Research Article

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Effect of PVA fiber on durability of cementitious composite containing nano-SiO₂

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Abstract: In the current investigation, the influence of polyvinyl alcohol (PVA) fibers on flowability and durability of cementitious composite containing fly ash and nano-SiO₂ was evaluated. PVA fibers were added into the composite at a volume fraction of 0.3%, 0.6%, 0.9%, and 1.2%. The flowability of the fresh cementitious composite was assessed using slump flow. The durability of cementitious composite includes carbonation resistance, permeability resistance, cracking resistance as well as freezing-thawing resistance, which were evaluated by the depth of carbonation, the water permeability height, cracking resistance ratio of the specimens, and relative dynamic elastic modulus of samples after freeze-thaw cycles, respectively. The results indicated that addition of PVA fibers had a little disadvantageous influence on flowability of cementitious composite, and the flowability of the fresh mixtures decreased with increases in PVA fiber content. Incorporation of PVA fibers significantly improved the durability of cementitious composites regardless of addition of nano-particles. When the fiber content was less than 1.2%, the durability indices of permeability resistance and cracking resistance increased with fiber content. However, the durability indices of carbonation resistance and freezing-thawing resistance began to decrease as the fiber dosage increased from 0.9% to 1.2%. The fiber reinforced cementitious composite exhibited better durability due to addition of nano-SiO₂ particles. Nano-SiO₂ particle improves microscopic structure of fiber reinforced cementitious composites, and the nano-particles are beneficial for PVA fibers to play the role of reinforcement in cementitious composites.

Keywords: PVA fiber; Nano-SiO₂; Cementitious composite; Durability; Microstructure

1 Introduction

A mass of concrete structures are deteriorating all over the world because of the increasing degradation of the service environment. The service performance of appreciable quantity of concrete structures degrades rapidly before the structures reach their design service life [1]. The average service life of many structures can't reach half of the design service life due to the poor durability properties of traditional concrete materials. Taking measures to enhance durability of cementitious materials has important significance to guarantee the design service life of engineering structure. For concrete structures, the most popular influence factor of insufficient durability is derived from the crack propagation inside concrete materials [2]. There are different reasons can result in cracking inside the concrete structure, such as concrete shrinkage, insufficient reinforcing bars, temperature stress, chemical attack, loading effect, curing condition, uneven foundation subsidence, improper concrete proportion, and so on. It is proved that a lot of cracks inside the concrete can provide convenient access for the corrosive ions to penetrate into the internal part of concrete structures. If the size of cracks is not too large, the influence of the crack on concrete erosion can be neglectful. While the crack width is more than 100 μm, the concrete erosion speed will increase greatly because of the cracks. Therefore, some measures must be taken to restrict cracking inside the concretes to improve durability of engineering structures.

To improve the cracking resistance of cementitious composites and enhance the durability of structures and members, some kinds of fibers are usually used in cementitious composites [3]. Generally, there are many types of

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fibers which are often used in cementitious composites, such as polyvinyl alcohol fiber (PVA fiber) [4], carbon fiber [5], polypropylene fiber [6], steel fiber [7], plant fiber [8], glass fiber [9] and basalt fiber [10]. Among these various fibers, polyvinyl alcohol fiber exhibits many advantages for applying in cementitious composites. The cementitious composite reinforced with PVA fiber is usually called ECC (Engineered Cementitious Composite) [11]. The ultimate tensile ductility of typical ECC will reach 3-5%, and the tiny crack width of 60 μm can be maintained at the same time [12]. ECC shows strain hardening properties under tensile stress through by forming microcracks. When the microcracks are appearing, the force can be transferred by the fibers crossing the microcracks, which enables the matrix of ECC to obtain strain capacity of more than 300 times larger than that of the traditional cementitious composite [13]. Due to the excellent toughness and tiny width of cracks, ECC has been used to enhance durability of the structure because the larger ultimate tensile strain and small microcrack width [14].

