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Enhancement of durability of glass fiber-reinforced cement with PVA

QIAN Xiao-qian(钱晓倩)†, ZHAN Shu-lin(詹树林)

(*Department of Civil Engineering, Zhejiang University, Hangzhou 310027, China*)

† E-mail: qianxq@mail.hz.zj.cn

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Abstract: The main thrust of this research was to determine the effectiveness of polyvinyl alcohol (PVA) powder in enhancing the durability of short GFRC materials. Accelerated aging of the materials was achieved through low-pressure steam curing in a moist chamber. The strength and ductility of GFRC were measured by the direct tension test, which showed that incorporation of PVA powder into GFRC could improve its mechanical behaviour and turn it from brittle to ductile. To investigate the mechanism of the tensile strength enhancement, the fiber-matrix interface was examined by polarizing optical microscopy and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). It was found that PVA powder tended to migrate to the fiber-matrix interfacial zone and thus prevented the accumulation of calcium hydroxide in this area. PVA film around the fiber resulted in a more ductile interfacial microstructure and better bonding between fiber and matrix, which should be responsible for enhancing the tensile property and preventing the aging of GFRC. Furthermore, PVA powder reduced the microhardness and brittleness at the interface.

Key words: Glass fiber-reinforced cement(GFRC), Durability, Strength, Toughness, Polyvinyl alcohol(PVA), Polymer, Interface

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INTRODUCTION

Widespread applications of GFRC led to the development of alkali-resistant glass fibers with better resistance to alkaline attack in Portland cement-based matrices. However, the aging problem has not been completely eliminated by such fibers. Strength reduction is encountered in practice when GFRC is exposed to humid environments for a long period. Their ductility is also reduced, which shortens their service life.

The effect of aging of GFRC composites that displayed a crack advancing from a notch to intersect a perpendicular glass fiber strand (Bentur et al., 1986). Composites displayed ductile behaviour in the presence of unbroken filaments bridging across the crack. It was observed that the spaces between individual glass filaments within the strands were free of hydration products. Composites displayed brittle behaviour after aging because the crack advance broken the filaments. It was observed that hydration products existed in the individual filaments. Although the mechanism of the aging problem is not clear, the loss in strength and ductility of GFRC under wet environments could be attributed to chemical and physical factors (Hayashi et al., 1985). Chemical attack by some alkalis in moist cement environments makes the GFRC materials lose some of their tensile strength. The accumulation of calcium hydroxide physically fills up the spaces between and around the filaments of the glass fibers as GFRC ages in moist condition. It is the brittle property of calcium hydroxide that leads to the stress concentration under loading, and therefore leads to embrittlement of GFRC (Shah et al., 1988). SEM observations also showed no visible chemical degradation of the alkali-resistance glass fiber (Bentur et al., 1987). They pointed out that evidences of chemical attack on the glass fiber could be found only after prolonged aging, long after embrittlement had occurred; even then, the damage on the glass surfaces due to chemical attack was limited.

In trying to improve the durability of GFRC, the effects of polymer additions on

preventing the aging of GFRC were investigated (Bijen, 1983). Test results showed that the durability of GFRC could be enhanced by adding polymer emulsion into the matrix. It was found that when fibers were mixed with polymer-modified motar, the glass fiber filaments were surrounded by the polymer particles and thus were prevented from accumulation of calcium hydroxide and chemical attack. However, investigation on the effect of an acrylic-polymer emulsion at different dosage on aged GFRC showed that the polymer addition could not enhance the flexural performance of GFRC with accelerated aging (Soroushian et al., 1990).

