

## **A Comparative Study of Different Inorganic Pastes for the Development of Fiber Reinforced inorganic Polymer (FRiP) Strengthening Technology**

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### **ABSTRACT**

The fiber reinforced inorganic polymer (FRiP) strengthening system exhibits much improved fire resistance and compatibility with the concrete substrate compared to the fiber reinforced polymer (FRP) strengthening system. Since an inorganic paste is used to replace organic resins as the matrices and the bonding adhesives in the FRiP strengthening system, its success depends greatly on the properties of inorganic pastes. This paper presents a comparative study on the performance of different inorganic pastes, which are based on magnesium phosphate cement (MPC), magnesium oxychloride cement (MOC), geopolymer (GP) cement and polymer modified cement mortar (PMM). The flow, pot life, compressive strength, flexural strength and bonding strength with cement mortar of the aforementioned binders and the tensile strength of the formed FRiP composites were carefully examined. It is shown that MPC and MOC binders are most promising candidates to be the matrix and the adhesive for the development of FRiP strengthening systems.

**Keywords** Fiber reinforced inorganic polymer composites; strengthening; inorganic paste, bond strength

### **INTRODUCTION**

Fiber reinforced polymer (FRP) is an effective technique for strengthening reinforced concrete (RC) and steel structures due to the numerous advantages of FRP composites such as the high strength to weight ratio, corrosion resistance, tailor ability and ease of installation (Teng et al. 2002). In spite of these advantages, there are few serious issues with the use of FRP strengthening system such as inflammability and smoke generation of the polymer matrix (i.e. usually an epoxy), and its moisture incompatibility with concrete substrate (Toutanji et al. 2006, Taljisten & Blankvard 2007, and Dai et al. 2009). To handle these problems, many researchers have tried to use inorganic resins, to replace the epoxy, as the matrix and bonding adhesive for fibers, to develop fiber reinforced inorganic polymer (FRiP) strengthening systems (Kurtz & Balaguru 2001, Badanoi 2003, Brockner et al. 2006, Toutanji et al. 2006, Misra & Mathur 2007, Taljisten & Blankvard 2007, Chau et al. 2009, Dai et al. 2009, Zhang et al. 2010, Ding et al. 2011, Hashemi & Al-Rahidi 2012).

An ideal inorganic matrix material for a bonded FRiP system needs to possess the following features (Wiberg 2003): (a) sufficient mechanical strength for load transfer; (b) the ability to impregnate and create a strong bond with fiber reinforcing materials; (c) the ability to bond strongly to the concrete substrate; (d) thermal and chemical compatibility with the concrete substrate; (e) good workability on the site, including good consistency and fast-curing ability; (e) environmental acceptability; and (f) limited shrinkage. The development of such an inorganic matrix material has been pursued by a number of research groups around the world over the past decade. Currently, four major types of inorganic matrices are being explored for the development of FRiP systems polymer modified mortar (PMM), geopolymers (GP), magnesium oxychloride cement (MOC) and magnesium phosphate cement (MPC). This research aims to present an overall comparison of the physical properties, mechanical properties, and the workability of the above four types of cementitious materials as well as the mechanical properties of the formed FRiP composites.

## EXPERIMENTAL PROGRAM

### Materials and Mix Proportions

The main raw materials used for preparing four inorganic matrices (i.e. MPC, MOC, PMM and GP) included dead burnt magnesia (DBM), light burnt magnesia (LBM), fly ash (FA), mono potassium phosphate (MPP), metakaoline (MK), slag (S) and Ordinary Portland Cement (OPC). Boric acid (BA) was used as the cement retarder. The magnesium chloride used was hygroscopic hexahydrate ( $MgCl_2 \cdot 6H_2O$ ) crystal with a purity of 98%. Water glass (WG) with a modulus ( $SiO_2/Na_2O$  ratio) of 1.4 was used to prepare GP. Type-I OPC was used to prepare PMM. An organic polymer (styrene butadiene rubber) with 37% solid contents was also used as the latex in PMM. Quartz sand passing through a sieve # 600 was used as the fine aggregate in PMM. Tap water was used as the mixing water. Manufacturer's data for the raw materials can be referred to the authors' previous study (Dai et al. 2013). The chemical compositions of major raw materials used in this study were obtained by the X-ray fluorescence spectrometry (XRF) analysis and are presented in Table 1. Fig. 1 shows their particle size distributions, which were determined by a laser particle size analyzer. Uni-directional carbon fiber sheet (Fig. 2) was used for making FRiP composites. According to the manufacturer's data, the modulus of elasticity of fibers is 240 GPa and the tensile strength is 3400 MPa.