During the last several years, the durability of ECC has been extensively studied. Sahmaran and Li [15] studied durability of ECC incorporating large volume of fly ash and concluded that the ECC specimens with high dosage of fly ash exhibited excellent mechanical properties and high tensile strain capacity after accelerated attack in sodium chloride and sodium hydroxide solutions. Many kinds of waste mineral admixture have great effect on durability of ECC. The freeze-thaw resistance of ECC can be obviously influenced by type and content of mineral admixture [16]. Liu *et al.* [17] discussed the effect of ground granulated blast furnace slag (GGBS) and silica fume (SF) on freezing-thawing performance of ECC containing fly ash and their results indicated that the ECC with larger content of fly ash replaced by GGBS and SF exhibited better frost resistance compared to the ECC containing no GGBS or SF. The results of Righi [18] concluded addition of rice husk ash with the content of 30% had positive influence on improving ductility and anti-cracking and decreasing heat at hydration and water absorption of ECC. Xu *et al.* [19] studied the durability of UHTCC under different cycles of freezing-thawing, and they concluded that UHTCC retained its strain-hardening and high tensile strain capacity after 300 cycles of freeze-thaw. Compared to the traditional cementitious composite, the durability of ECC is more excellent due to the addition of PVA fibers.

However, it is still necessary for the ECC used in the severe environment and strong corrosive environment to enhance its durability. With the development of nanotechnology, there is a broad prospect of the nano materials in the application of cementitious materials. The usage

of nano-particles in the cementitious composite has attracted the interest and attention of many researchers, and abundant research work over the past decade was conducted on properties of cementitious composite incorporating nano-particles. The results of Yesilmen [20] showed nano-sized mineral admixtures obviously improved ductility and flexural behavior of ECC. Through a series of experiments, Sikora *et al.* [21] used nano-Fe₃O₄ in cementitious composites and concluded the microscopic structure of cementitious composites was improved greatly, and the porosity was decreased, which increased density of the composites. Li *et al.* [22] explored coupling effect of hybrid fiber and nano-particles on workability, flexural performance and microscopic structure of cementitious composite with excellent ductility. Yang and Che [23] studied the influence of nano-CaCO₃ and microscale limestone powder on the porous structure and hydrated product of cementitious composites. Jiang [24] studied rheological performance of cementitious composites incorporating different kinds of micro and nanoparticles, and the results showed the dosage and kind of filler material had remarkable influence on the rheological performance of the composite. During the course of the hydration process of the nano-particles with the cement in the cementitious composite, the nano-particles improves behavior of hardened cement paste and interfacial bond behavior due to the nanometer effects [25].

Durability of cementitious composite is so important in the mix design and application of the cementitious composite, especially for the cementitious composite used in the severe environment and strong corrosive environment. However, so far, there is little report about the systemic study on influence of PVA fiber on durability of cementitious composites incorporating SiO₂ nano-particles. Investigation in these aspects is certainly necessary and helpful to promote the further usage of ECC incorporating nano-SiO₂ particles. The present paper reports the influence of PVA fiber on durability of cementitious composites containing nano-SiO₂.

2 Experimental program

2.1 Raw materials

Raw materials used in this study include cement, first grade fly ash [26], PVA fibers, silica sand, nano-particles, water-reducing agent and water. The cement was Portland cement (P.O42.5 by Chinese standards) [27] manufactured by Mengdian Cement Co. LTD of Henan Province in China.

The fly ash was provided by Datang Luoyang Thermal Power Co. LTD in China. The properties of cement and fly ash used are presented in Table 1. PVA fibers used in this investigation were made by Kuraray Company of Japan, and the performance parameters are shown in Table 2. Nano-SiO₂ used in this study was manufactured by Hangzhou Wanjing New Material Co. LTD, and Table 3 presents the properties of nano-SiO₂. The high range water-reducing admixture produced by Xingchen Co. LTD was used in this study to adjust the workability of fresh cementitious composites. The aggregate used was composed by silica sands with different grain size, and the total grain size range varies from 40 to 70 meshes, the corresponding grain size of which is 212–380 μm .

