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Effect of in-situ modification of poly-dopamine on workability and frost resistance of glass fiber reinforced cement materials

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ABSTRACT

In-situ modification of poly-dopamine performed good alkaline resistance for glass fibers and facilitated flexural strength of fiber-reinforced cement materials in previous studies. In this paper, the effect of in-situ modification of poly-dopamine on workability and frost resistance of glass fiber reinforced cement materials was further studied at varied fiber content and water-cement ratio. In terms of workability, the flow spread decreased with the increment of fiber content and the decrease of water-cement ratio. Meanwhile, the glass fibers modified by polydopamine had little influence on the workability of slurry of cement compared with untreated fibers, evidencing the suitability for construction utilization of in-situ polydopamine-modified glass fibers. Modification of polydopamine glass fibers reinforced cement exhibited better antifreeze performance than untreated fibers reinforced cement, suggesting the effectiveness of nanomodification on fibers. Compared with conventional cement paste, both untreated glass fibers reinforced cement and polydopamine modified glass fibers reinforced cement exhibited enhanced freeze-thaw cycles. When water-cement ratio was 0.3 and the volume content of polydopamine modified glass fibers was 5%, the antifreeze performance was optimal. In short, this work opens up new ideas for improving the frost resistance of cement.

1. INTRODUCTION

In 1824, the British Joseph Aspdin invented Portland cement. Subsequently, cement-based materials were widely used in civil engineering, water conservancy, road and bridge construction and other projects [1,2]. However, due to the poor freeze-thaw resistance, the cracking of cement-based materials has a serious impact on the building structure, which is not conducive to its durability and long-term safe service in cold regions [3]. Therefore, improving the frost-resistant property of cement-based materials is one of the key factors to improve their service life.

Glass fibers with the merits of high tensile strength, high modulus of elasticity, wide range of raw materials, good weathering resistance and easy to be formed into various shapes, have been gradually applied in cement-based materials [4]. Through the "bridging" effect, they can not only overcome the shortcomings of traditional cement-based materials, but improve the mechanical properties and frost resistance of cement-based materials. In view of the interfacial bonding between fibers and cement, a variety of surface modification schemes have been proposed, including etching [5], coating [6], surface grafting [7] and plasma treatment [8]. However, the above methods have many shortcomings, such as complex process, high cost and easy damage of glass fibers.

Nano materials have many singular features and new special features because of their small size effect, surface effect, quantum size effect and macroscopic quantum tunnel effect, which have been developed and applied in many fields including national defense, chemical industry and biology. As an efficient and controllable modification method, the "whisker" structure formed by nano materials and glass fibers can not only increase surface roughness and specific surface area of the glass fibers, but also improve the interface between glass fibers and cement-based materials [9]. Wei et al. modified basalt fibers with nano silica epoxy composite coating [10]. The results showed that the tensile strength of modified basalt fibers and the interfacial shear strength of basalt fibers/resin composite increased by 30% and 15%, respectively. They believed that the introduction of nano silica particles could improve the surface roughness of the fibers and the interfacial adhesion between the fibers and the matrix. In our recent work, dopamine-modified glass fibers were self-polymerized by a facile method at ambient temperature, compared with untreated glass fibers, the alkaline resistance and flexural strength of dopamine-modified glass fibers reinforced cement increased by 37.1% and 58.2%

respectively [11]. To comprehensively evaluate the effect of in-situ modification of poly-dopamine, its influence on workability and durability of glass fiber cement-based materials is also essential for practical applications.

Founded on the polydopamine-modified glass fibers prepared previously, in this paper, as-prepared nano-modified glass fibers were incorporated into the cement slurry for investigating the effect of in-situ modification of poly-dopamine on workability and frost resistance of glass fiber reinforced cement materials by comparison with cement paste and that mixed with untreated glass fibers.

2. MATERIALS AND METHODS

2.1 Materials

Untreated 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. Their apparent density was 2.68 g/cm^3. Self-prepared polydopamine modified glass fibers were gained by synthesis approach previously reported [11]. A certain amount of 0.3 mol/L Tris(hydroxymethyl)aminomethane (Tris) solution was prepared. 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 reaching at 8.5. Then fixed the vessel containing buffer solution on water bath thermostat and added glass fibers with fiber to solution ratio of 0.12 g/ml. Appropriate amount of 2×10^{-3} g/ml dopamine hydrochloride was subsequently added in oxygen-rich environment and reacted for 12 h under shaking. After the reaction, the glass fibers were washed with distilled water until the pH value of the solution became neutral, and finally put them into the oven and dried at 60 ^{o}C for 48 h. Distilled water was obtained from water purification system (Millipore Direct-Q8, Germany). P.O 42.5 cement was purchased from Shandong Shanshui Cement Co. Ltd with the specific surface area of 336 m^2/kg.