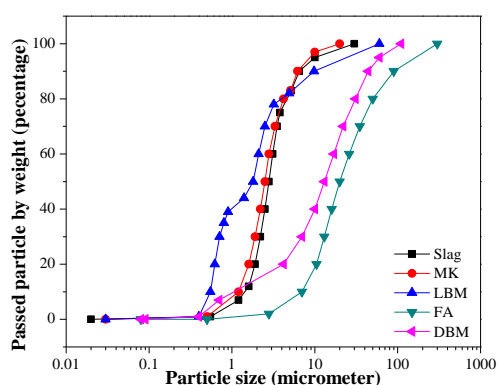


Fig.1. Particles size distribution curves

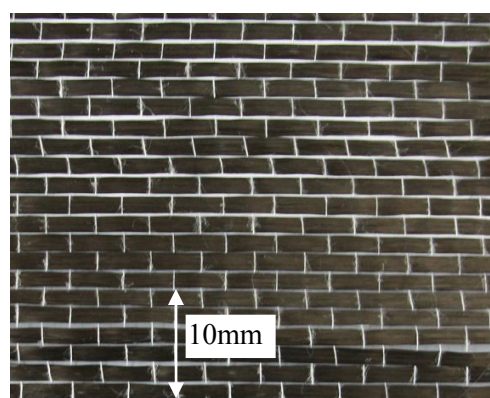


Fig.2. Uni-directional carbon fiber sheet

Table 1. Chemical composition of major raw materials (by weight %)

Chemical composition	DBM	LBM	OPC	MK	FA
MgO	83.18	93.38	2.54	0.659	-
CaO	6.467	1.5	63.15	24.28	7.78
SiO <sub>2</sub>	6.42	3.42	19.61	56.73	46.12
Fe <sub>2</sub> O <sub>3</sub>	1.278	0.313	3.32	4.113	5.61
P <sub>2</sub> O <sub>5</sub>	1.25	0.089	-	-	1.38
Al <sub>2</sub> O <sub>3</sub>	1.19	0.85	7.33	7.29	32.7
TiO <sub>2</sub>	-	0.027	-	1.81	1.81
K <sub>2</sub> O	-	0.025	-	3.46	1.59
MnO	-	0.011	-	-	-
ZnO	-	0.019	-	-	-
Cl	-	0.096	-	-	-
SO <sub>3</sub>	-	-	-	1.32	-
Na <sub>2</sub> O	-	-	2.13	-	-
LOI*	0.215	0.27	2.97	0.338	3.01

\*LOI – Loss on ignition

Table 2. Mix proportions of inorganic matrices (by weight)

MPC	DBM	MPP	BA	FA	Water
	1	1	0.10	0.60	0.60
MOC	LBM	FA	MgCl <sub>2</sub> * Solution		
	1	1	1.2		
GP	Slag	MK	WG	Water	
	1	0.50	0.20	0.60	
PMM	OPC	SCM <sup>a</sup>	Latex	Sand	Water <sup>b</sup>
	0.80	0.20	0.05	1	0.30

\* MgCl<sub>2</sub> concentration – 22° Baume

<sup>a</sup> SCM=(10%FA+5%S+5%MK)

<sup>b</sup> Water from latex was included

For all four types of inorganic pastes, Dai et al. (2003) conducted experimental studies to optimize their mix proportions. Table 2 presents the optimized mix proportions of all inorganic pastes with the aim to achieve the same compressive strength of 45 MPa. In the present study, all the test specimens were demolded after 24 hours and cured in an environment with a temperature of  $25 \pm 2^\circ\text{C}$  and relative humidity of  $55 \pm 5\%$  and tests were performed on the 7<sup>th</sup> day.