Small amount of PVA powder could significantly increase the aggregate-paste bond strength and reduce the size of the interfacial transition zone (Chu et al., 1995). Changes in the microstructure of hydrated cement paste around steel and brass fibers induced by the addition of 1.4% PVA were studied (Chu et al., 1994; Najm et al., 1994). It was found that PVA's enhancement of bond strength was attributable to the formation of a ductile, fine-grained interfacial layer, and the effect of PVA on the nucleation of CH and C-S-H at the fiber surface. This interfacial layer led to a significant improvement in the bond strength as well as in the frictional resistance, which enhanced the pull-out work. Investigation on the enhancement of the smooth surface reinforcing steel bar with the addition of PVA powder showed that the interfacial parameters, especially for fracture energy, were greatly improved by incorporating PVA powders into the matrix and by coating the rebar surface with the PAV powder plus cement (Li et al., 1998a; Li et al., 1998b).

However, assessing which changes of the microstructure and interface in GFRC may lead to the embrittlement phenomenon is still not an easy task (Zhu et al., 1997) and till now, the effect of PVA powder on the aging of GFRC is still not very clear. The objectives of this investigation are: (1) to study the durability characteristics of PVA fiber-reinforced cement (PFRC), GFRC and PVA powder modified GFRC, and (2) to identify the failure mechanisms in PFRC, GFRC and PVA powder modified GFRC using polarizing optical microscopy, SEM with EDAX and microhardness technique.

EXPERIMENTAL DESIGN

To study the aging effects of GFRC, thin plate specimens manufactured by extrusion technique were selected. The 6mm thick specimens was subjected to an accelerated aging test of one year at 20℃ in wet condition, which according to time-temperature equivalency procedures (Litherland et al.), was equivalent to accelerated aging of one day in wet storage at 80 ℃. Durability characteristics were assessed through tensile test. The three sheet samples prepared for each batch were produced by the extrusion technique so that the most of the short fibers could be aligned into the loading direction by the high shear stress (Li et al., 1998b; Shao et al., 1997).

1. Materials, mix proportions and construction

The materials used in this investigation were: (1) short alkali-resistant glass fibers and PVA fibers (Table 1); (2) type I Portland cement; (3) ground blast-furnace slag (Table 2); (4) 1% superplasticizer by solid weight ratio of the cementitious binder to improve the workability and extrudability of the mixture. The mix proportions are listed in Table 3.

Table 1 Properties of the short glass and PVA fibers

Parameters	Glass fiber	PVA fiber
Density (g/cm^3)	2.53	1.3
Tensile strength (MPa)	3600	1500
Elastic modulus (GPa)	70	36
Length (mm)	12	6
Diameter (micros)	8	14
Aspect ratio	1500	430

Table 2 Chemical compositions of slag (%)

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	SO_3	Loss
34.48	16.56	2.78	0.44	0.44	0.20	39.50	2.40	1.48	0.50

Table 3 Mix proportions

	Slag/C	SS1/B	SS2/B	PVAF	GF	PVA/B	W/B
Batch #1	1.0	0.20	0.13	–	–	–	0.28
Batch #2	1.0	0.20	0.13	2%	–	–	0.28
Batch #31.0	0.20	0.13	–	2%	–	0.28	
Batch #4	1.0	0.20	0.13	–	2%	2%	0.28

Note: C, Cement; SS1 and SS2, 600 – 300 μm and 150 – 90 μm silica sand respectively; PVAF and GF, PVA and glass fiber volume ratio respectively; B, binder (cement + slag); W, water; PVA, PVA powder.

To disperse the short fibers uniformly and improve the interfacial zone between matrices and fibers, the cementitious slurry was prepared first, and then mixed with slag and cement, and PVA powder if applied. When this cementitious slurry was prepared, the short fibers were added to it and mixed for about 3 minutes. Then, all the other componentswere added and mixed another 3 minutes. The mixed dough-like fresh cementitious composites were then fed into the pugmill chamber of a single screw vacuum extruder (PVL100.3, KEMA). After further mixing, de-airing, and compacting in the extruder, the composites were pushed through a sheet die with cross sectional area of 300mm x 6mm. The extrudates were cured under a plastic cover, and after 24 hours, were placed in a KOTA Isothermal Testing System Chamber (SSE-28CI-A) for a 28-day equivalent low-pressure steam curing as ACI Recommended Practice 517.

