Properties of GRC modified by emulsion

Z. LIU, Q. CUI and Q. LI
China Building Materials Academy, China

Abstract

Mechanical properties and durability have always been the key issues in the development of Glass fiber Reinforced Cement (GRC). Various approaches have been taken in many countries to solve the problem. In some countries siliceous materials and polymer emulsion are added to ordinary Portland cement to modify the cement mortar, while the approach of alkali-resistant glass (AR-glass) fiber reinforced sulphoaluminate cement is being adopted in China. In this paper, acrylic polymer emulsion is added into two kinds of cement mortars to develop the high strength and crack-resistant GRC product. By testing the mechanical properties and durability of GRC samples, the optimal dosage of polymer emulsion in different cement mortars is obtained. From the observation of the microstructure using scanning electronic microscopy (SEM), the mechanism of polymer emulsion modifying GRC is analyzed, and hence the internal relation between the microstructure and macroscopic properties is revealed.

Keywords
GRC, AR-glass fiber, ordinary Portland cement, sulphoaluminate cement, acrylic polymer emulsion, macroscopic properties, microstructure

INTRODUCTION

GRC is a kind of high performance cement-based composite, mechanical properties and durability have always been the key issues in the development of GRC[1]. Various approaches have been taken in many countries to solve the problem. In some countries siliceous materials and polymer emulsion are added to ordinary Portland cement to modify the cement mortar, while the approach of alkali-resistant glass fiber reinforced sulphoaluminate cement is being adopted in China[2].

The practice of adding polymer emulsions to cement mortar is now widespread and the mechanical properties of many such GRC products are well reported. Among the various advantages claimed for these polymer emulsions, a better workability of the matrix and an improvement in the mechanical strengths and durability of the GRC product are perhaps the most important[3-5]. The incorporation of polymer emulsions usually lowers the stiffness of cement mortar, which can reduce the stress. For the manufacture of GRC product it has been found that the addition of polymer emulsion allows a certain slurry of much lower water/cement (w/c) ratio.

Many different types of polymer emulsions have been examined for their suitability as a component in GRC and composite samples have been exposed to different environments. Allen and Channer[6] suggested that acrylic polymer emulsion protected the glass fibers to a certain extent from the corrosive action of cement, thereby enhancing the long-term durability of such composites. In this study, we add the acrylic polymer emulsion to two kinds of cement mortars, which are sulphoaluminate cement and ordinary Portland cement (OPC) plus fly ash, to develop the high strength and crack-resistant GRC product. By testing the mechanical properties and durability of GRC samples, the optimal dosage of polymer emulsion in different cement mortars is obtained.

MATERIALS AND METHODS

Materials

(1) Cement: 42.5 grade sulphoaluminate cement, grade 42.5 OPC, their oxide compositions are listed in Table 1.
(2) Fly ash: In the study on polymer modified GRC, the matrix of some samples consist of 50 weight% OPC and 50 weight% fly ash. Its oxide compositions and fineness data are given in Table 1.
(3) Glass fiber: An AR-glass fiber mesh with 16.7% content is used in the study. The main properties of the mesh are listed in Table 2.

Table 1. *Data for cement and fly ash*

Oxide (weight %)	Sulphoaluminate Cement	OPC	Fly Ash
	9.03	22.60	44.50
	2.86	2.10	4.50
	25.15	7.06	35.00
CaO	44.97	56.72	9.10
MgO	1.16	3.58	0.58
	9.88	2.68	0.48
	0.34	1.14	1.16
	0.08	0.18	0.64
	0.30	0.93	1.40
IL	5.60	3.04	3.08
Fineness(/kg)	415	355	460

Table 2. *Main properties of AR-glass fiber mesh*

Hole size/ mm	Surface density/ g/	Elastic modulus/ GPa	Breaking strength/ N/50mm		Breaking extent/ %	
			Warp	Weft	Warp	Weft
5×5	164	80.4	1345	1367	2.7	2.8

(4) Polymer emulsion: A commercially produced acrylic polymer emulsion is used in the study. The main properties of the polymer emulsion are listed in Table 3.

