Study on in-situ modification of poly-dopamine on glass fibers and its effect on shrinkage performance of cement materials

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Abstract. Cement-based materials are one of the essential construction materials that had been widely used in infrastructure and facilities. However, it experienced shrinkage problems, which led to the cracking of concrete buildings and deterioration of the durability. The incorporation of glass fibers can improve the shrinkage resistance of cement materials by enhancing the interface between cement and fiber. Aiming at improving the shrinkage resistance of cement, in this study, glass fibers were in-situ modified with poly-dopamine in aqueous solution. The effect of dopamine hydrochloride concentration and the pH of the solution were investigated with the optimal condition attained to be 2×10⁻³ g/ml and 8.5, respectively. Scanning electron microscope (SEM) and X-ray photoelectron spectroscopy analysis (XPS) were utilized for the characterization of as-prepared poly-dopamine modified glass fibers. Subsequently, as-prepared and untreated glass fibers were mixed with cement at varied volume fraction and water-cement ratio for the study of shrinkage performance. The glass fiber-reinforced cement had a lower shrinkage than cement without glass fibers. Compared with the cement without glass fibers, when the water-cement ratio was 0.4 and the volume content of in-situ modified glass fiber of poly-dopamine was 7%, the reduction in 28-day shrinkage of poly-dopamine in-situ modified glass fiber-reinforced cement was large extent, reducing by 42%. The shrinkage resistance performance of in-situ modified glass fibers reinforced cement with poly-dopamine was better than that of untreated glass fibers. In short, this work developed novel approach for in-situ modification of glass fibers and found a new path to improve the shrinkage resistance of cement material.

1. Introduction
Since the introduction of Portland cement in the 1920s, cement-based materials had been widely used in bridges, dams, roads and houses, due to their high compressive strength, non-combustibility, low cost and molding ease [1, 2]. However, the shrinkage problem of cement-based materials limited their further development. Cracks appeared on the cement surface with the development of shrinkage. The performance of the cement and the service life of the cement-based materials can be seriously affected [3]. Therefore, enhancing the shrinkage resistance of cement-based materials is vital to improve their service life.

The incorporation of glass fibers can not only effectively help strengthen the tensile strength and toughness, but also inhibit the cracking and reduce the shrinkage of cement-based materials [4, 5]. The glass fibers formed a three-dimensionally distributed support system inside the cement with the "bridge" function. Interface bonding between the glass fibers and the cement was improved. In turn,
the expansion of microcracks inside the cement-based material was limited, thereby improved the mechanical properties and the shrinkage resistance of the cement-based materials [6].

Glass fibers had the advantages of high tensile strength, high modulus of elasticity, good weather ability and ease of molding into various shapes. After they were added to the cement, the shrinkage of cement was effectively suppressed [7, 8]. However, there were some obvious disadvantages. For instance, the interface between glass fibers and cement needed to be strengthened. In order to solve this problem, many methods for surface modification of glass fibers had been proposed, such as etching [9], oxidation [10], and coating [11]. However, these methods had shortcomings such as easy damage to glass fibers, harsh experimental conditions and complicated operation steps. In order to overcome these shortcomings, surface modification of glass fibers with nanomaterial had become an effective choice due to its diverse facile synthesis manner and adjustable control in structure and morphology. The nanomaterial modified glass fiber formed a "root-whisker" structure, with the glass fiber as the "root" and the nanomaterial as the "whisker" [12], which improved the surface roughness of the glass fiber. Due to this structure, it had an excellent effect for improving the interfacial adhesion between the glass fiber and the cement. Gao [13] used carbon nanotubes and nano-clay to coat on glass fibers for glass reinforced cement. The results showed that the tensile strength of glass fibers treated with carbon nanotubes was increased by 70 %, and the interfacial bonding strength with cement matrix was also significantly improved. In the study of Lu et al [14], the graphene oxide/carbon fiber (GO/CF) hybrid fibers were fabricated by a newly designed electrophoretic depositing method. GO/CF hybrid fibers were capable of higher roughness and improved wettability, which provided the interfacial bonding strength with cement hydrates. In the study of Faranak [15] et al., the nano-crystalline cellulose produced by the treatment of bagasse fibers with bacteria was deposited on the surface of the bagasse fibers, which improved the interfacial adhesion between the bagasse fibers and the cement matrix.