2. Tensile strength test

For tensile tests, the specimens were obtained by cutting the extruded board into 75 mm × 250 mm × 6 mm plates. Each end of the specimen was glued onto two aluminum plates fixed by pins to loading fixtures connected to MTS hydraulic grips. On each side of a specimen, an LVDT was attached to measure the deformation of the specimen (Fig.1). These two LVDTs were connected through two AC conditioners to the digital controller of an MTS machine. The average displacement of these two LVDTs was used as a feedback signal to form a closed loop control.

3. Microscopic examination and microhardness of the interfacial zone

To examine the microstructure of the fiber-matrix interface, a polarizing optical microscope (Olympus BH-2, Japan) for qualitative analysis was used first and then SEM with EDAX (Philips XL 30) was employed for analysis of the chemical elements. Based on comparative morphology studies of concrete samples prepared by various methods, it could be concluded that the fractured surfaces revealed the fine crystal formations and reserved the soluble components along the interface (Marusin et al., 1995). The fracture surfaces along the fiber direction were used the optical microscope examination. The samples for low-energy secondary electrons (SE) with EDAX were sliced from the concrete sheet in a direction perpendicular to the fiber direction using a diamond saw, polished and coated with gold and stored in a vacuum desiccator until the examination (Jin, 1998).

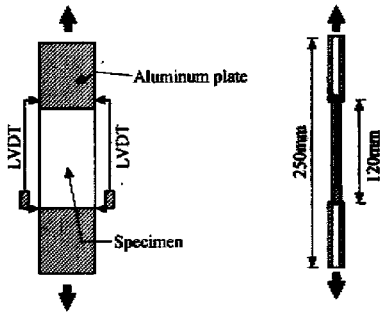

Fig.1 Setup of the direct tensile test

Fig.1 Setup of the direct tensile test

Microhardness along the fiber-matrix in-

terface was measured with Microhardness Tester (MHT-4, Zeiss). A Vickers indentation shape was used. The sample preparation for this test was very similar to that for the SEM observation but without the gold coating step.

RESULTS AND DISSUCTIONS

1. Tensile strength

The stress vs strain curve of the plain mortar sheet (batch #1) is shown in Fig.2. The peak stress was very low compared with those of the GFRC sheets (batches #2 – #4). The plain mortar sheet was also very brittle. The ultimate tensile strain was only around 2.0×10^{-4}. Almost no post-peak strain was recorded.

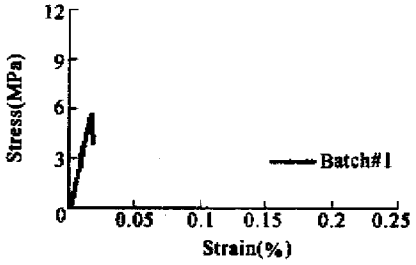

Fig.2 The tensile stress and strain curve for batch #1

For the PFRC sheet (batch #2), in addition to around 20% increases in the peak stress, the ultimate tensile strain and the tensile toughness were significantly increased (Fig.3). After the first throughout transverse

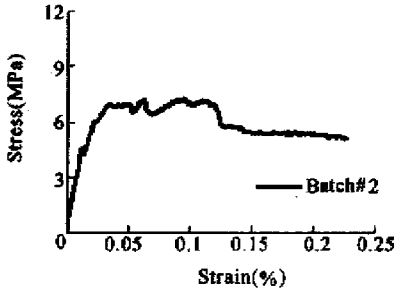

Fig.3 The tensile stress and strain curve for batch #2

matrix crack (the corresponding point at the stress-strain curve is called beyond over point-BOP), the short PVA fibers were able to bridge the crack and sustain the extra loading. A strain hardening response characterized by the multiple matrix cracking was observed. The ratio of the ultimate strain to the BOP strain is being > 8 may be attributable to the good fiber-matrix bonding and ductile properties of PVA fibers.

