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Chemical Resistance of Polyvinylalcohol Reinforcing Fibers

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Abstract: This paper describes a research project performed on the chemical stability of polyvinylalcohol (PVA) fibers used as reinforcement in cementitious composites. PVA fibers were treated with sodium hydroxide and hydrochloric acid solutions for different periods of time, respectively. Subsequently, both the mass loss ratio and the retained strength were measured. The surface morphology of the fibers was characterized using a scanning electron microscope (SEM), and the crystal structure of the fibers was measured using X-ray diffraction (XRD). Finally, original and treated fibers were used to prepare the cementitious mortar respectively, and the effects of fibers with different treatments on the mechanical properties of composites were tested. The results indicate that chemical treatment causes small mass loss and change of surface morphology. The chemical treatment has no significant influence on the strength of PVA fibers; however, the decrease of grain size in PVA fibers has a beneficial effect on the strength. For the fibers treated by alkaline solution, the tensile strength is somewhat higher than that by acid solution under the same conditions. The chemical treatment can bring small deviations in the consistency of the strength between fibers and mortars. This may be attributed to the kinking of fibers during the chemical treatment process.

Key words: *Chemical resistance; Fiber-reinforced mortar; Fibers.*

Introduction

Due to the brittleness and high cracking potential of normal concrete, much of the world is experiencing an alarming trend toward serious deterioration of civil infrastructures exposed to a combination of mechanical and environmental loads [1, 2]. High performance fibers are frequently applied to prepare fiber-reinforced composites (FRC) featuring high toughness and crack-stopping capability [3, 4]. An ultra ductile cementitious composite, called engineered cementitious composite (ECC), which is highly crack-resistant with a tensile strain capacity over 300 times that of normal concrete, has attracted the serious concern of researchers [2, 5]. ECC utilizes essentially the same ingredients as normal concrete; however, it does not include coarse aggregates, and it employs a small amount of polyvinylalcohol (PVA) fibers, which have high strength and modulus of elasticity apart from the strong bonding strength between fiber and cement matrix. Because of its unique tensile property and enhanced durability, ECC has seen increasing field applications recently in transportation infrastructures [2, 5].

Chemical corrosion on cementitious composites is often unavoidable, as structural elements and systems, such as concrete pavements, bridge piers, off-shore platforms, and equipment in marine applications, may be exposed to various corrosive medium in practical applications [4]. Thus, various investigations have been conducted recently on the durability performance of ECC mixture. According to these investigations, ECC mixtures are highly durable under accelerated weathering tests [6-8], freeze–thaw cycles with/without de-icing salts [9], and reinforcement corrosion [10]. However, most of the previous studies focused on the fabricated materials in which the fibers were covered by matrix [4, 11], which means that little attention was devoted to the fibers themselves. In fact, the resistance of the fibers to corrosion investigated previously was mainly dependent on the matrix's corrosion-resistance in fiber-reinforced composites.

On the study of extracted fibers, Akers et al. indicated that the alkaline environment would cause some changes in the crystal structure of PVA fibers [12]. Damage may be noticed after a prolonged exposure in a severe environment. As the main bearing materials in composites, chemical resistance of PVA fibers will have an important impact on the durability of FRC. Therefore, it's necessary to investigate the performance of acid and alkali resistance of PVA fibers. Furthermore, long-term durability and performance data will promote the extensive use of this fiber. Since it's difficult to simulate the actual corrosion course of the environment, in this investigation, the PVA fibers were soaked in high concentrations of NaOH or HCl solutions for a few days to accelerate their aging and corrosion, excluding the influence of the matrix and revealing clear and accurate response of the fibers to the chemical corrosion. Tensile strengths, surface morphology, and crystal structure of the fibers were then measured successively. Besides, the original and treated fibers were both used to prepare fiber-reinforced mortar in order to analyze the potential effect of chemical treatment of this fiber on the strength of composites.

Experimental

Materials

In the experiments, ordinary Portland cement (type P.O. 42.5, China), low-calcium fly ash (Grade I, China), clean sand with fineness modulus of 1.75 and PVA fibers (diameter = 40 μm, tensile strength = 1600 MPa, elastic modulus = 42 GPa, Kuraray, Japan)

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Table 1. Proportions of PVA Fiber-reinforced Mortar.