Table 3. Main properties of acrylic polymer emulsion

Appearance	Solid content (weight %)	pH	Viscosity(cps)	Minimum film-forming temperature(℃)	Glass transition temperature(℃)
Milky white	47	9.7	45	12	6

(5) Anti-foam agent: A commercial anti-foam agent is incorporated in the polymer-containing mixes at a level of 0.1% of the weight of sulphoaluminate cement or OPC plus fly ash.

(6) Sand: River sand, fineness modulus is 3.14, maximum grain size is 2mm, fine content is 1.2%.

(7) Admixture: Superplasticiser made by China Building Materials Academy.

(8) Water: Tap water

METHODS

GRC formulation

We make the GRC samples according to GB/T 15231-2008 (*Test methods for the properties of glass fiber reinforced cement*). The fluidity of the cement mortar increases and the w/c ratio decreases after the polymer emulsion added. We adjust the water to keep the similar fluidity about 285±3mm by JC/T 986-2005 (*Cementitious grout*). Table 4 lists the GRC formulation in this study.

In the manufacture of polymer modified GRC samples, the proportion of polymer solids used is 0-21% of the weight of cementitious materials. S0 is the control sample made of sulphoaluminate cement without polymer emulsion while P0 is the control sample made of OPC plus fly ash without polymer emulsion. The double layers glass fiber meshes are fixed at the position about 2mm away from the upper and bottom surfaces of the GRC sample. For each formulation, several GRC panels are prepared and cured in four conditions:1) S0 is cured in cabinet for 3 days at 95% relative humidity(RH) and 20℃; 2) S1-7 are cured in cabinet for 3 days at 65% RH and 20℃ to allow the polymer to dry out and form a film; 3) P0 is cured in cabinet for 28 days at 95% RH and 20℃; 4) P1-7 are cured in cabinet for 28 days at 65% RH and 20℃. After curing, the panels are cut into test samples measuring 250mm×50mm×10mm and 120mm×50mm×10mm, as shown in Figure 1 and Figure 2.

Table 4. GRC Formulation

No	Cement	Fly ash	Sand	w/c	Polymer solid/cementitious materials (weight %)	Superplasticiser	Anti-foam agent
S0	100	0	100	0.350	0	0.6	0.1
S1	100	0	100	0.315	3	0.6	0.1
S2	100	0	100	0.300	6	0.6	0.1
S3	100	0	100	0.287	9	0.6	0.1
S4	100	0	100	0.275	12	0.6	0.1
S5	100	0	100	0.269	15	0.6	0.1
S6	100	0	100	0.265	18	0.6	0.1
S7	100	0	100	0.256	21	0.6	0.1
P0	50	50	100	0.395	0	0.8	0.1
P1	50	50	100	0.380	3	0.8	0.1
P2	50	50	100	0.373	6	0.8	0.1
P3	50	50	100	0.338	9	0.8	0.1
P4	50	50	100	0.315	12	0.8	0.1
P5	50	50	100	0.295	15	0.8	0.1
P6	50	50	100	0.290	18	0.8	0.1
P7	50	50	100	0.289	21	0.8	0.1

Figure 1. *Flexural strength test samples*

Figure 2. *Impact strength test samples*

Flexural strength test
Flexural strength tests are carried out by a WD4100 electronic testing machine, in four-point loading, with a span of 210 mm and a loading speed of 5 mm/min. The limit of proportionality (LOP) and modulus of rupture (MOR) are recorded, as shown in Figure 3.