## Test Methods

Six types of tests were conducted to evaluate the performance of the inorganic pastes. The evaluated performance included flowability, pot life, compressive strength and flexural strength of the inorganic pastes; their bonding strength with cement mortar and fiber sheets, and the tensile strength of the FRiP composites. SEM analyses were also conducted to investigate the micro level interaction between fiber sheets and different inorganic matrices.

The flowability/workability of inorganic pastes was determined using the mini-cone slump flow test (Topçu & Uygunoğlu 2010). A small cone with the upper diameter of 36 mm, the

lower diameter of 60 mm and a height of 60 mm was used to calculate the diameter of flow of each inorganic matrix over a horizontal glass plate. The pot life of each inorganic paste was determined using the Vicat's apparatus, following ASTM C-191. The compressive strength of different inorganic pastes was determined based on tests of 30mm×30mm×30mm cube specimens. The flexural strength of each inorganic paste was determined using prisms with the dimensions of 40mm×40mm×160mm and following ASTM C-348. To evaluate the bonding strength of different inorganic pastes with cement mortar, flexural tests on composite beams, which consisted of two mortar prisms joined together with help of a 3 mm thick layer of inorganic paste, as shown in Fig. 3.

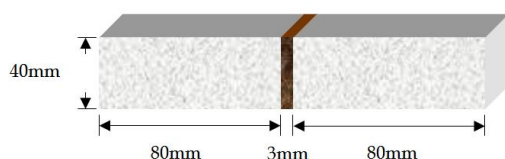


Fig.3. Specimen for bonding strength tests

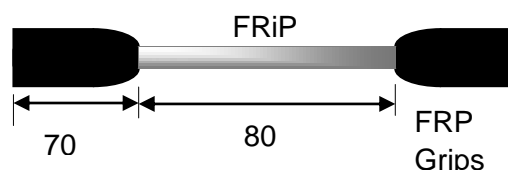


Fig.4. FRiP tensile coupon

The tensile strength of FRiP composites made of different inorganic matrices was evaluated using coupons as shown in Fig.4. The coupons were 3 mm in thickness and made in a dumbbell shape. The dry fiber sheets were sandwiched in the coupons. The two ends of the tensile coupons were made of FRP composites to avoid local failure there ahead of the central part. Pullout tests were conducted to investigate the bond performance of dry fiber sheets in different inorganic matrices. The inorganic matrices were prepared in the form of 70.7mm×70.7mm×70.7mm cube in which one layer of dry carbon fiber sheet was embedded at the center (Fig.5). In order to implement uniform stresses in the fiber sheets during the pullout tests, the dry fiber sheets out of the cubes were impregnated with a two-part epoxy matrix. A constant embedded length of 55 mm was adopted for all the pullout specimens. The bond strength of the fiber sheets was then calculated by dividing the maximum pull-out force by their surface area in the matrices.



Fig.5. Specimens for pullout test and test setup

## RESULTS AND DISCUSSION

### Physical Properties of Matrices

The physical properties of inorganic pastes like flowability and pot life are important parameters influencing the performance of FRiP strengthening systems. With a higher flowability of the matrix, better impregnation of fiber sheets can be achieved, resulting in higher bond between fiber sheets and matrices (Dai et al. 2013). In addition, the matrix should be sticky enough to be applicable to vertical surfaces of the RC members or the soffit

of RC beams or slabs. Workability of different inorganic pastes is mainly a function of water content. Higher flow was associated with higher water content (Wagh et al. 1997, Ding & Li 2005, Ohama 1995). Adding fly ash, up to a certain limit, also helps to improve the flow of paste, because of its small and spherical grains (Ding & Li 2005, Chan & Li 2006, Wu & Sun 2005).