Mixture	Mix Proportion（kg/m^3）					
	Cement	Fly Ash	Water	Sand	Water-reducing Admixture	Fibers
C	632.5	632.5	354.2	468.1	5.20	0
I	632.5	632.5	354.2	468.1	6.33	6.5
Ⅱ	632.5	632.5	354.2	468.1	7.59	13.0

Table 2. Fibers with Different Treatments.

Sample	Solution	Treating Time	Sample	Solution	Treating Time
N1	2 mol/L NaOH	6 days	H1	2 mol/L HCl	6 days
N2	2 mol/L NaOH	12 days	H2	2 mol/L HCl	12 days
N3	4 mol/L NaOH	6 days	H3	4 mol/L HCl	6 days
N4	4 mol/L NaOH	12 days	H4	4 mol/L HCl	12 days

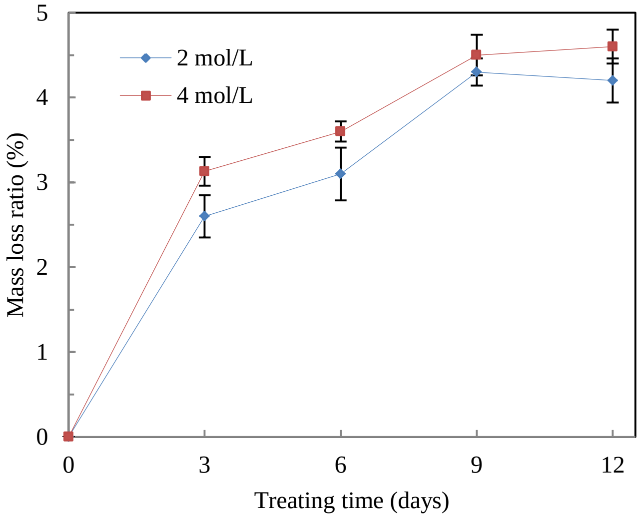


Fig. 1. Mass Loss Ratio as a Function of Treating Time (NaOH).
Note: Error bars indicate one standard deviation among three specimens.

were used to prepare the fiber-reinforced composite. The chemical admixture used was a polycarboxylic acid high-range water-reducing admixture. The mixture proportions of PVA fiber-reinforced mortar are shown in Table 1, where the volume fraction of fiber is 0, 0.5% and 1.0%, respectively. The amount of high-range water-reducing admixture in each mixture was slightly adjusted to achieve consistent workability. The flow of all the mixtures was within the range of 170-180 mm, according to ASTM C1437–07. The products used to prepare the solutions were laboratory reagents: ACS-ISO 98% pure NaOH pellets and 37% HCl solutions.

Methods

The fibers coded in Table 2 were soaked in NaOH or HCl solutions respectively, with the treating time ranging from 3 to 12 days at the increments of 3 days under the temperature of 25°C. To reveal the influence of corrosion medium concentration on the performance of PVA fibers, the concentrations of 2 mol/L and 4 mol/L were both adopted for the two solutions. After the treatment, the fibers were immersed in water for 24 hours to remove the residual chemical medium and dried in an oven. Then, the mass losses were determined. To make the measurement accurate, the fibers were dried to constant weight at 50℃. This test may be regarded as a rather extreme accelerated aging test involving such high concentrations of corrosion medium.

A single fiber was tested on a universal testing machine (Instron 3369) according to ASTM D3822-01 with the cross head speed of 0.5 mm/min. Since the tensile strength of single fiber was sensitive to the accuracy of measurement, and the extraction of fibers from a bundle may cause the weakest ones to fracture in the process, at least 20 specimens were tested for each set of fibers.

The surface morphologies of the fibers before and after the treatment were characterized using a Hitachi S-4800 (Japan) SEM. In addition, XRD (X'Pert MPD PRO diffractometer, Holand) was employed to investigate the influence of chemical solutions on the crystallization of PVA fibers using CuKα radiation (λ=0.154059 nm). Measurement conditions were as follows: the X-ray tube worked at 40 kV and 30 mA and the data were collected from 10° to 70° (2θ) during 10 min for the original and treated fibers.