Table 1: Properties of cement and fly ash

Composition (%)	Cement	Fly ash
<i>Chemical compositions</i>		
SiO ₂	21.05	52.12
Al ₂ O ₃	5.28	17.86
Fe ₂ O ₃	2.57	6.57
CaO	63.14	9.12
MgO	3.58	3.26
Na ₂ O	0.17	2.38
K ₂ O	0.58	2.05
SO ₃	2.39	0.23
<i>Physical properties</i>		
Specific gravity	3.13	2.13
Specific surface (cm ² /g)	3266	2464

2.2 Mix proportions

In order to reveal the impact of PVA fiber content on durability of cementitious composites incorporating nano-SiO₂, the ratios of water to binder and cement to sand were constant, and the mix proportions in theory were obtained by changing PVA fiber. After the appropriate amendment on some of the proportioning parameters, the final mix proportions were determined. The ratios of water to binder and cement to sand in this study were selected as 0.38 and 2.0, respectively. In this study, a low volume fraction ($\leq 1.2\%$) of PVA fiber and the 2.0% content of nano-SiO₂ were used. The fly ash and nano-particles were added by replacing the equivalent cement. Altogether there are 10 mix proportions were designed, which are presented in Table 4. The letters N and S represent the mix proportions containing no nano-particle and nano-SiO₂, respectively.

2.3 Specimen preparation

In order to obtain cementitious composites with excellent fresh and hardened properties, the key point is to ensure that the fibers and nano-particles disperse uniformly in the matrix during the course of mixing of the cementitious composites. The fresh cementitious composites were prepared using a Hobart mixer with the maximum mixing capacity of 10 L. First, the silica sands, fly ash, cement and nano-particles were dry stirred for 2 min. Then the water-reducing admixture and half of the water were equally added into the mixture by twice and the composites were stirred for 1 min each time. After that, the rest of the water was added to the mixture and stirred for further 1 min. Before added into the mixture, the fibers were added in four parts in advance. Then each part of PVA fibers and the mixture were stirred for 2.5 min. Altogether, after mixing for 15 min, the homogeneous fresh cementitious composite with good fluidity and well fiber dispersion was obtained. Immediately after mixing, some of the fresh composite was used to measure the flowability of the cementitious composite. Then the other fresh composite was placed in various molds to prepare test specimens. The strengthening effect of cementitious composite to the concrete structures is dependent on the fluidity of fresh cementitious composite. It was observed from the workability tests that the flowability of cementitious composite was reduced due to the adding of PVA fibers and nano-particles. As a result, the fluidity of fresh composite must be checked in preparing the fresh cementitious composite to guarantee well strengthening effect [28–30].

2.4 Flowability tests

The flowability tests were performed according to GB/T 50080-2002 [31]. The slump flow tests, conducted in conjunction with slump tests, were expected to provide a better evaluation on flowability of the fresh composite mixtures that is too fluid to hold its shape after the standard slump test [32]. The flowability of cementitious composite was evaluated by slump flow, which can be measured by slump flow test. After the slump cone was lift, the fresh composite began to extend under the effect of gravity. When the fresh composite stopped extending, the two diameters in two vertical direction of the extended surface of the fresh composite were measured respectively. The final average of the two diameters was regarded as the slump flow of the cementitious composite. The slump flow was tested for all the cementitious composite mixtures.

Table 2: Physical properties of PVA fiber

Specific gravity	Dry fracture elongation (%)	Fiber length (mm)	Fiber diameter (μm)	Tensile strength (MPa)	Water absorption (%)	Melting point (°C)
1.32	15	9	20	1400	<1	220

Table 3: Physical properties of nano-SiO₂

Average particle size (nm)	SiO ₂ content (%)	Specific surface area (m ² /g)	Bulk density (g/cm ³)	PH value
30	99.5	200	0.055	6