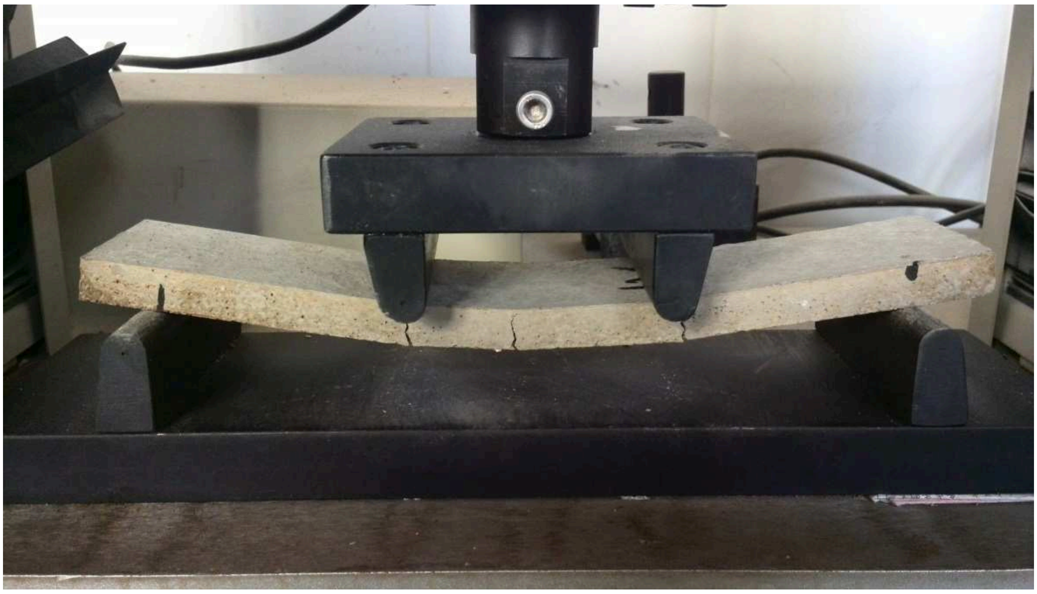

Figure 3. *Flexural strength testing*

Impact strength test
Impact strength tests are carried out by an XCJ-50 Charpy impact machine. The impact energy are recorded, as shown in Figure 4.

***Figure 4**. Impact strength testing*

RESULTS AND DISCUSSION

The test results of flexural and impact strengths of GRC samples after curing are shown in Figures 5, 6 & 7.