In order to monitor the possible effect of chemical treatment on the mechanical property of the composites, virgin and 6 and 12 days treated fibers were used to prepare cementitious mortars. De-molding was carried out between 22 and 24 hours after molding and then the specimens were cured in a standard curing room. All of the strength measurements were conducted according to ASTM C348-02 and ASTM C349-02 at the age of 28 days. Three specimens were made for each batch for flexural test. The six portions of prisms broken in flexure were used to conduct compressive strength test subsequently for each case.

Results and Discussion

Mass Loss of Treated Fibers

Fig. 1 presents the mass loss ratio as a function of alkali solution treating time for the two concentrations. The mass loss ratio increased sharply until 9 days, and then almost remained stable with further treating time. In addition, the mass loss for the concentration 2 mol/L was a little lower than that for 4 mol/L. The high level of hydroxyl ions may be more adverse to the durability of the fibers.

It is interesting to note that the color of the fibers changed from white to light yellow after the soaking treatment. PVA consists of

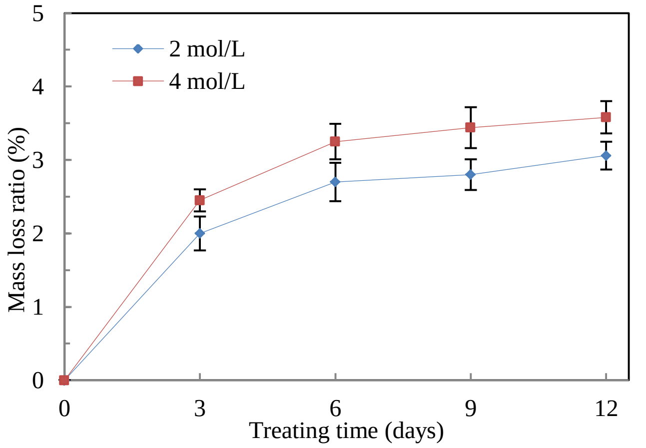


Fig. 2. Mass Loss Ratio as a Function of Treating Time (HCl).
Note: Error bars indicate one standard deviation among three specimens.

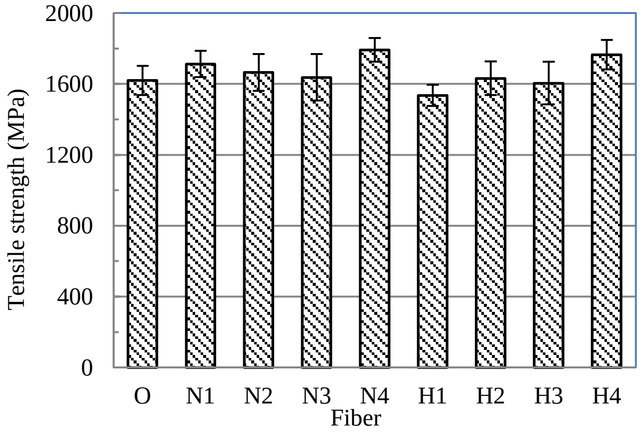


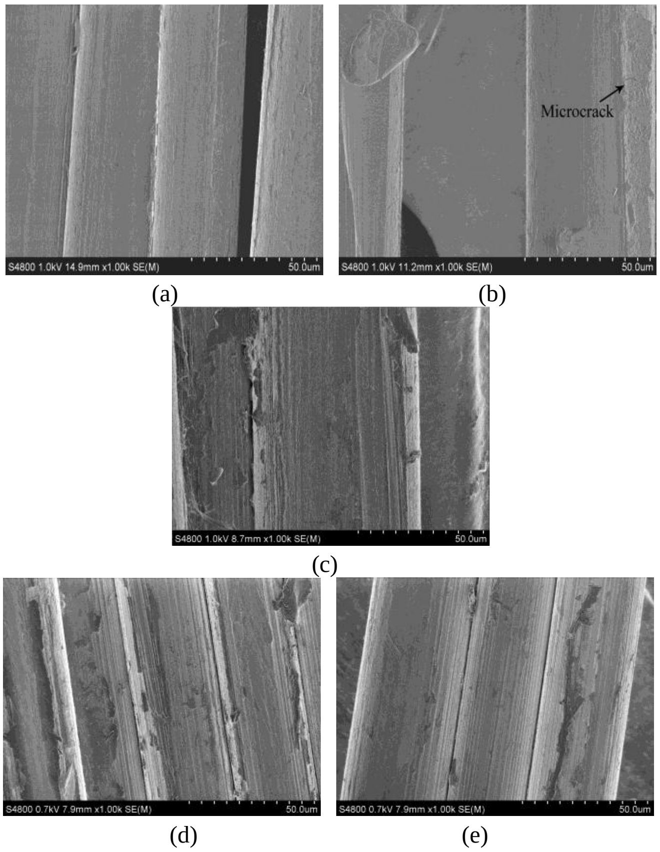
Fig. 3. Tensile Strength of Fiber with Different Treatments.
Note: Error bars indicate one standard deviation among three specimens.