2.5 Carbonation tests

According to the Chinese Standard [33], 100-mm cube specimens were cast for carbonation tests. After the specimens with moulds were vibrated on the vibrating table, they were cured at ambient temperatures on the flat ground. The specimens should be moved to standard curing room for further curing after they were demoulded. After 26 days of curing, the specimens were placed into the oven to be drying for 48 h, and then the specimens can be on testing after cooling. Before the specimen was placed into the carbonation box, one surface of the specimen was drawn lines with the space of 10 mm to determine the position of the measuring points. Then the other three surfaces of the specimen were sealed by a layer of paraffin. The temperature, relative humidity and CO₂ concentration of the carbonation box were controlled as $20 \pm 2^\circ\text{C}$, $70 \pm 5\%$, and 20%, respectively. The scheduled carbonation periods include 3d, 7d, 14 d, and 28d. When the carbonation time reached the scheduled carbonation period, the specimen was taken out to be split into two parts in perpendicular to the lines direction on the universal testing machine. Some solution of phenolphthalein and alcohol with the concentration of 1% was sprayed on the splitting surface, and the carbonation depths of the measuring points were measured. For each specimen, the average value of more than eight effective carbonation depths was selected as the final carbonation depth.

2.6 Permeability resistance tests

Permeability resistance tests of cementitious composites were carried out on the full-automatic permeability instrument in accordance with Chinese Standard [34]. The permeability height of pressure water of the circular truncated

cone specimen was measured. The top diameter, bottom diameter, and height of the specimen were 175 mm, 185 mm, and 150 mm, respectively. During the course of testing, the water pressure was controlled as 1.2 MPa. After the water pressure for 24 h, the specimen was taken from the permeability instrument and split into two pieces. The edge of water permeability on the splitting surface was marked using a waterproof pen. On the splitting surface, ten measuring points were selected evenly, and ten permeability heights were measured. The average permeability height of these ten values was determined as the final permeability height of the specimen. There are six specimens for each mix proportion and the average permeability height of the six specimens was calculated as the final permeability height of this mix proportion.

2.7 Plate cracking tests

Plate cracking tests of cementitious composites were carried out according to the Chinese Standard [35]. The rectangular plate specimens with size of $910 \times 600 \times 20$ mm were cast for plate cracking tests. The cracking resistant of cementitious composite was evaluated by the index of cracking resistance ratio, which was calculated based on the length and width of the cracks on the surface of the specimen. The cracks were divided into five grades according to their widths, and each grade of crack width has a weight value, which can be seen in Table 5. The cracking index of a crack can be defined as the product of its length and the corresponding weight value, and the cracking index of a specimen can be calculated as follows [35]:

$$W = \sum (A_i \cdot l_i) \quad (1)$$

where, W , the cracking index of a specimen, mm; l_i , the length of crack i , mm; A_i , the corresponding weight value of crack i . There will be some difference between the average cracking index of the cementitious composite for basic mix proportion and the mix proportion containing admixture. The index of cracking resistance ratio can be defined as the ratio of the above-mentioned difference to the average cracking index of the basic mix proportion, which can

Table 4: Mix proportions of the cementitious composites

Mix no.	Cement (kg/m ³)	Fly ash (%)	Nano-particle (%)	PVA fiber (%)	Silica sand (kg/m ³)	Water (kg/m ³)	Water-reducing admixture (kg/m ³)
N-0-0	650	35	0	0.0	500	380	3
N-0.3-0	650	35	0	0.3	500	380	3
N-0.6-0	650	35	0	0.6	500	380	3
N-0.9-0	650	35	0	0.9	500	380	3
N-1.2-0	650	35	0	1.2	500	380	3
S-0-2.0	648	35	2	0.0	500	380	3
S-0.3-2.0	648	35	2	0.3	500	380	3
S-0.6-2.0	648	35	2	0.6	500	380	3
S-0.9-2.0	648	35	2	0.9	500	380	3
S-1.2-2.0	648	35	2	1.2	500	380	3

be obtained as follows:

$$\gamma = \frac{W_0 - W_i}{W_0} \times 100 \quad (2)$$

where, γ , index of cracking resistance ratio, %; W_0 , the average cracking index of the cementitious composite for basic mix proportion, mm; W_i , the average cracking index of the mix proportion containing admixture, mm. The positive value of γ will show that the admixture has improving effect on the cracking resistant property of cementitious composite. On the contrary, the negative value of γ will show that the admixture has reducing effect on the cracking resistant property of cementitious composite.