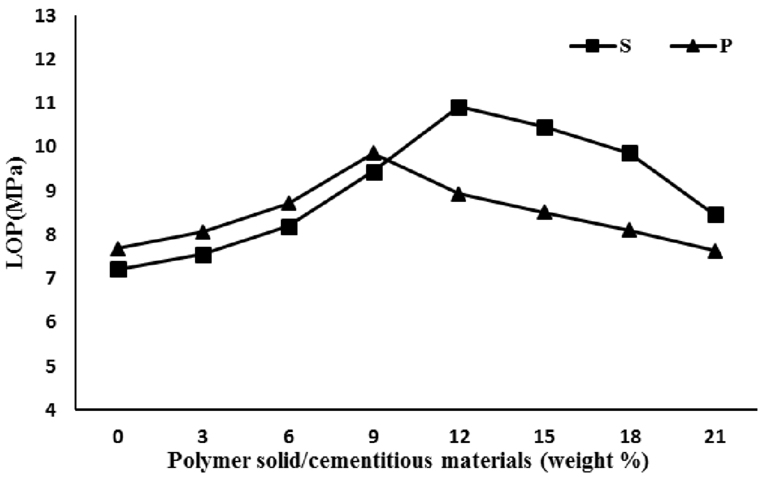

***Figure 5**. LOP of GRC sample after curing*

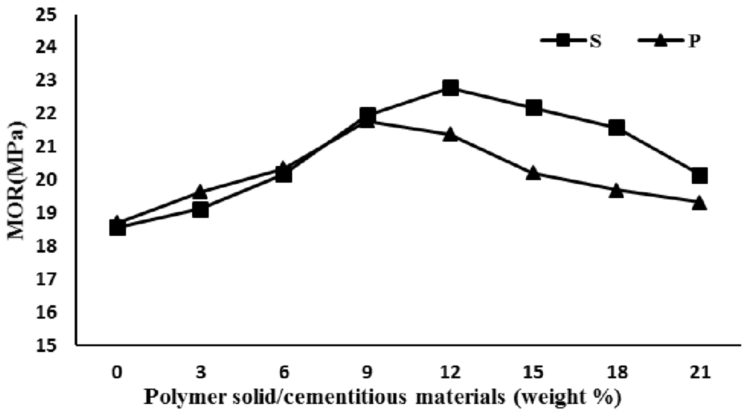

Figure 6. *MOR of GRC sample after curing*

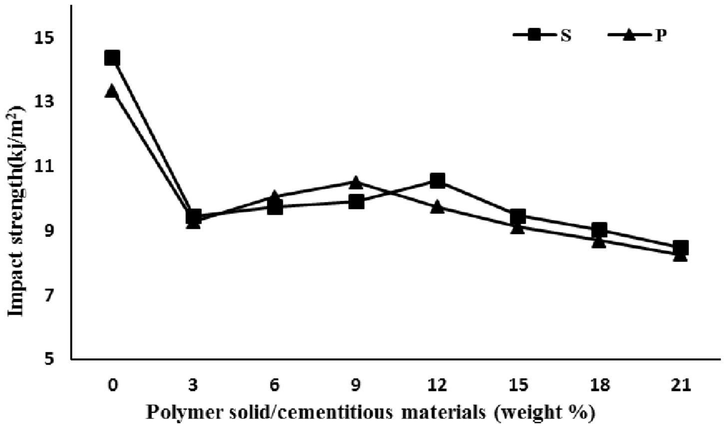

Figure 7*. Impact strength of GRC sample after curing*

Flexural strength of GRC

From Fig. 5 and 6, we can find that the flexural strengths of GRC samples have the similar change rules: 1) The LOP and MOR strengths of GRC samples firstly increase to the peak point and then decrease whereas all meet the requirements of JC/T 1057-2007 (*Glass fiber reinforced cement panel for exterior wall*) (LOP≥7.0, MOR≥18.0). 2). We get the biggest LOP and MOR strengths when the polymer solid is 12% of the weight of sulphoaluminate cement and 9% of the weight of OPC plus fly ash. 3) At 12 weight% polymer solid addition, improvements of S4 in LOP and MOR strengths over the control of up to 41.63% and 22.66%. At 9 weight% polymer solid addition, improvements of P3 in LOP and MOR strengths over the control of up to 28.39% and 16.41%. It is assumed that the polymer film aids in avoiding the formation of zones of stress concentrations in the matrix by distributing strains more uniformly. Some flaws may also be filled by the polymer particles.

Impact strength of GRC

From Fig. 7, we can find that the impact strength values of GRC samples with different cementitious materials are similar to those described above for LOP and MOR strengths: 1) The impact strengths of GRC samples with polymer emulsion firstly increase to the peak point and then decrease whereas all are smaller than the control samples without polymer emulsion and meet the requirement of JC/T 1057-2007(*Glass fiber reinforced cement panel for exterior wall*) (impact strength≥8.0 KJ/). This is because acrylic polymer emulsion reduces the elastic modulus of GRC samples.

Freezing-thaw cycle resistance of GRC
GRC samples are removed out from curing condition and put into the 20℃ water for 1 day. Then freeze the samples for 2 hours at -20℃ and thaw them for 1 hour at 20℃ as a whole cycle. We test the mechanical properties of GRC samples after 25 cycles. The mechanical properties of S4 & P3 before and after the freezing-thaw cycle are shown in Table 5.

Table 5 *Freezing-thaw cycle resistance of GRC*

No		LOP/ MPa	MOR/ MPa	Impact strength/ KJ/
	Before	10.92	22.79	10.55
S4	After	9.77	20.58	9.52
	Strength Loss/ %	10.53	9.70	9.76
	Before	9.86	21.78	10.51
P3	After	8.83	19.61	9.48
	Strength Loss/ %	10.45	9.96	9.80

From Table 5 we can find that the strength losses of LOP, MOR and impact strength of S4 are 10.53%, 9.70% and 9.76% respectively while the strength losses of P3 are 10.45%, 9.96% and 9.80%. There is no crack, spall or delamination in the GRC samples.

Accelerated ageing test of GRC
In line with the experimental program, some GRC samples are stored in a natural weather condition in an open and approximately horizontal position in Beijing while other samples are placed in 50℃ water. After the specified ageing time is reached, GRC samples are taken out from the ageing environment, then the flexural and impact strength tests are carried out. The mechanical properties of GRC samples are shown in Figures 8, 9 & 10.

From Figures 8, 9 & 10 we can find that the LOP and MOR strengths of GRC samples firstly increase to the peak point and then decrease by time no matter exposed in air or hot water. The mechanical properties of GRC samples in hot water are higher than the ones in air during the first week because the cement grains in hot water continue hydration reaction more quickly. As the ageing time going on, the mechanical properties of GRC samples in hot water are lower than the ones in air. The impact strength of GRC samples always decreases by time no matter in air or hot water. After ageing in air for 180 days, the retention ratios of LOP, MOR and impact strengths of S4 are 82.78%, 87.45% and 78.96% while P3 are 84.48%, 87.97% and 76.12%. After ageing in hot water for 180 days, the retention ratios of LOP, MOR and impact strengths of S4 are 78.57%, 82.36% and 69.38% while P3 are 82.25%, 83.47% and 66.60%.