In this paper, in-situ modification of the glass fibers via self-polymerization of dopamine was studied with the optimal preparation conditions explored by controlling the concentration of the dopamine hydrochloride solution and the pH value of the solution. The effect of surface modification of glass fiber was explored by SEM and XPS. Subsequently, as-prepared nano-modified glass fibers were incorporated into the cement slurry for investigation of shrinkage deformation by comparison with cement paste and that mixed with nano-modified glass fibers.

2. Materials and methods

2.1. Materials

Tris(hydroxymethyl)amino alkane and analytical grade dopamine hydrochloride (Sigma-Aldrich) was purchased from Shanghai Jingchun Biochemical Technology Co. Ltd. without any additional purification. Hydrochloric acid (HCL) was purchased from Laiyang Economic and Technological Development Zone Fine Chemical Plant. Distilled water was obtained from water purification system (Direct-Q® 3.5.8). Glass fibers were purchased from Taishan Glass Fiber Co, Ltd. It was processed into chopped glass fibers that the length was 12 mm and the diameter was 14 μm. Its apparent density was 2.68 g/cm³. P.O 42.5 cement was purchased from Shandong Shanshui Cement Co. Ltd with the specific surface area of 336 m²/kg.

2.2. Poly-dopamine in-situ modified glass fiber

A certain amount of 0.3 mol/L Tris(hydroxymethyl)amino methane (Tris) solution was prepared in the container fixed in a water bath thermostat. An appropriate amount of 0.2 mol/L dilute hydrochloric acid solution was subsequently added to get Tris-HCl buffer solution. At the same time, the pH of the buffer solution was measured with a pH meter until the pH reached at 7.5, 8.0, 8.5, 9.0 and 9.5, respectively. Another set of solutions without drop addition of hydrochloric acid was used as a blank sample. 10 g of glass fibers were then added to the container, followed by varied quantity of dopamine hydrochloride added under an oxygen atmosphere. The amount of dopamine hydrochloride was
controlled to be $1 \times 10^{-3}$, $1.5 \times 10^{-3}$, $2 \times 10^{-3}$, and $2.5 \times 10^{-3}$ g/ml. After 12 h of reaction, the glass fibers were washed with distilled water until the pH value of the solution became neutral, which were finally placed in an oven and dried at 60°C for 48 h.

2.3. Characterization of glass fiber
The surface morphology of the glass fibers was observed by FEI QUENTA FEG 250 field emission scanning electron microscope manufactured by American FEI Company with the acceleration voltage was 20KV. The surface elements and chemical state of the glass fibers were characterized by an ESCALAB 250 X-ray photoelectron spectrometer manufactured by Thermo Fisher SCIENTIFIC.

2.4. Mixtures preparation
Glass fiber-reinforced cement materials were prepared by mixing the cement, water, untreated glass fibers (OF) and in-situ modified glass fibers of poly-dopamine (DF) in various proportions. Three water-cement ratios of 0.3, 0.35 and 0.4 were designed to prepare glass fiber-reinforced cement materials. For each mixture with specific water-cement ratio, the dosage of glass fibers was designed to be 0, 1, and 7% to investigate the influence of the incorporation of glass fibers and the effect of nano-modification on glass fibers. Cement was introduced in the mixing container and mixing was carried out at a high speed of 285 rpm by vertical axis planetary concrete mixer with the gradual addition of glass fibers and water simultaneously. Fresh mixtures were placed into 280 mm × 25 mm × 25 mm molds with the copper rod fixed at both ends, compacted, removed from the molds after 24 h of casting and immersed in curing water tank for 28 days. The temperature and relative humidity were controlled at 20 ± 3°C and 50 ± 4% respectively.

2.5. Test methods
The shrinkage of fiber-reinforced cement was tested according to JC/T 603-2004. The shrinkage was calculated by the shortage length of the specimen divided by its original length.