Table 5: Weight value for crack width

Crack width d (mm)	Weight value A
$d \geq 3$	3
$3 > d \geq 2$	2
$2 > d \geq 1$	1
$1 > d \geq 0.5$	0.5
$d < 0.5$	0.25

2.8 Freezing-thawing cycle tests

Freezing-thawing cycle tests of cementitious composites were carried out according to the Chinese Standard [36], and $100 \times 100 \times 400$ mm beam specimens were cast for fast freezing-thawing cycle tests. The specimens were placed into water to be immersed for 4 d after they were cured for 24 d in the curing room under the standard curing condition. The specimens were put into the specimen box of the freezing-thawing test machine after measuring of initial

dynamic elastic modulus. The water surface inside specimen box should be 20 mm higher than the top surface of the specimen. The dynamic elastic modulus of specimens was measured after each 25 cycles of freezing-thawing, and the relative dynamic elastic modulus could be obtained. In this study, relative dynamic elastic modulus of the specimen subject to 300 cycles of freeze-thaw was determined to evaluate the freezing-thawing resistance of cementitious composite.

3 Results and discussions

3.1 Flowability of cementitious composite

Figure 1 shows the slump flow measurements of the cementitious composite mixtures containing no nano-particles and 2% nano-SiO₂ and with different amounts of PVA fiber additions. The figure displays that the slump flow of the mixtures decreased with increasing PVA fiber dosage. The slump flow of fiber reinforced cementitious composite containing 2% nano-SiO₂ is lower than that of the fresh cementitious composite containing no nano-particles for the same fiber volume dosage. These results were consistent with what obtained by Hossain [37]. The mixture containing 1.2% PVA fibers had approximately 50% reduction in slump flow when compared with the control mixture (without PVA fibers) whether nano-SiO₂ particles are added or not. The decreasing trend in slump flow values may be due to the addition of fibers that created a network structure in the cementitious composite, which restrained the mixture from segregation and flow. In addition, some cement particles may adsorb on the fiber surfaces to wrap the fibers around [38], thus reducing the amount of effective paste to contribute to the cementitious composite flow.

Figure 1: Effect of PVA fiber on slump flow

3.2 Carbonation resistance of cementitious composite

Carbonation is the neutralization process of cementitious composite, in which the alkalinity of cementitious composite will decrease. High alkalinity is the essential condition to protect the reinforcing steel bars inside the cementitious composite from corrosion, and is also essential condition to maintain the various hydration products steady and keep fine cementing properties for the composite [39]. As seen in Figure 2, when a certain amount ($\leq 1.2\%$) of PVA fibers were added into the cementitious composite containing 35% fly ash and the cementitious composite containing 35% fly ash together with 2% nano-SiO₂, the carbonation depth of the specimen was further reduced. The minimum carbonation depth decrease occurred in the composite containing 0.9% PVA fibers without nano-particles, and the composite containing 1.2% PVA fibers and 2% nano-SiO₂, respectively. Generally, the larger PVA fiber dosage resulted in smaller carbonation depth for all the mixtures. However, for the cementitious composite without nano-particles, overmuch PVA fibers may have adverse influence on reduction of carbonation depth. The carbonation depth was observed to reduce when the test age increased from 3 days to 28 days. However, it shall be noted that the variation in carbonation depth was not obvious for the composites containing different dosages of PVA fibers when the test age was less than 14 days. This indicated that the addition of PVA fiber had very limited benefit to carbonation resistance of the cementitious composite at low carbonation stage.

The carbonation can be illustrated as the diffusion process of CO₂ from the outside surface into the internal of the cementitious composite. The carbonation depth increases with the increase of diffusion depth of CO₂. A large

(a) Mixtures without nano-particle

(b) Mixtures containing 2% nano-SiO₂

Figure 2: Effect of PVA fiber on carbonation depth

number of small pores and microcracks inside the cementitious composite provide necessary channels for CO₂ diffusion. After PVA fibers were added into the cementitious composite, large amounts of fibers uniformly dispersed in the matrix formed a network, which can restrict sinking of aggregate and prevent the segregating of the fresh composite. The bleeding of the cementitious composite can also be reduced by the fiber network. As a result, the pore channels inside the composite were reduced. Meanwhile, a great deal of PVA fibers will reduce the size of the capillary pore inside the matrix or even block the capillary pore. Furthermore, the PVA fibers can restrict the generation and propagation of the cracks in the matrix, and hold back connection of cracks [40]. For the cementitious composite containing no nano-particles, there is a critical content of PVA fiber to enhance the carbonation resistance of