Table 3 presents the flow of different inorganic pastes which had the same compressive strength. It is shown that MOC paste exhibits the highest flow among these matrices while GP leads to the lowest. The lower flow of GP may be due to inclusion of high percentage of MK, which reduced the activation of aluminosilicate by reducing alkali for geopolymerization (Bernal et al. 2012). The flow of MPC is similar to that of MPC. The flow of PMM is slightly lower because of addition of sand which gives granularity to the paste.

Pot life of matrices was determined using Vicat's Needles. Different inorganic pastes have different pot life. In this study, MPC has the shortest pot life even with the addition of Boric acid retarder. This is because of the furious acid-base reaction between magnesia and phosphate solution (Wagh et al. 1997). The pot life of MPC was recorded as 22 minutes while the pot life of MOC is very high. The latter mainly depends on the concentration and quantity of MgCl<sub>2</sub> solution. A higher solution content and concentration of MgCl<sub>2</sub> lead to longer pot life and vice versa (Misra & Mathur 2007). GP's pot life is also short, depending on water glass modulus and contents. In case of PMM, the pot life is nearly 2 hours, which is similar to that of conventional cement mortar. The relative density of all four types of inorganic pastes was also calculated by weighing the samples in air and water as indicated in Table 3.

Table 3. Physical properties of inorganic pastes

Matrix \ Property	Flow (mm)	Pot Life (Minutes)	Relative density (g/cc)
MPC	150	22	2.015
MOC	160	280	1.73
PMM	140	110	1.94
GP	100	40	1.89

### Mechanical Properties of Inorganic Matrices

Compressive strength of all the inorganic matrices was kept similar. Appropriate mixing ratios of raw materials were selected to achieve the 7d compressive strength of  $45 \pm 2$  MPa.

### Flexural strength

Flexure strength is indirect measure of tensile strength of inorganic matrices. Fig.6 shows the comparison of the flexural strength of different matrices. MOC matrix has the highest value followed by PMM, MPC and GP matrices (Fig.6). The high strength of MOC may be attributed to acicular microstructure of the hardened paste and better compaction of crystalline and amorphous hydration products. The higher flexure strength of PMM is due to addition of polymer as well as sand. Sand is high density particles which increase the toughness of the materials, resulting in higher flexural strength. The flexural strength of MPC was slightly lower than that of PMM. GP has shown the lowest flexure strength.

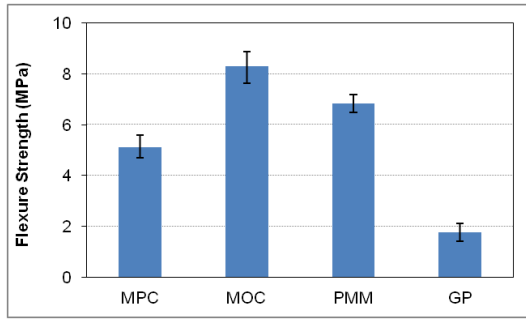


Fig. 6. flexural strength

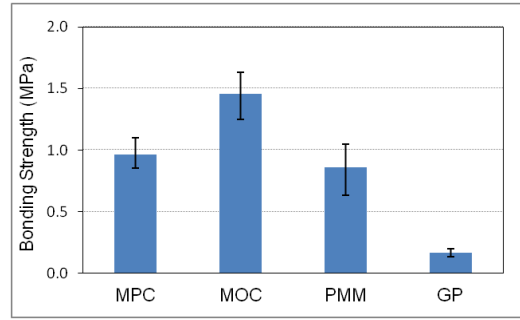


Fig.7. bonding strength with cement mortar

### Bonding strength with cement mortar

Figure 7 shows the bonding properties of different inorganic pastes with cement mortar based on the flexural tests shown in Fig.3. In most of the cases fracture occurred at the interface between matrix and cement mortar. MOC showed the highest bonding strength among all the matrices followed by MPC (Fig. 7). The bonding strength of PMM was similar to that of MPC. GP showed the lowest bonding characteristics with cement mortar substrates. It should be noted that all the tests were performed 7 days after the casting. It is expected that bonding strength of these inorganic pastes with cement mortar substrates increases with the curing time.

