Study on the Preparation of Modified Polypropylene Fiber Reinforced Cement-Based Composite

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Abstract. The concentrated HNO3 is applied to carry out the surface modification of polypropylene fibers for the preparation of PP fiber reinforced concrete composite. The modification effect of the oxidation reaction is evaluated by the mechanical testing of the PP fiber reinforced concrete composite. The stretching vibration of O-H and C=O bond centered at the wave number of 3300 cm⁻¹ and 1720 cm⁻¹, respectively, indicates the oxygen-containing groups are generated on the surface of the modified polypropylene fiber. The contact angles of the modified polypropylene fiber are also significantly reduced to about 81°, compared with the untreated polypropylene fiber (112°). SEM analysis suggests that the corrosion effect of HNO3 modified polypropylene fiber on the surface is quite obvious since the surface becomes very rough and has grown pore structure near the surface area. Finally, the modification PP fiber reinforced cement composite has an increment of 11.5% on the fracture strength properties compared by the untreated PP fiber. The results indicated that the oxidation process by the concentrated HNO3 could substantially improve the mechanical properties of modified PP fiber in the concrete composite. The reason should be the elevated hydrophilic properties of the modified PP fiber improve the interface bonding strength which is crucial for the performance of the composite.

1. Introduction
Fiber reinforced is an important method for high performance cement-based composite materials. The fiber reinforcement could effectively reduce the formation of cracks in the process of cement hardening, and inhibit the growth of cracks under external load, so as to improve the mechanical properties of concrete. Adding fiber materials to cement-based materials can improve and overcome the shortcomings of cement-based materials, thus the crack resistance, impermeability and other properties of cement-based materials could be extensively improved [1].

Recently, the synthetic fibers used to strengthen cement-based composites mainly include polypropylene fiber, polyvinyl alcohol fiber, polypropylene fat fiber, polyethylene fiber, polyamide fiber, etc. [2, 3]. From the early use of polyamide fiber to the synthetic fiber, polypropylene fiber has been widely concerned because of its good reinforcement effect, wide source and low price. At present, the research focus of synthetic fiber reinforced cement-based materials is mainly on corrosion resistance, elastic modulus of synthetic fiber and cement-based materials, and the combination of synthetic fiber and collective interface [4]. In the process of application and research of fiber-reinforced cement-based
materials, there are two or more hybrid fiber-reinforced cement-based materials with different properties, materials and types of fiber-reinforced matrix. The selected fibers can learn from each other's strengths and weaknesses, and the results composite may obtain better performance [5, 6].

In this paper, the concentrated HNO₃ is applied to carry out the surface modification of polypropylene (PP) fibers for the preparation of PP fiber reinforced concrete composite. The modification effect of the oxidation reaction is evaluated by the mechanical testing of the PP fiber reinforced concrete composite.

2. Experimental Section
The PP fibers was soaked in strong acid solution prepared from 10 mL concentrated HNO₃ and 35ml distilled water. According to the time gradient, they were divided into five groups: 0 min, 10 min, 20 min, 30 min and 120 min. After treatment, the modified PP fiber was washed with distilled water and dried in the oven at 60 °C for 24 hours.

The polymer emulsion, inorganic cement material, additives and water were mixed in a certain proportion. The sample slurry was poured into the sample mold uniformly coated with demoulding agent according to the preparation method of GB/1727-79, and 28 days was deactivated in the curing box of HBY-30 type CA mortar. After the sample is dried, clamp the two ends of the sample in the center of the fixture of the tensile machine, start the dl-2000 electronic tensile testing machine (the tensile speed is 2 mm/s) until the test piece is pulled off, and read out the value at the time of pulling off.

3. Results and discussion
The Fourier transform infrared spectrometer is applied to evaluate the concentrated HNO₃ oxidation effect of PP fiber for 0-120 minutes (Figure 1). It can be seen from the Figure 1 that the infrared spectrum of PP fiber is much different before and after modification. After the modification by concentrated nitric acid, there is a strong absorption band forms by the stretching vibration of O-H bond at the wave number of 3300 cm⁻¹, and there is a absorption peak of C=O centered at the wave number of 1720 cm⁻¹. The results indicate the oxidation process is effective in the modification reactions while concentrated nitric acid was applied, the oxygen-containing group is generated. In addition, the strength of characteristic absorption peak increases gradually with the time of modification of HNO₃, indicating that the modification effect becomes more and more obvious with the increasing oxidation time.