cementitious composite. The critical dosage of PVA fiber can also be called optimum content. When the fiber content exceeds the optimum content, the fiber number will be overmany and the fiber spacing will be too small, which will result in interlapping for the adjacent interface region of fibers. Thus the amount of weak interface will increase and the microstructure of the interface region will be too loose, which will be harmful to improve the carbonation resistance of the matrix. After 2% nano-SiO₂ was added into the cementitious composite, the nano-particles promoted the hydration more completely, and more silica gel was generated. The silica gel and the unreacted SiO₂ nano-particles filled in the internal pores of the matrix and improved the density degree, which might go against the diffusion of CO₂. Therefore, the carbonation resistance of cementitious composite containing nano-SiO₂ increased with increment in fiber dosage.

3.3 Permeability resistance of cementitious composite

Permeability resistance is an important parameter to evaluate the durability of cementitious composite. Usually, the service environment of cementitious composite structures is rather complex, and most of the structures are directly exposed to the air. Because there are a large number of microcracks and capillary-size pores inside the cementitious composite, the pressure water can enter the matrix through these permeability channels, which will cause enlarging and propagation of the microcracks and result in durability reduction of the structures [41]. In particular, the water permeating into the cementitious composite will participate in some complex chemical reactions to generate some corrosive materials, which will result in dis-soluble erosion inside the structures and the structures are prone to durability failure [42]. In contrast, the permeability height of cementitious composite specimen generally declined with increasing PVA fiber dosage, which can be seen from Figure 3. Especially after 0.3% PVA fibers were added in the cementitious composite, there was a sharp reduction in permeability height of the specimen. It is noted that larger amount of PVA fiber addition resulted in larger reduction in permeability height of the specimen. It should be noted that the permeability height of the specimen of cementitious composite containing 2% nano-SiO₂ was lower than that of the cementitious composite containing no nano-SiO₂ for the same PVA fiber volume dosage. For the cementitious composite without nano-particles, the permeability height of specimen containing no PVA fiber was 40.2 mm, but it was only 15.4 mm for the composite spec-

Figure 3: Effect of PVA fiber on permeability height

imen reinforced with 1.2% PVA fiber. It can be concluded that the volume content in the PVA fiber had significant effect on the permeability resistance of cementitious composite specimen.

A large number of tiny and thin PVA fibers with large specific surface area constructed a uniform and disordered support system. When the cementitious composite matrix was shrink, this disordered support system consumed energy effectively and restricted cracking of the matrix, which reduced the inner microcracks and defects of the cementitious composite effectively. As a result, it is so difficult to form the through porous capillary channels or cracks inside the composite due to the existing of fibers. With the improved inner structure of the matrix, the permeability resistance of cementitious composite was enhanced [43].

3.4 Cracking resistant property of cementitious composite

Shrinkage cracking is a usual disadvantage of cementitious composite, which will result in reduction in strength and durability of cementitious composite, and accelerate corrosion of the reinforcing steel bars inside the composite. Controlling the early plastic cracking and crack propagation of cementitious composite to improve the cracking resistant property of the composite has great significance on improving the durability of cementitious composite. The influence of PVA fiber content on cracking resistance ratio of cementitious composite and cementitious composite containing 2% nano-SiO₂ is shown in Figure 4(a) and 4(b), respectively. The results showed the PVA fiber additions

(a) Mixtures without nano-particle

(b) Mixtures containing 2% nano-SiO₂**Figure 4:** Effect of PVA fiber on cracking resistance ratio

obviously increased cracking resistance ratio of the cementitious composite. As is seen from Figure 4(a), for the cementitious composite without nano-particles, the amount of the net cracking resistance ratio increase caused by 0.3% PVA fibers was about 66%, which was much larger than the net increase of cracking resistance ratio of cementitious composite containing 2% nano-SiO₂. For both series mixtures, the cementitious composite containing 1.2% PVA fibers exhibited the highest cracking resistance ratio increase. As is found from Figure 4(b), for cementitious composite containing 2% nano-particles, the increase in cracking resistance ratio was determined as 90% compared to the control composite mix.