carbon, hydrogen, and oxygen as in the following structural formula [13]:

$$-\left(CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}\right)_m-\left(CH_2-\underset{\displaystyle OCOCH_3}{\underset{|}{CH}}\right)_n- \tag{1}$$

Thus, under alkaline conditions, ester groups on the side chain hydrolyze into hydroxyl and acetic acid [14]. Furthermore, acetic acid reacts with sodium hydroxide and generates sodium acetate which presents the fiber in a light yellow color.

The relationship between mass loss ratio and acid solution treating time at the two different concentrations is shown in Fig. 2. As shown, an acid medium led to the sharp rise of mass loss ratio before 6 days. After that, it rises slowly until the maximum treating time. When Fig. 1 and Fig. 2 are compared, the mass loss ratio of fibers in HCl solutions is much smaller than that in NaOH solutions, about 10%~27%. The reason is that, under acidic conditions, the hydrolyzation of the ester group is a reversible reaction and the reaction degree is much lower than that under alkaline conditions [14]. Therefore, the mass loss in Fig. 2 is smaller than that in Fig. 1, and the fibers treated by HCl solutions show less color change.



(a) (b)
(c)
(d) (e)

Fig. 4. SEM Images of Fibers (a) O, (b) N2, (c) N4, (d) H2, and (e) H4.

Tensile Strength

The effects of chemical treatment on the tensile behavior of PVA fibers are shown in Fig. 3. The results indicate that the tensile strength of different fibers still remained at a high level despite the mass loss under different chemical treatments. It can be concluded that the accelerated aging tests conducted above have no significant evidence of deteriorating the tensile property of PVA fibers. Prolonging the immersion time had almost no impact on the maintenance of the tensile strength. At a certain concentration and processing time, the strength of fibers treated by NaOH solution was 11%-20% higher than that by HCl solution.

SEM Analysis

The SEM pictures show some changes on the surface of the fibers after chemical treatment. The surface morphologies of 12-days treated and untreated fibers are shown in Fig. 4.

As seen, the surface of untreated fiber is uneven, and some small burrs are observed on the fibers. These burrs likely play an important role for bonding strength between PVA fibers and the cement matrix. After 12 days treatment by 2 mol/L NaOH solution, transverse microcracks appeared on the surface of the fibers. Under tensile condition, they may become the points of stress

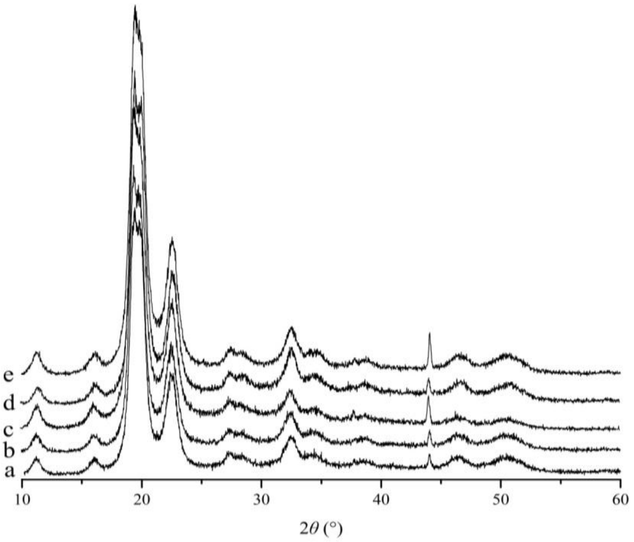


Fig. 5. Diffraction Patterns of Fibers (a) H4, (b) H2, (c) O, (d) N2, and (e) N4.

concentration. When replacing the concentration of 2 mol/L with 4 mol/L, transverse microcracks disappeared and longitudinal striations appeared on the surface. The longitudinal striations are formed by the expansion of micro-scratches produced in the process of manufacture.