Fig.4 gives the tensile stress and strain relationship for aged GFRC sheet (batch #3).

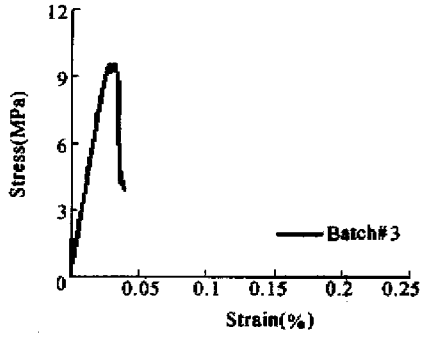

Fig.4 The tensile stress and strain curve for batch #3

Due to the higher strength and larger aspect ratio of the short glass fiber, the GFRC sheet had a much higher ultimate stress than the PFRC sheet (batch #2) at the same fiber volume ratio. However, the tensile strain corresponding to the peak stresses of this aged GFRC sheet (batch #3) was very small, only around 3.0×10^{-4}, and after the peak stress, the composites show a brittle failure mode, no strain hardening response. During the test, the specimens broke suddenly without any warning when the stress peaks were reached. Compared to the brittleness of the aged GFRC sheet, the modified with PVA powder GFRC sheet had significantly increased tensile strain and toughness (Fig.5). Strain hardening appeared and the failure mode changed. The ratio of the ultimate strain to the BOP strain reached to nearly five (Fig.5). The macro-structural test showed that the aging effect of GFRC could be prevented by the addition of small amount of PVA powder. The properties of the interfacial zone between the fiber and matrix were studied in our efforts to explore the micromechanism of this macrophenomenon.

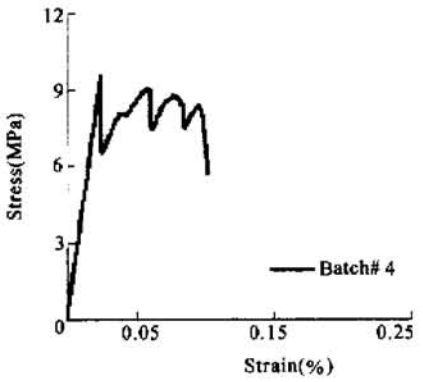

Fig.5 The tensile stress and strain curve for batch # 4

2. Microscopic examination of the fiber-matrix interface

Fractured surfaces of the batch # 2, batch # 3 and batch # 4 sheets were observed with a Polarizing Optical Microscope with magnification of 500 × . Typical micrographs of short fibers are shown in Figs.6, 7 and 8. In the optical micrograph of GFRC without PVA powder (Fig.7), the smooth surface of the glass fiber can been seen. No etching pits and local damages were found. This observation is consistent with the SEM images by Bentur and Diamond (Bentur et al., 1986).

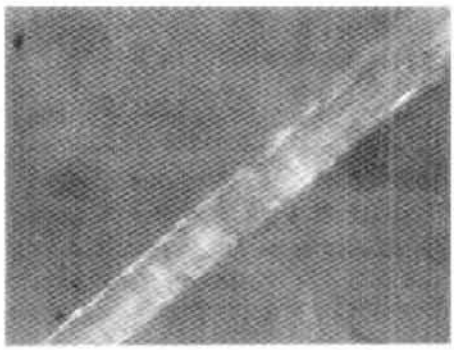

Fig.6 Typical PVA fiber (batch # 2) in the optical microscopic image (500 ×)

Fig.7 Typical glass fiber (batch # 3) in the optical microscopic image (500 ×)