2.2 Mixtures preparation

Glass fibers reinforced cement materials were prepared by mixing cement, water, untreated glass fibers/dopamine-modified glass fibers in various proportions. Three water-cement ratios of 0.3, 0.35 and 0.4 were designed to prepare glass fibers reinforced cement materials. For each mixture with specific water-cement ratio, the dosage of glass fibers was designed to be 0%, 1%, 3%, 5% 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 100 × 100 × 10 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.

2.3 Test methods

The workability of glass fibers reinforced cement slurry was characterized by average diameter of flow spread. The frost resistance of glass fibers reinforced cement materials was tested according to GB/T 15231-2008. The sample was first soaked in water at least 10 ^{o}C for 24 h, and then placed in a freezer at -(20 ± 2) ^{o}C for 2 h. Subsequently, the sample was removed and melted in clean water at (20 ± 5) ^{o}C for 1 h, which was one freeze-thaw cycle. At the end of one cycle, the surface was dried with a wet towel, and checked for any damage phenomenon such as layer, peeling, et al. The freeze-thaw cycles were used to characterize freeze-thaw resistance.

3. RESULTS AND DISCUSSION

3.1 Workability

Figure 1 showed the effect of water-cement ratio on workability of untreated glass fiber and dopamine-modified glass fiber reinforced cement materials. As shown in Figure 1 (a), when water-cement ratio was 0.3, the flow spread of cement paste was 131 mm. Along with the inclining fiber content the flow spread of gradually decreased for both dopamine-modified glass fiber reinforced cement. When fiber content was 7%, the flow spread of polydopamine modified glass fibers reinforced cement and untreated glass fibers reinforced cement reached the minimum value, which were 89 mm and 88 mm respectively. When water-cement ratio was 0.35, as depicted in Figure 1 (b), the flow spread of cement paste was 154 mm, while those of polydopamine modified glass fibers reinforced cement and untreated glass fibers reinforced cement were 125 mm and 123 mm respectively with the fiber content of 7%, which also showed that the flow spread decreased with the increase of fiber content. Similarly, for the water-cement ratio of 0.4, as shown in Figure 1 (c), the flow spread of cement paste was 175 mm, and that of polydopamine modified glass fibers reinforced cement and untreated glass fibers reinforced cement were 147 mm and 146 mm respectively with the fiber content was 7%. It can also be clearly observed that with the increasing water-cement ratio, the flow spread was gradually added. For example, when the fiber content was 3%, the flow spread of polydopamine modified glass fibers reinforced cement for water-cement ratio of 0.3, 0.35 and 0.4

were 124 mm, 149 mm and 170 mm respectively, and that of untreated glass fibers reinforced cement were 125 mm, 140 mm and 171 mm respectively. In addition, it is worth noting that at the same water-cement ratio and fiber content, the flow spread of polydopamine modified glass fibers reinforced cement and untreated glass fibers reinforced cement were almost identical, indicating that modification of polydopamine on glass fibers had little effect on the workability of fiber-reinforced cement materials.

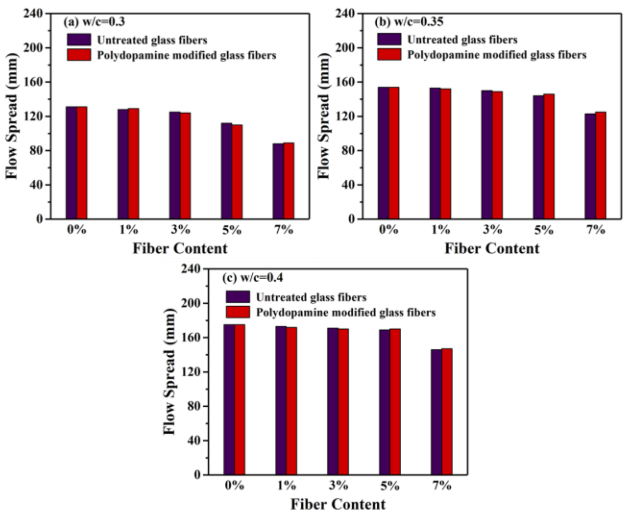

Figure 1. Effect of untreated glass fibers and polydopamine modified glass fibers on workability of cement materials with different water-cement ratio and fiber content.