3. Results and discussion

3.1. Effect of dopamine hydrochloride concentration on in-situ modification glass fibers of poly-dopamine
Figure 1 shows the effect of dopamine hydrochloride concentration on the self-polymerization of dopamine on glass fibers. Comparing figure 1 (a) with figure 1 (c), rough surface with some nanoparticles is distinctly observed on modified glass fibers. XPS results from figure 2 (a) show that in addition to silicon (Si), oxygen (O), sodium (Na) and zirconium (Zr), which are the elements of glass fibers, carbon (C) and nitrogen (N) are also be found which are originated from poly-dopamine. It can be seen from figure 2 (b) that the peak sites located at 285.1 eV and 284.5 eV could be assigned to C-H/C=C and C-C [16, 17], respectively, which is the presence of carbon in poly-dopamine. These indicated that the poly-dopamine is successfully modified on the surface of the glass fibers.

![Figure 1](image_url)

*Figure 1. Effect of dopamine hydrochloride concentration on surface morphology of poly-dopamine in-situ modified glass fibers (a: $1 \times 10^{-3}$ g/ml; b: $1.5 \times 10^{-3}$ g/ml; c: $2 \times 10^{-3}$ g/ml; d: $2.5 \times 10^{-3}$ g/ml; e: untreated).*
As shown in figure 1(a), when the dopamine hydrochloride solution concentration is $1 \times 10^{-3}$ g/ml, nanoparticles are grown on a small portion of the glass fibers, and when the concentration of the dopamine hydrochloride solution is increased to $1.5 \times 10^{-3}$ g/ml, the nanoparticles on the surface of the glass fibers are gradually increased, as shown in figure 1(b), but there are still some small areas on the surface of the glass fibers that are not completely covered. When the concentration of the dopamine hydrochloride solution is increased to $2 \times 10^{-3}$ g/ml, the nanoparticles are uniformly and densely grown on the surface of the glass fibers as shown in figure 1(c). The concentration of dopamine hydrochloride is further increased to $2.5 \times 10^{-3}$ g/ml. It is found that the surface morphology of the glass fibers is similar to that obtained after the reaction in $2 \times 10^{-3}$ g/ml of dopamine hydrochloride solution, as shown in figure 1(d). As a consequence, it can be concluded that the effect of poly-dopamine in-situ modification of glass fibers gradually improved with increasing dopamine hydrochloride concentration. When the concentration of dopamine hydrochloride is $2 \times 10^{-3}$ g/ml, the modification effect is the best. Increase the concentration of dopamine hydrochloride, the modification effect is not improved. Therefore, the concentration of dopamine is selected as $2 \times 10^{-3}$ g/ml as the optimal reaction condition.

![Figure 2](image2.png)

**Figure 2.** XPS spectra of in-situ modified glass fiber with poly-dopamine shown in figure 1(a) (a: wide scan; b: C 1s).

![Figure 3](image3.png)

**Figure 3.** Effect of pH value of solution on surface morphology of DF (a: pH = 7.5, b: pH = 8.0, c: pH = 8.5, d: pH = 9.0, e: pH = 9.5, f: untreated).

### 3.2. Effect of pH control on in-situ modified glass fiber of poly-dopamine

With the concentration of dopamine hydrochloride set at $2 \times 10^{-3}$ g/ml and reaction time at 12 h, the pH value of the solution is varied to investigate its effect on nano-modification process of the fibers. As can be seen from figure 3(a)-(f), the untreated glass fibers surface is relatively smooth. When the pH is 7.5, the nanoparticles begin to appear on the surface of the glass fiber, but the amount is small and the
distribution is extremely uneven. When the pH is 8.0, more nanoparticles are grown on the surface of the glass fibers but still not evenly distributed on the surface of the glass fibers. When the pH is 8.5, nanoparticles having substantially uniform particle size are uniformly distributed on the surface of the glass fiber. When the pH is 9, aggregation of nanoparticles appear on the surface of the glass fiber with small portion of large particle size shown, suggesting the decreased degree of distribution uniformity. When the pH is 9.5, some of the nanoparticles aggregate together to form larger size particles, which make the uniformity extremely poor. The effect of surface modification of glass fiber changes well firstly, and then changes badly with the increasing of pH value and it is the best when the pH is 8.5. Considering the influence of particle size and distribution uniformity, the best reaction condition with the pH is 8.5.