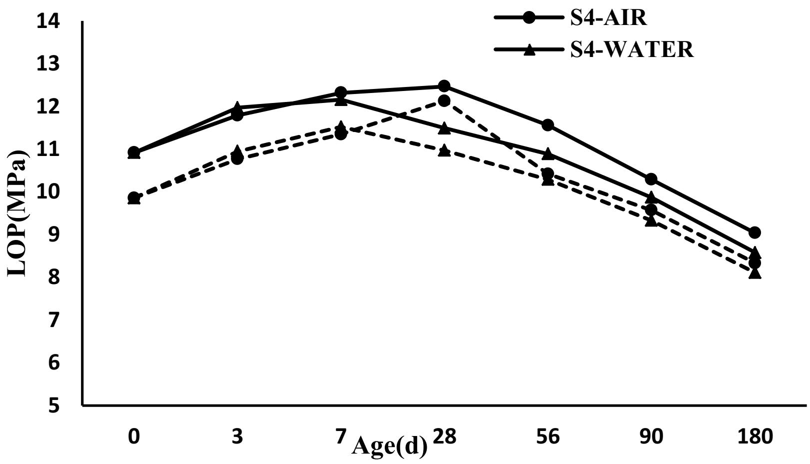

Figure 8. *LOP of GRC samples after accelerated ageing test*

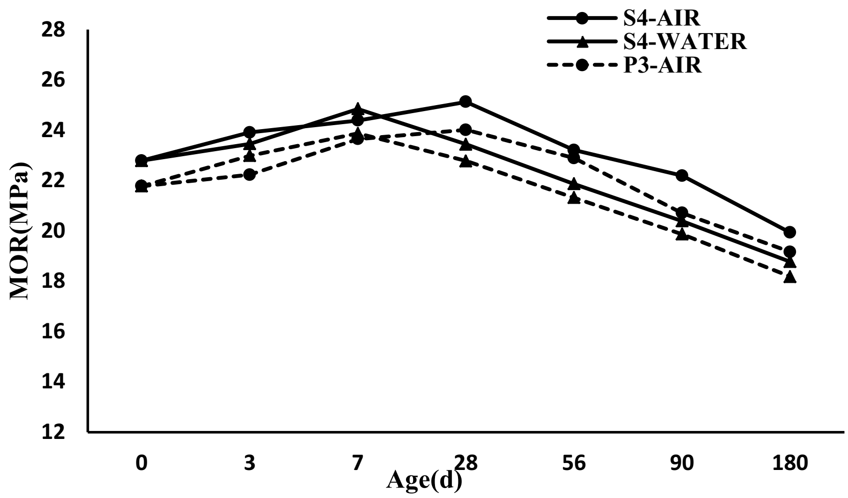

Figure 9*. MOR of GRC samples after accelerated ageing test*

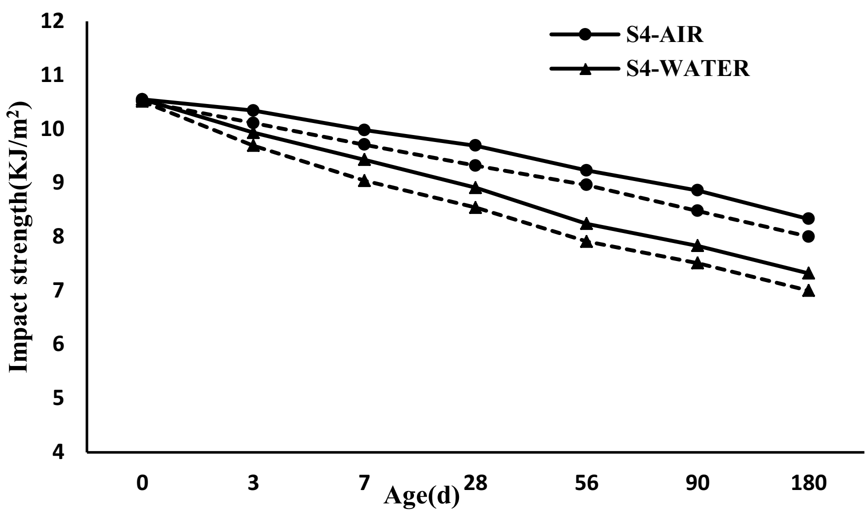

Figure 10. *Impact strength of GRC samples after accelerated ageing test*

Observation of glass fiber surface and cement mortar
A broken sample is placed immediately in pure alcohol. Prior to observation a surface layer of GRC is removed and a small sample is taken. The surface needs to be fresh and contain cement hydration products and glass fiber. The surfaces of glass fiber and cement mortar subjected to different ageing conditions are observed by SEM and are shown in Figures 11 to 18.