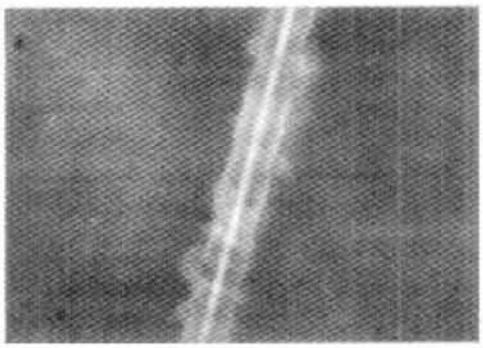

Fig.8 Typical glass fiber with PVA Powder(batch # 4) in the optical microscopic image (500 ×)

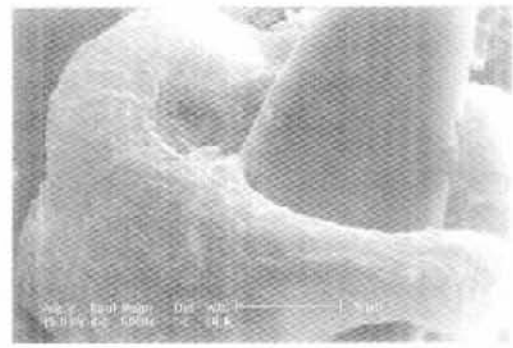

Fig.9 Typical SEM image of thin PVA film at glass fiber-matrix interface (batch # 4)

When PVA powder was added, the observable glass fiber surfaces were completely different from those without PVA powder. Fig.8 of typical glass fiber from a fractured specimen (batch # 4) shows polymer depositions attached to the glass fiber surface. The surface energy of the glass fiber filament could attract water-soluble polymer molecules, and thus led to accumulation of the polymer on the filament surface (Bijen, 1983). The slurry coating adopted in this study could accelerate this process. The resulting thin and ductile polymer (PVA) film formed around the glass fiber (Fig.9), prevented formation and accumulation of hydration products (especially the brittle calcium hydroxide) at the interface and strengthened the bond between the fiber and matrix. Thestress transition between fiber and matrix was smoother and the stress concentration was reduced. As shown in the

macrostructural tensile test, the tensile strain and toughness were considerably increased (Fig.5). Similar explanation can be found in Chu et al.'s study (Chu et al., 1994), in which the steel and brass fiber-matrix interfaces with PVA powder were investigated. The PFRC sheet was observed to have a rough PVA fiber surface (Fig.6). This phenomenon can be explained by the nucleation among PVA and CH and C-S-H (Chu et al., 1995) and results in a very good bonding between fiber and matrix and thus good tensile ductility of the specimen.

To further verify the polymer depositing phenomena, SEM with EDAX was used to investigate the chemical components at the fiber-matrix interface. The weight percent of elements was measured first then converted to molar number percent. The calcium/silica ratio (Ca/Si ratio) was analysed to identify the hydration products in the interfacial zone. As known, the Ca/Si ratio of the main hydration products was about 3: 1. However, if slag was used, this ratio would significantly decrease because the Ca/Si ratio of the CSH gel resulting from pozzolanic reaction was less than 1.5: 1; the pozzolanic reaction would consume a large amount of calcium hydroxide. Fig.10 and Fig.11 presented the average Ca/Si ratio at the glass fiber-matrix interface for the batch #3 and #4 samples respectively. To increase reliability, at least three Ca/Si values at the same distance away from the glass fiber were measured and their average value was adopted. From the figures, it could be seen that the interfacial zone was about 20 μm. For the batch #3 (Fig.10), the Ca/Si ratio was about 1.0 in the interfacial zone and 1.47 in the matrix. For the batch #4 (Fig. 11), this ratio was about 0.7 in the interfacial zone and 1.44 in the matrix. Thus, It could be concluded that PVA powder did not change the main chemical components of the hydration products in the matrix even though some researchers found that it changed the air content of the paste and mortar (Chu et al., 1994; Ohama, 1995). However, PVA powder changed the hydration products at the glass fiber-matrix interface. After addition of PVA powder, the Ca/Si ratio in the interfacial zone decreased, from 1.0 to 0.7. This implies that the amount of calcium hydroxide is reduced in this area.