After the treatment of 2 mol/L HCl solution for 12 days, external stripping was clearly observed because the surface layer of the fiber was damaged by the HCl solution. However, when treated with a 4 mol/L HCl solution, the surface morphology of treated fibers was similar to that of virgin fibers. The surface layer of the fibers may have dissolved into the solution absolutely. Thus, no fragments could be seen on the new surface, and the actual bearing area would reduce if the fibers are used to prepare fiber-reinforced composites then.

According to the analysis in this section, it's difficult to clarify the maintenance of tensile strength for PVA fibers. The effects of mass loss and surface damage of fibers on the tensile strength appear likely to be small. Therefore, the crystal structure is discussed further in the following section.

XRD Analysis

The diffraction patterns of 12-days treated and untreated fibers are shown in Fig. 5. The corresponding 2θ of $\bar{1}01$, 101 and 200 peaks are 19.5°, 20.1° and 22.7° respectively. It can be seen that the intensities of diffraction peaks $\bar{1}01$ and 200 for fibers treated with alkaline solution show slight growth as compared to the original fibers. However, the acid solution caused a slight decrease.

Since the $\bar{1}01$, 101 and 200 peaks are the only peaks resolved to high accuracy, the grain sizes for these peaks are given in Table 3. In addition, Table 3 also lists the crystallinity of each sample treated for 6 and 12 days respectively. According to Table 3, the grain size of each peak for treated samples is smaller than that of original fibers. The decrease in grain size is believed to reduce the interface defects between the crystal region and the amorphous region [15, 16] and control the deformation transition, which is favorable to the strength of PVA fibers. Thus, this occurrence partially offsets the damaging effect of mass loss and micro defects on the surface structure of fibers, explaining why the strength of some samples is even higher than the original strength.

Table 3. Effect of Different Treatments on the Crystal Structure of PVA Fibers.

Fiber*	Parameter[#]	Peak		
		$\bar{1}01$	101	200
O	G	9.7	9.5	8.3
	C		60.3	
N1	G	7.5	7.2	8.1
	C		59.8	
N2	G	8.6	7.8	7.8
	C		62.4	
N3	G	7.8	6.9	8.2
	C		60.7	
N4	G	8.5	8.3	7.6
	C		65.8	
H1	G	7.4	6.9	8.0
	C		57.2	
H2	G	7.1	7.2	7.5
	C		56.9	
H3	G	6.9	6.5	6.2
	C		56.7	
H4	G	7.0	6.6	5.9
	C		57.1	

*Virgin fiber is denoted by O.

[#]G: grain size (nm); C: crystallinity (%).

The crystallinities of fibers treated by alkaline solution were larger than those of original fibers, except for the sample treated by 2 mol/L NaOH solution for 6 days, which is almost equal to the original fibers. Nevertheless, acid solutions led to a slight decrease of crystallinities for H1, H2, H3 and H4 in the table. This illustrates that the hydrolyzation of ester groups caused the molecular structure to be more regular than the original one and prompted the further development of crystal. However, some crystal components dissolved and precipitated when treated in acid solution, which resulted in the slight decrease of crystallinity. From Fig. 3 with reference to Table 3, the strength of fibers treated by alkaline solution was somewhat higher than that by acid solution under the same condition due to the higher crystallinity.

Strength of Fiber-reinforced Mortar

The strength results of mortar prepared with original and treated fibers are shown in Figs. 6 and 7. According to the results of compressive strength represented in Fig. 6, the compressive strength was hardly affected by the chemical treatment of fibers. This is logical since the role of fibers is very small and matrix accounts most of the compressive resistance during the course of compression. As the addition of fibers introduced extra voids in the matrix, the compressive strength of fiber-reinforced mortar was a little smaller than that of standard mortar (C).