It can be concluded that incorporation of PVA fiber greatly improved cracking resistant property of cementitious composites. On the one hand, PVA fiber improved the cohesiveness of fresh cementitious composite due to

the excellent hydrophilia and adhesive property with binding materials. On the other hand, PVA fibers belong to synthetic fibers with wonderful ductility. The fibers inside the composite were crossing to form a net structure, which reduced the fluidity of cement paste and restricted the sinking of aggregates. The function of supporting aggregates for PVA fibers has great contribution on improving cracking resistant property of cementitious composite. Meanwhile, PVA fibers can fill and block the pores caused by cement hydration, reduce the amount of connected pore channels and decrease the size of the pore channel. As a result, the pore size distribution was optimized, and thus the compactness of cementitious composite was significantly enhanced. Furthermore, the bridging function shared responsibility for the inner shrinkage stress, which reduced the stress concentration on the crack tip of the cementitious composite. So the crack was prevented from further propagating, and the possibility for the microcracks to become through cracks was reduced [44]. The high activity of SiO₂ nano-particles promoted cement hydration to be more thorough, and the compactness of cementitious composite was improved. As a result, the number of pores inside the composite was well controlled, and the porosity and size of the internal pores were decreased. The existing of SiO₂ nano-particles promoted the reinforcement of PVA fibers on cracking resistant property of cementitious composite. Therefore, the addition of PVA fibers greatly improved the cracking resistant property of cementitious composite.

3.5 Freeze-thaw resistance of cementitious composite

From the point of view of microstructure, the interior of cementitious composite is not voidless and continuous, and there are a large number of capillary-size pores with the diameter of 0.01-10 μm on the interface between the aggregate and the cement gel [45]. Under the damp environment, most of the capillary-size pores will be filled with water, which will be frozen when the temperature of the cementitious composite is too low. The internal stress resulted from freezing will directly act on the pore structure, which will result in irreversible micro-crack damage inside the composite. With the action of freezing-thawing cycles, the internal stress will affects the matrix repeatedly, and the internal micro-crack damage will expand and accumulate, which finally leads to freezing-thawing damage of the cementitious composite [46]. Not only that, the internal stress of the pore structure derived from freezing-thawing cycles on the interface between the reinforcing steel-bars

and the composite matrix is also the primary cause of steel-bars corrosion and bond failure between steel-bars and the composite matrix [47].

Figure 5(a) illustrates the effects of PVA fiber dosage on relative dynamic elastic modulus of cementitious composite after the samples underwent 300 cycles of freeze-thaw. As is shown in Figure 5(a), the incorporation of PVA fibers increased the relative dynamic elastic modulus effectively. The maximal relative dynamic elastic modulus improvement also occurred in the composite containing 0.9% of PVA fibers. In comparison to the control cementitious composite (0% PVA fiber), the net rate of increase in the relative dynamic elastic modulus was 16.5% for the composite reinforced by 0.9% fibers after the samples underwent 300 freeze-thaw cycles. Figure 5(b) presents the relation curves between the relative dynamic elastic modulus and freeze-thaw cycles of various dosage of PVA fibers reinforced cementitious composites containing 2% SiO_2 nano-particles. From the figure, it was observed that the change rule in relative dynamic elastic modulus of the cementitious composite containing 2% nano- SiO_2 with increment in fiber dosage is similar with that of the cementitious composites without SiO_2 nano-particles. After the samples underwent the same freeze-thaw cycles, the cementitious composite reinforced with 0.9% PVA fibers exhibited maximum relative dynamic elastic modulus. For 300 freeze-thaw cycles, the relative dynamic elastic modulus of cementitious composite containing % SiO_2 nano-particles increased from 86.6% to 91.4% and increased by 5.5% compared to the cementitious composite without fibers. The variation in relative dynamic elastic modulus in Figure 5 showed low content (0.9%) in PVA fiber improved the freezing-thawing resistance of cementitious composite, while a larger amount ($> 0.9\%$) of PVA fibers reduced the freezing-thawing resistance of cementitious composite.