### Pullout strength of fiber sheets

Pullout strength of fiber sheets from inorganic matrix is a decisive parameter of the matrix feasibility for the FRiP strengthening technology. It was found that the pullout bond strength of fiber sheets in different inorganic matrices varies greatly even given same matrix compressive strength. MPC and MOC pastes have shown the highest pullout strength while GP again the lowest. The higher pullout strength achieved in cases of MPC and MOC pastes may be attributed to the better impregnation characteristics of matrices into fiber sheets and the roughly textured and acicular hydration products (refer to Figs. 10a and 10b). Fiber sheets in PMM matrices achieved pullout strength higher than those in GP but less than those in MPC and MPC (Fig. 9). The granularity of the paste probably jeopardized its impregnation into dry fiber sheets, resulting in relatively lower pullout strength.

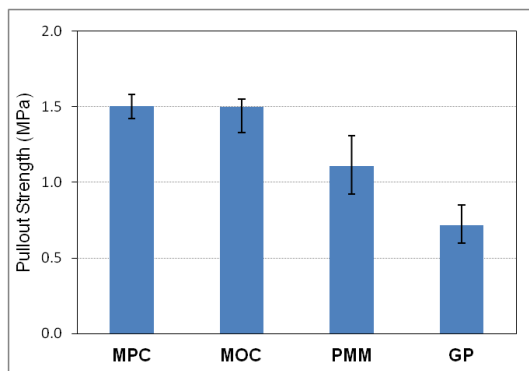


Fig. 8. Pullout strength of fiber sheets

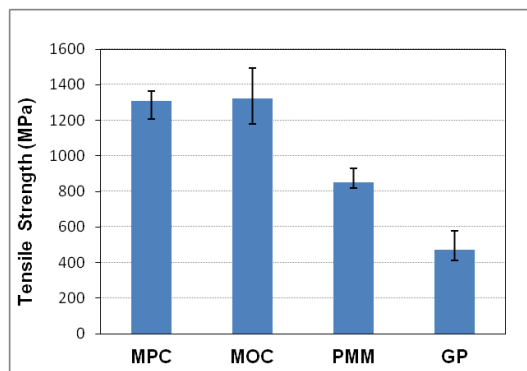


Fig.9. Tensile strength of FRiP composites

## Tensile strength of FRiP composites

The tensile strength of FRiP composites is important for the successful development of the FRiP strengthening technology. The matrix plays an important role in transferring force among fibers and the stress uniformity in fibers at the ultimate state. It should be mentioned that slip out of fibers from the matrix instead of fiber rupture was observed at the peak pullout loads. Fig.9 shows the tensile strength of FRiP composites with different inorganic matrices. It is shown that FRiP composites made from MOC and MPC have higher tensile strength. Fiber sheets in geopolymer matrix have the least tensile strength. The higher tensile strength of fiber sheets in MOC and MPC matrices is attributed to the better flow, high bonding properties, high tensile strength and better microstructure of these two matrices as mentioned in previous sessions. Since the vulnerability of MOC to water exposure may be a big concern (Deng 2003, Chan and Li 2009), MPC may become the most suitable candidate as the matrix material and bonding adhesive for the future development of the FRiP strengthening system. The tensile strength of PMM-based FRiP composites is inferior to that of MOC and MPC-based ones but superior to that of GP-based one as found in other mechanical tests.