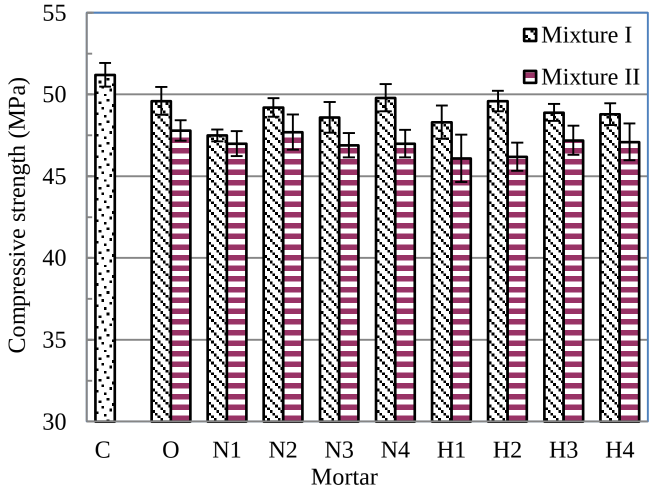


Fig. 6. Effect of Chemical Treatments on the Compressive Strength of Mortar.

Note: Errors bars indicate one standard deviation among three specimens.

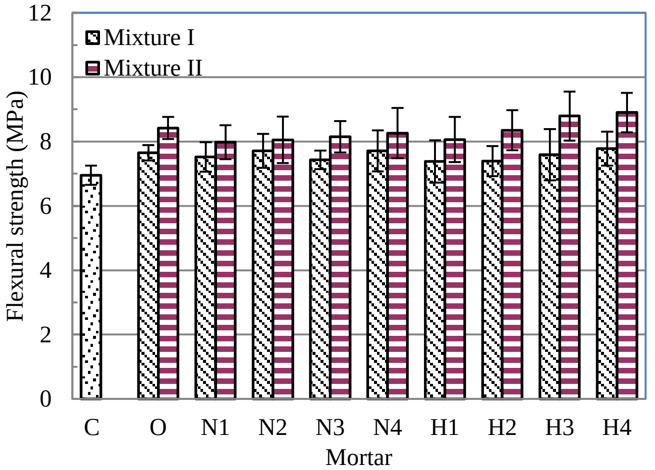


Fig. 7. Effect of Chemical Treatments on the Flexural Strength of Mortar.

Note: Errors bars indicate one standard deviation among three specimens.

As shown in Fig. 7, the addition of PVA fibers greatly increased the flexural strength of mortar. The strength of mortar prepared with treated fibers was almost the same as those prepared with original fibers, and H3-II and H4-II showed a slight increase in strength over that of O-II. However, a high-strength fiber sample did not necessarily correspond to the high-strength mortar, as indicated in Fig. 3. It should be noted that kinking of the fibers took place during the process of immersion and washing. This resulted in the poor dispersion of fibers in the mortar, ultimately leading to the influence on the mortar's mechanical property to some extent [17]. In addition, the morphology changes on fiber surface may have enhanced the bonding strength between the fibers and the matrix. Considering all these factors, the researchers conclude that as the reinforcement material of FRC, chemical treatment on PVA fibers causes limited effects on the mechanical properties of composites.

Conclusions

This research focused on PVA fibers themselves and obtained response behaviors of the fibers and composites. In particular, the following conclusions can be drawn:

(1) After the chemical treatment, the mass loss of PVA fibers increases sharply. The mass loss remains mostly stable after 9 days for NaOH solution treatment and 6 days for HCl solution. Under the same conditions, the mass loss, after acid treatment, is smaller than that of alkaline treatment mainly because of the hydrolyzation of ester groups in alkaline conditions.

(2) The decrease of grain size after chemical treatment can regulate the deformation transition between the crystal region and the amorphous region and enhance the tensile strength. Thus, the tensile strength of different fibers after treatment still remains at a high level; some are even slightly higher than the original strength. Due to the higher crystallinity, the strength of fibers treated by alkaline solution is 11%-20% higher than those treated by acid solution under the same conditions.

(3) The kinking of fibers produced during the process of chemical treatment causes and uncertain level influence to the strength of cementitious mortar. However, the influence is very limited, therefore, the chemical treatment on PVA fibers does not cause significant change of mechanical properties of the composite.