Before freezing-thawing cycle tests started, the surface of all the specimens is very smooth and there is no small pit on the surface. As the tests went on, there were a certain amount of small pores on the specimen surface of the cementitious composite containing no PVA fibers. Spalling in patches of the hardened cement paste occurred under the action of expansion pressure resulted from the freezing of the water in the small pores during the course of freezing-thawing cycles. On the contrary, the surface of the specimen of PVA fibers reinforced cementitious changes little during the course of freezing-thawing cycles. The overlapping each other of disordered PVA fibers inside the composite restricted the running over of the internal air, and the air content in the cementitious composite increased, which relieved the hydrostatic pressure and seepage pressure in the course of low temperature cycles [48]. Because

(a) Mixtures without nano-particle

(b) Mixtures containing 2% nano- SiO_2

Figure 5: Effect of PVA fiber on relative dynamic elastic modulus

the diameter of PVA fiber is very small, the fiber amount of unit mass is large and the space between two fibers. As a result, the energy loss of the cementitious composite during freeze-thaw damage was increased, and the expansion and cracking of cementitious composite was effectively restricted, which was beneficial to improve the freezing-thawing resistance of cementitious composite. However, the amount of fibers in unit of composite will be too large and the space between two fibers is too small if overdosage of PVA fibers were used. Then there are too many planes of weakness inside the fiber reinforced cementitious composite, and the microstructure of the transient zone of interface will be loose, which has disadvantages on improving freezing-thawing resistance of cementitious composite.

3.6 Microstructure of cementitious composite

With the development of hydration process of cementitious composites, the grain amount of cement is decreasing and the thickness of hydrated products layer around the cement grains becomes larger and larger [49]. Figure 6(a) and 6(b) exhibits microstructures of common cementitious composites and cementitious composites reinforced by PVA fibers containing nano-SiO₂ particles, respectively. As is observed from Figure 6(a), there are large amounts of areas with large pores in the cementitious composite due to the absence of nano-particles. The bonding between the fiber and cement paste is not strength enough, which implies that ITZ is relatively weak. The porosity of the composite is so high that large amounts of Ca(OH)₂ has large space to grow. The microstructure of PVA fiber reinforced cementitious composite becomes much denser due to the filling effect for nano-particle and the small particle for hydrated products C-S-H gels. As is shown in Figure 6(b), with addition of 1.0% SiO₂ nano-particles, the number of pores in the composite is very small. Besides, the quantity of disadvantageous crystals was obviously reduced, such as needlelike ettringite and calcium hydroxide, by including SiO₂ nano-particles into PVA fiber reinforced composite. As a result, the ITZ was strengthened, which is more advantageous for the PVA fibers to play the role of their reinforcement.

4 Conclusions

Based on the current study presented above, the main conclusions were drawn:

- (1) Addition of PVA fibers in cementitious composite decreased slump flow of the fresh composite. The amount of slump flow decrease increased with increasing amount (0.3–1.2% by volume) of PVA fibers. The incorporation of nano-SiO₂ particles in cementitious composites caused further loss of flowability.
- (2) Incorporation of PVA fibers significantly improved the durability of cementitious composites regardless of addition of nano-particles. When the fiber content was less than 1.2%, the durability indices of permeability resistance and cracking resistance increased with fiber content. However, the durability indices of carbonation resistance and freezing-thawing resistance began to decrease as the fiber dosage increased from 0.9% to 1.2%. The fiber reinforced

(a) PVA fiber reinforced composite without nano-particle

(b) PVA fiber reinforced composite containing 2% nano-SiO₂

Figure 6: SEM micrographs of PVA fiber reinforced cementitious composites

cementitious composite exhibited better durability due to addition of nano-SiO₂ particles.

- (3) The microstructure of PVA fiber reinforced cementitious composite becomes much denser due to filling effect of nano-SiO₂ and particles of hydrated products C-S-H gels. Nano-SiO₂ particle improves microscopic structure of fiber reinforced cementitious composites, and the nano-particles are beneficial for PVA fibers to play the role of reinforcement in cementitious composites.

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