![Figure 1. The FT-IR spectra of HNO₃ treated PP fiber](image)

Jc2000c contact angle measuring instrument was used to test the PP fiber samples, and the inspection apparent diagram is shown in the figure 2.
Figure 2. The contact angle testing of the PP fiber oxidized by HNO₃ for 10 (a), 20 (b), 30 (c), 120 (d) and 0 (e) minutes

It can be seen from the Figure 2 that the surface of the fibers has rarely changed which is not suitable for the contact angle. With the increase of modification time, it can be found that the size of contact angle changes obviously with the increasing modification time. The contact angle of PP fiber samples are measured, it is found that the contact angle of PP fiber decreases with the increasing immersion time in HNO₃, indicating that the hydrophilicity of the fiber surface becomes better. The contact angles reduces from 112° to about 81°, indicating that the effect of HNO₃ modified PP fiber is very obvious.

Table 1. The contact angle of the PP fiber oxidized by concentrated HNO₃

| Type        | Oxidation Time /min | HNO₃/ml | DI water/ml | contact angle/° |
|-------------|---------------------|---------|-------------|----------------|
| PP fiber    | 0                   | 0       | 0           | 112.2077       |
| PP fiber    | 10                  | 10      | 40          | 102.3404       |
| PP fiber    | 20                  | 10      | 40          | 96.52414       |
| PP fiber    | 30                  | 10      | 40          | 90.96300       |
| PP fiber    | 120                 | 10      | 40          | 81.20265       |

Figure 3. The SEM images of the PP fiber (a, c) and PP fiber oxidized in HNO₃ for 30 minutes (b, d)

The modification time will have a great influence on the oxidation modification effect of the fiber. Table 2 shows that the contact angle of the fiber was becoming smaller with the increasing oxidation time. In the period of 0-30min, the contact angle of the polypropylene fiber decreases greatly. After 30min, the change of the contact angle of the PP fiber tends to be gentle, which shows that the effect of modification tends to be saturated gradually.
The Figure 3 is the SEM images of PP fiber samples which shows the micro morphology changes after modification. It can be clearly seen from the Figure 3 that the surface of the original surface of PP fiber is very smooth; however, after the treatment of HNO₃, the surface becomes very rough and has grown pore structure near the surface area, which shows that the corrosion effect of HNO₃ modified polypropylene fiber on the fiber surface is very obvious, and in terms of increasing the surface roughness of the fiber, it can also improve the hydrophilicity of the PP fiber surface.

![Figure 3. SEM images of PP fiber samples](image)

**Figure 3.** The fracture strength of untreated PP fiber and HNO₃ treated PP fiber reinforced cement-based composite

The fracture strength is performed by mechanical universal testing machine, based on the composite formula of 2:5 (poly ash ratio), 0.05 wt% defoamer and 1 wt% water reducing agent. After modification, the oxidized PP fiber reinforced cement composite shows much better fracture strength (Figure 4). The modification PP fiber reinforced cement composite has an increment of 11.5% on the fracture strength properties compared by the untreated PP fiber. The results indicated that the oxidation process by the concentrated HNO₃ could substantially improve the mechanical properties of modified PP fiber in the concrete composite. The reason should be the elevated hydrophilic properties of the modified PP fiber improve the interface bonding strength which is crucial for the performance of the composite.

**4. Conclusion**

In this paper, the modified PP fiber reinforced concrete composite was prepared to evaluate the mechanical properties of the composites compared by the untreated PP fiber reinforced concrete composite. The results suggest that the oxidation process by the concentrated HNO₃ could substantially improve the mechanical properties of modified PP fiber in the concrete composite. The reason should be the better hydrophilic properties of modified PP fiber which has been analyzed by FT-IR (The stretching vibration of O-H and C=O bond centered at the wave number of 3300 cm⁻¹ and 1720 cm⁻¹, respectively, indicates the oxygen-containing groups are generates on the surface of the modified polypropylene fiber) and contact angle testing (The contact angles of the modified polypropylene fiber are also significantly reduced to about 81°, compared with the untreated polypropylene fiber (112°)).

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