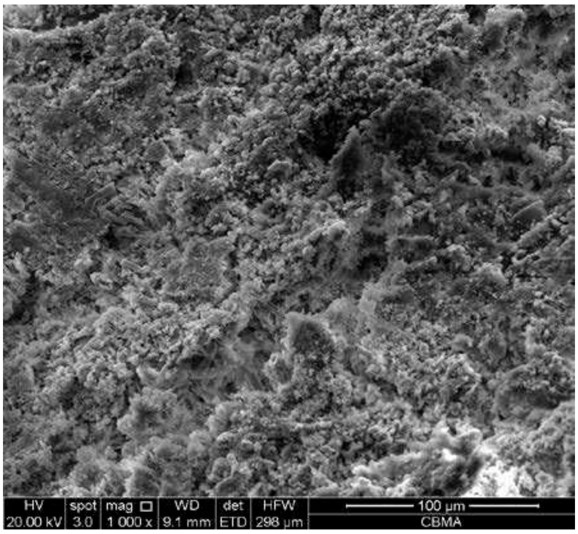

Figure 11. *Cement mortar in S4 (cure at 65% RH, 20℃, 3 days)*

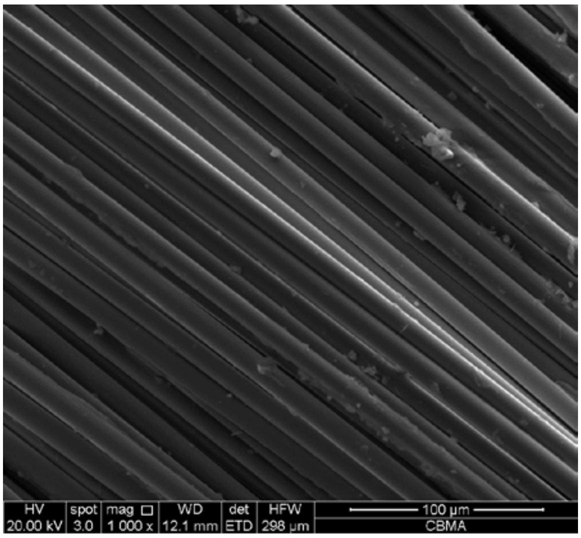

Figure 12*. Glass fiber in S4 (cure at 65% RH, 20℃, 3 days)*

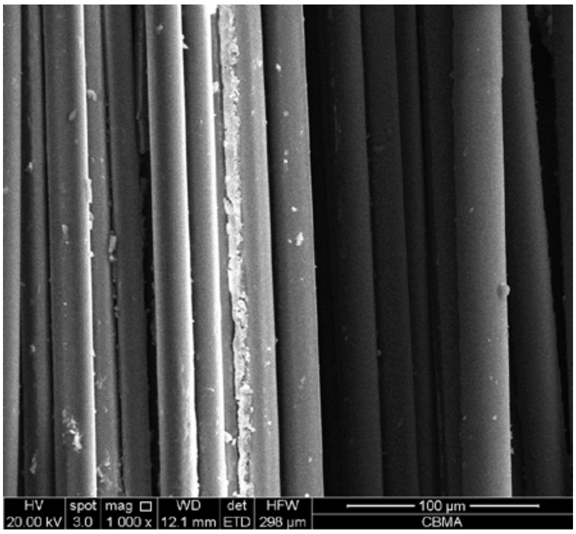

Figure 13. *Glass fiber in S4 (in air, 180 days)*

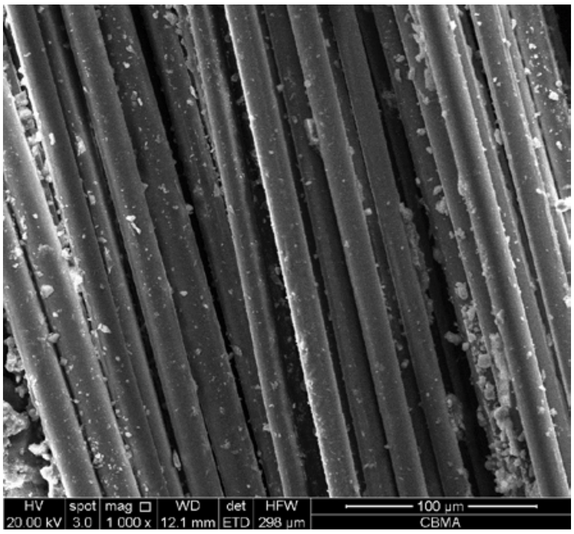

Figure 14. *Glass fiber in S4 (in hot water at 50℃, 180 days)*

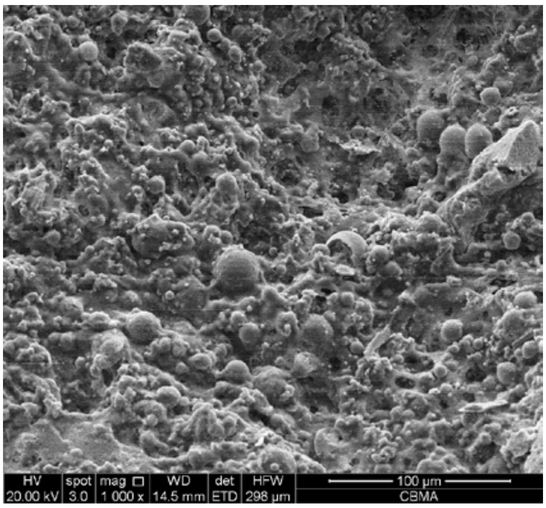

Figure 15. *Cement mortar in P3 (cure at 65% RH, 20℃, 28 days)*

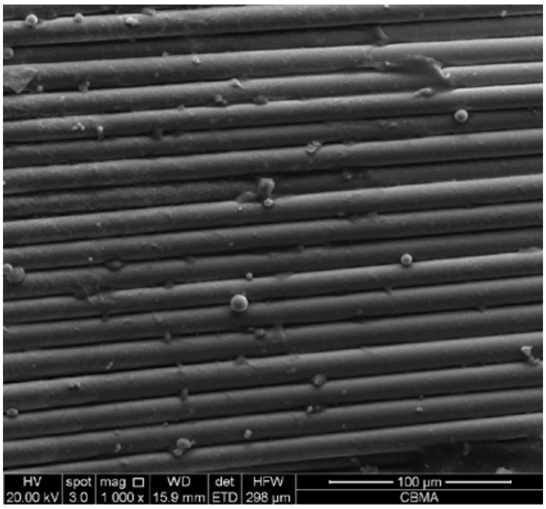

Figure 16. *Glass fiber in P3 (cure at 65% RH, 20℃, 28 days)*

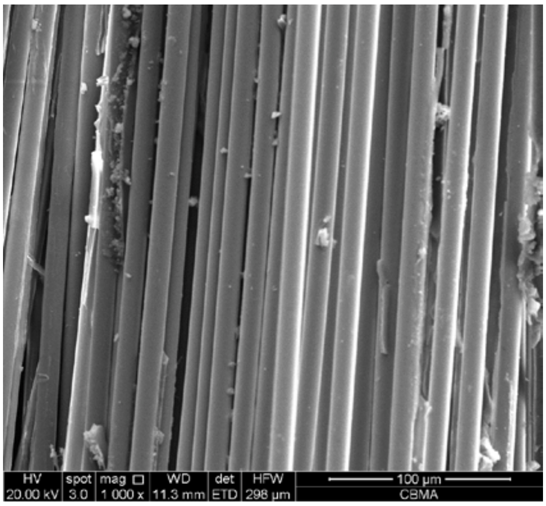

Figure 17*. Glass fiber in P3 (in air, 180 days)*

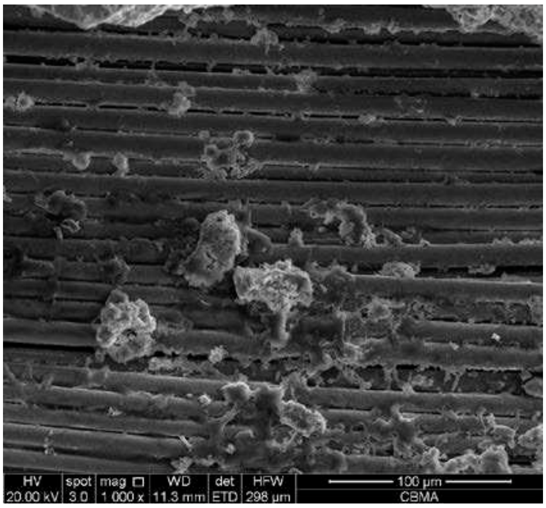

Figure 18. *Glass fiber in P3 (in hot water at 50℃, 180 days)*

From Figure 11 and Figure 15 it can be seen that initially a film of the polymer is formed around cement grains which prevents normal hydration of the cement and the polymer modified cement mortar is very compact. At the same time, the adhesive nature of the film plays a part in providing a vehicle for stronger adhesion among the constituents. From Fig. 12 and 16 it can be seen that for 3 days and 28 days curing, the outline of glass fiber in S4 and P3 is very clear and its surface has a few attachments. However, for GRC samples aged in