3.2 Frost Resistance

Figure 2 illustrated the effect of untreated glass fibers and dopamine-modified glass fibers on the frost resistance of cement materials with different water-cement ratio. As shown in Figure 2 (a), when water-cement ratio was 0.3, the number of freeze-thaw cycles that cement paste could bear was 13 times. When glass fibers were added, the number of freeze-thaw cycles was significantly increased. When fiber content was 5%, the freeze-thaw cycles of polydopamine modified glass fiber reinforced cement was 49 times, while that of untreated fibers reinforced cement was 31 times. This may be due to the smaller water-cement ratio, which affected the dispersion of fibers, resulting in the degradation of polydopamine modified glass fibers reinforced cement. As demonstrated in Figure 2 (b), when water-cement ratio was 0.35, cement paste was damaged after 7 freeze-thaw cycles. Polydopamine modified glass fibers reinforced cement and untreated glass fibers reinforced cement could withstand freeze-thaw cycles for 39 times and 30 times respectively when fiber content was 7%. As shown in Figure 2 (c), when water-cement ratio was 0.4, cement paste only insisted 5 freeze-thaw cycles, while polydopamine modified glass fibers reinforced cement and untreated glass fibers reinforced cement could insist 14 and 9 freeze-thaw cycles respectively when fiber content was 7%. And the frost resistance of glass fibers reinforced cement was related to the water-cement ratio. It can be seen from the figures that the smaller the water-cement ratio, the more the freeze-thaw cycles withstood. Untreated glass fibers and dopamine-modified glass fibers could effectively improve the frost resistance of cement materials, and the larger the fiber content, the better the frost resistance. Under the same conditions, dopamine-modified glass fibers improved the frost resistance of cement materials better than untreated glass fibers. When the water cement-ratio was 0.3, 0.35 and 0.4, the maximum number of freeze-thaw cycles that polydopamine modified glass fibers reinforced cement could bear were 18, 9 and 5 times more than that of untreated fibers reinforced cement respectively. By comparison, under the water-cement ratio of 0.3 and volume of polydopamine modified glass fibers of 5% the antifreeze performance was optimal.

Figure 3 showed the morphology of glass fibers reinforced cement surface defects after several freeze-thaw cycles. Figure 3 (a) displayed the surface morphology of untreated glass fibers reinforced cement after 8 freeze-thaw cycles when water-cement ratio was 0.35 and fiber content was 1 %. As seen in the black wireframe area in the figure, after the freeze-thaw cycles, the surface of cement sample had been peeled off. Figure 3 (b) illustrated the surface morphology of untreated glass fibers reinforced cement with 7 % fiber content after 33 freeze-thaw cycles when water-cement ratio was 0.3. As shown in the black oval area in the figure, in the case of high fiber content, the surface defects of untreated fibers reinforced cement after freeze-thaw cycles were not peeled off, but small holes. Moreover, these small holes were mostly distributed in the concentrated area of glass fibers, which meant that there were more defects in this area than in others. This may be due to the uneven distribution of high content of untreated glass fibers in the low water-cement ratio, resulting in local aggregation of untreated glass fibers and relatively denser internal three-dimensional space network. Under the same vibration conditions, the internal network space of fibers might not be fully filled with cement paste, and thus there were some defects of holes in the internal of untreated glass fibers reinforced cement. Once more pores were present, under the action of "frost heaving and thawing", the pore water in the holes would freeze and expand, the volume of the holes would gradually increase under the exertion of stress or the holes would cumulatively break, forming the surface defects as shown in Figure 3 (b).

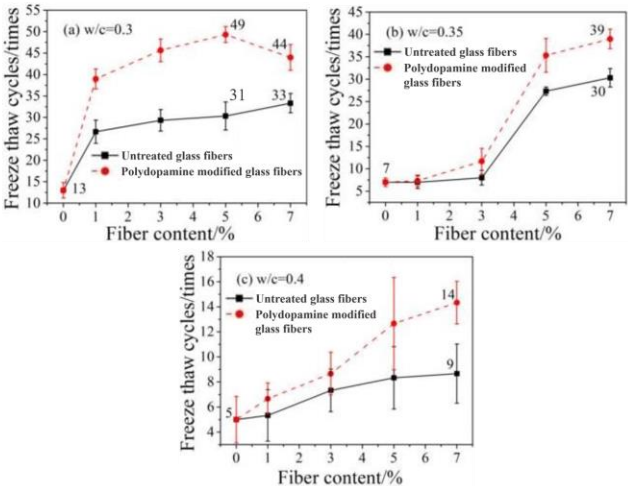

Figure 2. Effect of untreated glass fibers and polydopamine modified glass fibers on frost resistance of cement materials with different water-cement ratio and fiber content.

Figure 3. Surface morphology of untreated glass fiber reinforced cement after freeze-thaw cycles.

4. CONCLUSIONS

In conclusion, in-situ modification of polydopamine on glass fibers insensitively influenced the workability of cement materials, which confirmed the advance and feasibility of modification technique for practical applications. Similar with untreated glass fibers reinforced cement, the increment of water-to cement ratio as well as declining of fiber content resulted in better workability. The polydopamine modified glass fibers reinforced cement possessed larger freeze-thaw cycles than the untreated glass fibers reinforced cement, suggesting the effectiveness of nano modification on the fibers. At different water-cement ratios, compared with cement paste, the enhanced freeze-thaw cycles of glass fibers reinforced cement evidenced positive significance of glass fibers to cement materials. It is anticipated that as-developed in-situ modification approach via self-polymerized dopamine on glass fibers provides a meaningful strategy for advancing modification of glass fibers and promotes the development of high-performance fiber-reinforced cement.

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