adhesion in flexure of PMMA mortars bonded in Seawater, tap water and air. Regardless of the type of water, the adhesion in flexure of PMMA mortars with Silane or Silane-treated sands increases sharply till curing periods of 3 to 6 hours, and becomes nearly constant at a curing period of 24 hours. Irrespective of the placing conditions, PMMA mortars at curing periods of 3 to 6 hours develop about 80% or higher of 672-hour (28-day) adhesion in flexure. At curing periods of 24 and 672 hours, the adhesion in flexure of PMMA mortars bonded in Seawater and tap water is about 70 to 90% of that in air. Like the flexural and compressive strengths, the adhesion in flexure of PMMA mortars bonded in Seawater is higher than that of PMMA mortars bonded in tap water. This phenomenon may be due to the reasons as stated above. The use of Silane-treated sands is found to be a much effective technique to improve the adhesion in flexure of PMMA mortars rather than the addition of Silane to their binders. It is considered that

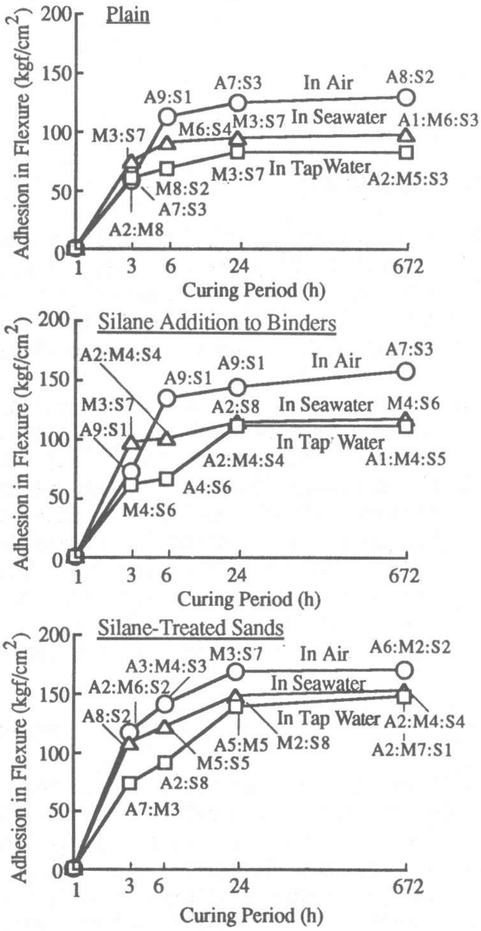

Fig. 6 Curing Period vs. Adhesion in Flexure of PMMA Mortars with Silane Coupling Agent or Silane-Treated Sands, Placed in Seawater, Tap Water and Air.

a coupling action of the Silane between the binders and aggregates or filler may also be caused at the interfaces between the fresh PMMA mortars and PMMA mortar substrates when PMMA mortars are bonded in Seawater or tap water. The failure modes in the adhesion test in flexure of PMMA mortars bonded to PMMA mortar substrates in Seawater are almost cohesive failure in the bonded PMMA mortars and mortar substrates, which proves good adhesion between the bonded mortars and the mortar substrates in Seawater.

Fig. 7 shows the effects of Silane addition and the use of Silane-treated sands on 24-hour relative adhesion in flexure of PMMA mortars bonded in Seawater and tap water. Like their relative flexural and compressive strengths, the relative adhesion in flexure of PMMA mortars becomes large in bonding in Seawater rather than in tap water, and this trend is also marked in PMMA mortars with Silane-treated sands.

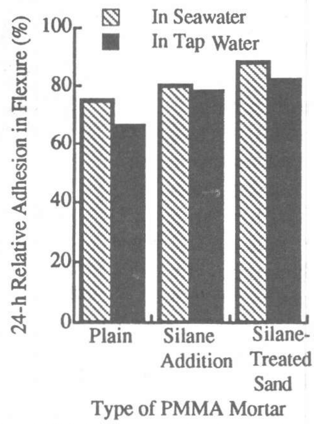

Fig. 7 24-h Relative Adhesion in Flexure of PMMA Mortars Bonded in Seawater and Tap Water.

5. CONCLUSIONS

(1) The working life of PMMA mortars placed in Seawater and tap water can be controlled like that of PMMA mortars placed in air.
(2) PMMA mortars placed underwater develop about 80% or higher of 672-hour (28-day) flexural and compressive strengths, and adhesion in flexure to PMMA mortar substrates at curing periods of 3 to 6 hours regardless of placing conditions.
(3) The flexural and compressive strengths, and adhesion in flexure of PMMA mortars placed and bonded in Seawater and tap water develop 60 to 90% of those of PMMA mortars placed and bonded in air.
(4) The developments of the flexural and compressive strengths, and adhesion in flexure of PMMA mortars (to PMMA mortar substrates) are remarkable in their placement or bonding in Seawater rather than in tap water. This trend is also marked in PMMA mortars with Silane-treated sands.
(5) For the purpose of improving the strength and adhesion of PMMA mortars placed or bonded in Seawater and tap water, the use of the sands treated with Silane rather than Silane addition to the binders can be recommended.

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