air and hot water at 50℃ for 180 days, the outline of glass fiber is different. The surface of glass fiber is still smooth for the samples in air whereas the surface of glass fiber has visible corrosion marks for the samples in hot water. This microscopic analysis results support the test results for mechanical properties.

In the presence of hot water, particularly over long time and under the alkaline conditions prevailing in cement hydration, the film loses its integrity and the alkali attack on the glass fiber can progress, reducing its strength considerably.

CONCLUSIONS

1) The optimal dosage of acrylic polymer emulsion is 12% of the weight of sulphoaluminate cement and 9% of the weight of OPC plus fly ash. The LOP, MOR and impact strengths of GRC samples are biggest at the optimal dosage and the adhesive nature of the polymer film plays a part in providing a vehicle for stronger adhesion among the constituents.
2) The polymer modified GRC samples have good freezing-thaw cycle resistance. The retention ratio of mechanical properties are around 90% after 25 cycles because a film of the polymer is formed around cement grains which prevents normal hydration of the cement.
3) The polymer modified GRC samples have good durability. The retention ratio of mechanical properties are over 75% in air and 65% in hot water after 180 days. In the presence of hot water, particularly over long time and under the alkaline conditions prevailing in cement hydration, the film loses its integrity and alkali attack on the glass fiber can progress, reducing its strength considerably.

ACKNOWLEDGEMENTS

Financial support from the National Science & Technology Support Program (2014BAL03B04) approved by the Ministry of Science and Technology in China is gratefully acknowledged. Thanks are also due to the State Key Laboratory of Green Building Materials for assistance in test.

REFERENCES

[1] Shen Rongxi, Cui Qi, Qinghai. New Fiber Reinforced Cement-based Composite [M]. Beijing: China Building Materials Industry Press, 2004.
[2] Wang Yanmou. China Glass fiber Reinforced Cement [M]. Beijing: China Building Materials Industry Press, 2000.
[3] Polymers in concrete. Proceeding International congress on Polymer Concrete. London. UK. 1975(The Construction Press Ltd.Lancaster.1976).
[4] Polymers in concrete. Proceeding 3rd International congress on Polymers in Concrete. Koriyama. Japan.1981(Nihon University,1982)two volumes.
[5] West, J.M., deVekey, R.C. and Majumdar, A.J. Acrylic polymer modified GRC composites 16 No1(January 1985). pp 33-40
[6] Allen,H.G. and Channer,R.S. Some mechanical properties of polymer modified Portland cement sheets with and without glass fiber reinforcement. Ibid. pp 282-289.