Figure 4. Effect of poly-dopamine in-situ modified glass fiber (DF) and untreated glass fiber (OF) on shrinkage properties of cement materials with different water-cement ratio.

3.3. Shrinkage performance

Figure 4 shows the development of the shrinkage of different cement samples for up to 28 days. As can be seen from the figure, the shrinkage of each sample is increased with the increase of curing age. Before the curing age is 7 days, the growth trend is relatively fast. After 7 days, the growth trend is gradually slowing down. The contraction is the most severe with the curing age at 28 days. The shrinkage of cement is in the following order with the same water-cement ratio and curing time: Control > 1 % OF > 1 % DF > 7 % OF > 7 % DF. It shows that the incorporation of glass fiber plays a positive role in improving the shrinkage resistance of cement. The reason why is that the glass fibers inside the cement matrix are formed into a three-dimensional disordered distribution support system, which limits the expansion of micro-cracks inside the cement by "bridge" action. Due to it, the shrinkage resistance of cement-based materials is improved [6]. After DF and OF are added, the shrinkage of poly-dopamine in-situ modified glass fiber-reinforced cement and untreated glass fiber-reinforced cement under different curing ages are decreased differently at the same water-cement ratio compared with the cement without glass fibers. As the amount of glass fiber is increased, the degree of decline in shrinkage is gradually increased. When the water-cement ratio is 0.4 and the DF content is 7 %, the reduction in 28-day shrinkage of poly-dopamine in-situ modified glass fiber-reinforced cement is large extent, reducing by 42 % compared with the cement without glass fibers. The reason s that the increase in the amount of glass fiber enhances the “bridge effect” on the inhibition of microcrack propagation inside the cement, thereby reducing the shrinkage of the cement [6]. The shrinkage of the cement without glass fibers is increased with the water-cement ratio. When the latter is 0.4, the 28-day shrinkage of the cement without glass fibers is the biggest, reaching 0.17 %. The reason why is that the water-cement ratio is increased, the degree of hydration of cement is improved, which leads the shrinkage rate of the cement is increased, which shows similar results as previously reported [18]. It is noteworthy that the shrinkage of poly-dopamine in-situ modified glass fiber-reinforced cement and untreated glass fiber-reinforced cement are decreased when the water-cement ratio changes from 0.3 to 0.35. The reason is that the dispersion of glass fibers in the cement matrix is influenced by the water-cement ratio after the glass fiber is incorporated, which may affect the shrinkage properties of the sample [19]. Under the same conditions, the shrinkage of
poly-dopamine in-situ modified glass fiber-reinforced cement is always lower than that of untreated fiberglass-reinforced cement, due to the "root-whisker" structure of DF. With this structure, the surface roughness of glass fibers is improved, which increases their specific surface area. The fiber-cement bonding strength is increased, and the shrinkage of the cement is lowered [11]. Poly-dopamine in-situ modified glass fiber-reinforced cement effectively suppresses the shrinkage of cement-based materials.

4. Conclusions
In summary, modified glass fibers having a “root-whisker” structure were prepared by in-situ growth of a long chain of poly-dopamine molecules on the surface of glass fiber. By controlling the concentration of dopamine hydrochloride and the solution pH, the optimal modification regime was screened out. The surface roughness of fibers was increased by this method. After the glass fiber was added to the cement, the shrinkage resistance of the cement material was significantly improved. As the amount of glass fiber was increased, the shrinkage resistance of cement was gradually enhanced. Poly-dopamine in-situ modified glass fiber-reinforced cement exhibited better resistance of shrinkage than untreated fiberglass-reinforced and ordinary cements. Glass fibers were successfully modified by in situ modification of poly-dopamine. After these were added to the cement, the shrinkage resistance of the cement was significantly improved.

Acknowledgments
The authors would like to acknowledge the financial support from the Supported by National Natural Science Foundation of China (51872121, 51632003 and 51902129), the Taishan Scholars Program and Case-by-Case Project for Top Outstanding Talents of Jinan.

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