(4) On the whole, the chemical stability of PVA fibers is more desirable than the rather extreme accelerated aging. This fiber may be a good alternative material in a severe chemical environment for long-term service.

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References

1. Ahmed, S.F.U., and Mihashi, H. (2007). A Review on Durability Properties of Strain Hardening Fibre Reinforced Cementitious Composites (SHFRCC), *Cement & Concrete Composites*, 29, pp. 365–376.
2. Qian, S.Z., and Li, V.C. (2011). Ductile Concrete – Engineered Cementitious Composites (ECC) for Durable Bridge Deck Repair and Rehabilitation, *Transportation Research Board 90th Annual Meeting*, Washington DC, Jan 23-27, 11-2566, pp. 1-16.
3. Bachtiar, D., Sapuan, S.M., and Hamdan, M.M. (2008). The Effect of Alkaline Treatment on Tensile Properties of Sugar Palm Fibre Reinforced Epoxy Composites, *Materials and Design*, 29, pp. 1285-1290.
4. Wei, B. Cao, H.L., and Song S.H. (2010). Tensile Behavior Contrast of Basalt and Glass Fibers after Chemical Treatment, *Materials and Design*, 31, pp. 4244–4450.
5. Xu, S.L., and Li, H.D. (2008). A Review on the Development of Research and Application of Ultra High Toughness Cementitious Composites, *China Civil Engineering Journal*,

41(6), pp. 45-60 (in Chinese).

6. Sahmaran, and M., Li, V.C. (2008). Durability of Mechanically Loaded Engineered Cementitious Composites under High Alkaline Environment, *Cement & Concrete Composites,* 30(2), pp. 72–81.
7. Li, V.C., Horikoshi, T., Ogawa, A., Torigoe, S., and Saito, T. (2004). Micromechanics-based Durability Study of Polyvinyl Alcohol Engineered Cementitious Composite (PVA–ECC), *ACI Materials Journal,* 101(3), pp. 242–248.
8. Xu, S.L., and Cai, X.H. (2010). Mechanics Behavior of Ultra High Toughness Cementitious Composites after Freezing and Thawing, *Journal of Wuhan University of Technology (Materials Science Edition),* 25(3), pp. 509-514.
9. Sahmaran, M., and Li, V.C. (2007). De-icing Salt Scaling Resistance of Mechanically Loaded Engineered Cementitious Composites, *Cement and Concrete Research,* 37(7), pp. 1035–1046.
10. Sahmaran, M., Li, V.C., and Andrade, C. (2008). Corrosion Resistance Performance of Steel-reinforced Engineered Cementitious Composites Beams, *ACI Materials Journal,* 105(3), pp. 243–250.
11. Shan, Y., and Liao K. (2001). Environmental Fatigue of Unidirectional Glass-carbon Fibre Reinforced Hybrid Composite, *Composites: Part B,* 32, pp. 355–363.
12. Akers, S.A.S., Studinka, J.B., Meier, P., Dobbt, M.G., Johnsont, D.J., and Hikasa, J. (1989). Long-term Durability of PVA Reinforcing Fibres in a Cement Matrix, *International Journal of Cement Composites and Lightweight Concrete,* 11(2), pp. 79-91.
13. Kuraray-am.com [Internet]. Tokyo: Kuraray Co., Ltd.; properties of PVA fibers. Available from: http://www.kuraray-am.com/pvaf/affinity.php
14. Wu, Y.H., Li, W.C., and Shen, X.M. (2002). *Organic Chemistry,* Press of University of Science and Technology of China, Hefei, China (in Chinese).
15. Xiao, C.F. (1997). *An Introduction of Chemical Fibres,* China Textile & Apparel Press, Beijing, China (in Chinese).
16. Li, L. (2006). Study on Structure and Properties of High Strength and High Modulus Poly(vinylalcohol) Fibre Prepared by Melt Spinning, PhD Dissertation, Sichuan University, China (in Chinese).
17. Akkaya, Y., Shah, S.P., and Ankerman, B. (2001). Effect of Fibre Dispersion on Multiple Cracking of Cement Composites, *Journal of Engineering Mechanics,* 127(4), pp. 311-316.