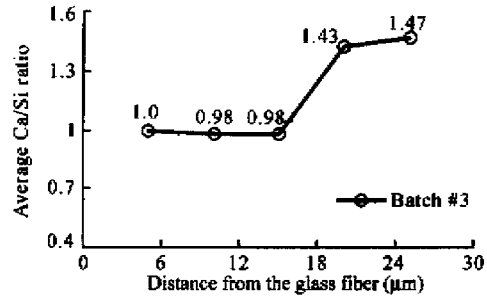

Fig.10 The average Ca/Si ratio of batch #3 in the glass fiber-matrix interface

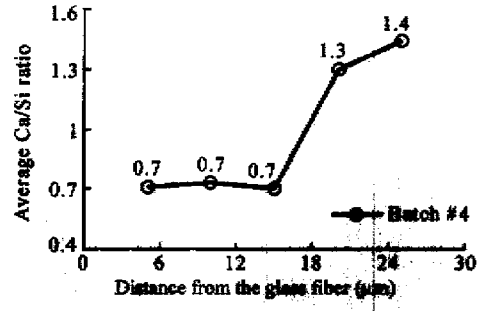

Fig.11 The average Ca/Si ratio of batch #4 in the glass fiber-matrix interface

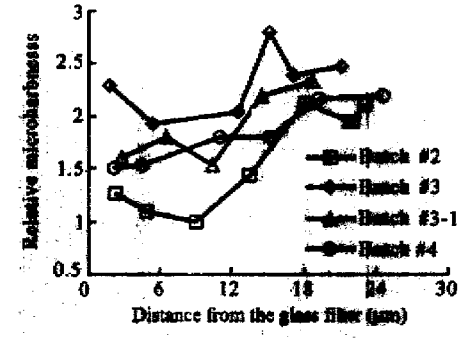

Fig.12 Relative microhardness comparison

3. Microhardness of the fiber-matrix interface

Fig. 12 shows relative values of microhardness are plotted against the distance from the boundary of the fiber. Batch #3-1 samples were the same as batch #3 samples in composition but were cured 28 days under normal condition (20 ℃, RH > 90%) after the samples were prepared. The higher values usually represent stiffer interfaces. Just as assessed by SEM with EDAX, the interfacial zones were also found to be around 20 μm for

these short micro-fibers. It was observed that the glass fiber-matrix interface was stiffer than the PVA- fiber-matrix interface. After the aging, the microhardness of the glass fiber-matrix interface increased, which led to an observed brittle failure mode. PVA powder can reduce the embrittlement of the glass fiber-matrix interface, and thus prevent the aging of GFRC. These microhardness values further explain the above tensile test results and also verify the microscopic examinations.

CONCLUSIONS

The aging of the interface between the alkali-resistant glass fiber and the cementitious matrix reduces the ductility and toughness of the GFRC. Addition of PVA powder can prevent or reduce the aging of GFRC. The following conclusions were drawn from the current study.

PFRC has very good ductility and toughness as shown by the tensile test. The ratio of post BOP strain to the BOP strain is very high. GFRC is very brittle when exposed to accelerated aging environment. No chemical damage is observable on the surface of the alkali-resistant glass fiber after the aging of GFRC. The observably tough surface of PVA fiber could have resulted from some chemical reactions between the fiber surface and the matrix. This may lead to good interfacial bonding and ductile tensile behaviour.

It was found that PVA powder could improve the interface of the glass fiber and matrix and also improve the tensile strain and ductility of GFRC significantly. The microstructural test and analysis showed that the mechanism of enhancement ductility and toughness could be attributed to the migration of the water-soluble PVA to the surface of the glass fiber. The thin PVA film formed on the glass fiber surface prevented the fiber from accumulating calcium hydroxide, and therefore resulted in a less brittle interfacial zone. It was the thin ductile film that caused the interfacial stress concentration to decrease.

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