## SEM analyses of FRiP composites

SEM analyses of FRiP composites were carried out to investigate the micro level interaction of matrices with fibers. As shown in Figs. 10a~10d, different inorganic matrices show different impregnation properties to fibers. Different inorganic matrices show different microstructures and impregnation properties to fiber sheets. MOC matrix has shown relatively higher impregnation characteristics with fiber sheets and tensile strength of the

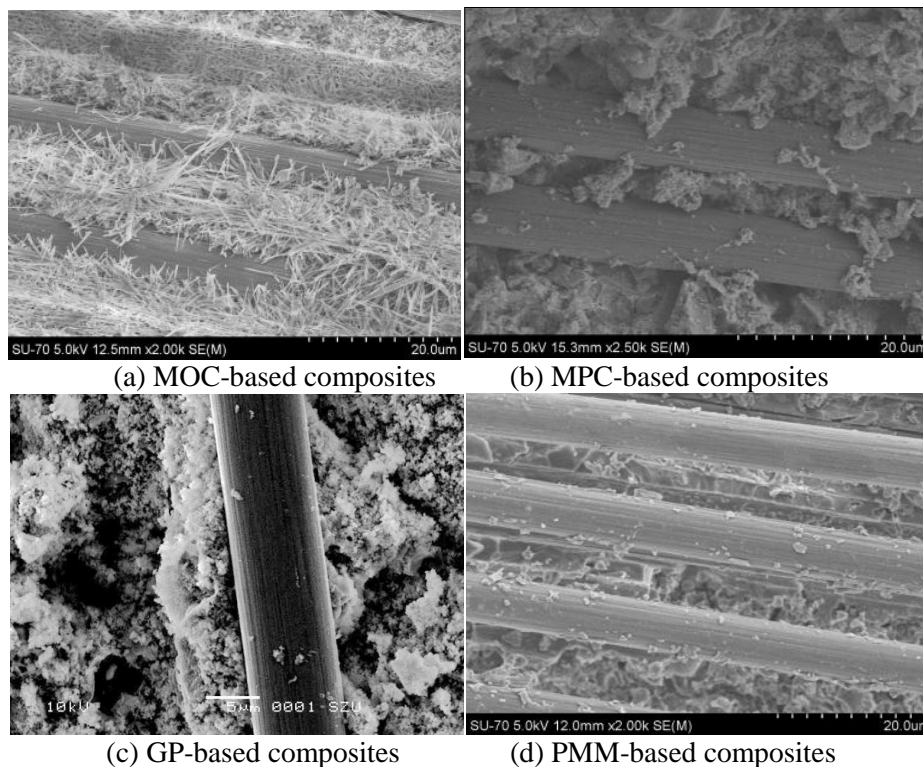


Fig. 10. SEM micrographs of different FRiP composites

formed FRiP composites. MPC also has shown a good impregnation property and favorable microstructure in the SEM micrograph (Fig. 10b). GP and PMM matrices show a relatively low impregnation into the fiber sheets (Fig.10c~10d), explaining well their lower bonding properties with fiber sheets and low strength of the formed FRiP composites.

## CONCLUSIONS

Based on a comparative experimental study on four typical types of inorganic cementitious materials, which can be used for develop FRiP strengthening systems for concrete structures, the following conclusions can be drawn up:

(1) MOC and MPC–based matrices exhibit significantly better performance in terms of the flow, mechanical strength, the bonding strength with cement mortar and fibers, and the tensile strength of the formed FRiP composites. Considering the vulnerability of MOC to water exposure, MPC becomes the most appropriate candidate for the future development of the FRiP strengthening system.

(2) Although quick setting of MPC is a favorable property for a matrix and adhesive material used in the FRiP strengthening technology, sufficiently long pot life and flow are necessary. Further optimization of the MPC matrix is deemed necessary in terms of its flowability, pot life, mechanical strength and bonding with fibers and concrete substrate.

(3) GP exhibits the most brittle behavior of all types of inorganic pastes. Compared to its compressive strength, its tensile strength is very low. PMM performs better than GP but is inferior to MPC and MOC in the FRiP strengthening system.

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