Effect of Temperature on Micromechanical Properties of Polyvinyl Alcohol Fiber–Matrix interface and Uniaxial Tensile Properties of High-Ductility Cementitious Composites

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Abstract: This study investigated the effects of temperature on the tensile strength of polyvinyl alcohol (PVA) fibers, micromechanical properties of the fiber–matrix interface, and macroscopic uniaxial tensile properties of high-ductility cementitious composites (HDCC). In particular, the following values of the temperature of different regions and the glass transition temperature of PVA fibers were selected: −30 °C, 0 °C, 20 °C, 60 °C, and 180 °C. Thermogravimetric analysis and differential scanning calorimetry of PVA fibers were carried out using a synchronous thermal analyzer. In addition, the micromorphology of failure fibers and the fiber–matrix interface was observed using a scanning electron microscope. The results showed that when taking the tensile strength at 20 °C as a reference value, after heat treatment at −30 °C, 0 °C, 60 °C, and 180 °C, the average tensile strength of PVA fibers was 86%, 89%, 88%, and 60% of that at 20 °C, respectively. The ultimate tensile strain value of HDCC was closely related to the treatment temperature: it was the largest at 0 °C; its values at −30 °C and 60 °C were essentially equivalent, its value at 20 °C was small, and its value was the smallest at 180 °C. It can be concluded that after the heat treatment, the tensile strength of PVA fibers decreases to some extent, and there is a piecewise linear relationship between the fiber tensile strength and temperature. Hence, an appropriate heat treatment can reduce the chemical debonding energy and increase the frictional bond strength at the onset of fiber slippage. At the same time, the effect of temperature on the ultimate tensile strain of HDCC is opposite to that on the chemical debonding energy of the fiber–matrix interface.

1. Introduction
High-ductility cementitious composites (HDCC), also known as engineered cementitious composites or bendable concrete, are favored by researchers and engineers owing to their high ductility, high durability, and good construction performance [1]. In recent years, HDCC has been widely used in repairing and strengthening, aseismic structures, bridge deck seamless joints, and other projects [2,3].

Polyvinyl alcohol (PVA) fibers, the core raw material of HDCC, is an organic synthetic fiber. If it is placed in a too high- or too low-temperature environment for a long time, its physical and mechanical properties change significantly compared to those at manufacture. Therefore, the design, preparation, and engineering applications of HDCC-based materials guided by the material parameters ac-
quired at normal room temperatures of workshops would inevitably produce large deviations in a high- or low-temperature environment.

At present, research on the temperature effect on HDCC performance focuses mainly on mechanical properties, ductility, temperature explosion resistance, and frost resistance [4-7]. However, there are few reports on the effect of temperature on physical and mechanical properties of PVA fibers and ductility of HDCC prepared using PVA fibers affected by temperature [8].

China has a vast territory, and the regional temperatures vary greatly. In the southern high-temperature regions, the surface temperature can reach 60 °C in summer, while in the high-latitude cold regions, the extreme low temperature in winter is less than −30 °C. The design and application of HDCC can be carried out in a targeted manner when considering the effect of material storage and service temperature on the physical and mechanical properties of fibers, which is conducive to using the excellent characteristics of HDCC to the fullest.

The effects of temperature on the tensile strength of PVA fibers, micromechanical properties of the fiber–matrix interface, and macro-uniaxial tensile properties of HDCC were studied by simulating the temperature of different regions and the glass transition temperature of PVA fibers. In this study, the following five temperature values were explored: −30 °C, 0 °C, 20 °C, 60 °C, and 180°C.

2. Materials and methods

2.1. Materials

The materials used in this test were P-II 42.5R Portland cement, grade I fly ash, calcium carbonate limestone powder with an average particle size of 20 μm, river sand with a maximum size of 1.18 mm, ordinary tap water, and a polycarboxylate-type high-performance water-reducing admixture with a water reduction rate of more than 40%. The selected physical and mechanical properties of the high tensile strength and high modulus PVA fibers are listed in Table 1.

| Ultimate tensile strength /MPa | Elastic Modulus /GPa | Ultimate elongation /% | Equivalent diameter /μm | Length /mm | Density /g/cm³ |
|-------------------------------|----------------------|------------------------|------------------------|------------|----------------|
| ≥1300                         | 35                   | 8~10                   | 40                     | 12         | 1.3            |

2.2. Mix proportions

Table 2 shows the mix proportions of HDCC. The matrix for a single PVA fiber pull-out test was prepared using fresh HDCC paste; PVA fibers in HDCC were removed.

| Mix number | Cement | Fly ash | Sand | Stone powder | Water | Water reducer | PVA Fiber |
|------------|--------|---------|------|--------------|-------|---------------|-----------|
| 0.25F60    | 496    | 744     | 360  | 90           | 310   | 3.8           | 26        |
| 0.25F80    | 248    | 992     | 360  | 90           | 310   | 3.0           | 26        |
| 0.3F60     | 480    | 720     | 348  | 87           | 360   | 2.2           | 26        |
| 0.3F80     | 240    | 960     | 348  | 87           | 360   | 2.0           | 26        |

The mix number (column 1) describes the water-to-binder ratio and mass percentage of fly ash in HDCC; for example, 0.25F60 denotes that a water-to-binder ratio of 0.25 has been used and 60% of cement has been replaced with fly ash.

2.3. Test methods

Heat treatment experiments. The fibers and HDCC specimens were treated with heat, and the five temperature conditions were −30 °C, 0 °C, 20 °C, 60 °C, and 180 °C. The temperatures of −30 °C and 0 °C were realized using a RS-420 cryogenic freezer, 20 °C was realized using a HBY-40B concrete constant temperature and humidity test box, while 60 °C and 180 °C were realized using a DZF-6050 vacuum dryer.
1) Heat treatment of PVA fibers. PVA fibers were treated with heat for 3 hours at the five specific temperatures mentioned above. Then, the power supply of the equipment was cut off, and the door of the test box was opened, so that the PVA fibers could be naturally heated/cooled to room temperature. Next, the tensile strength test of the PVA fibers was performed, and specimens were molded to explore the micromechanical properties of the fiber–matrix interface.

2) Heat treatment of HDCC specimens. HDCC specimens were formed using heat-treated PVA fibers and cured in a test box with a temperature of (20±3) °C and a relative humidity ≥95% for 28 days. Then, the specimens were wrapped tightly with a cling film to prevent moisture loss from their surfaces. The specimens were kept at a constant temperature for 1 hour at the five specific temperatures mentioned above. After this, the power supply of the equipment was turned off and the door of the test box was opened. After the HDCC specimens were naturally heated/cooled to room temperature, the uniaxial tensile test of the specimens was performed.

The tensile strength and micromechanical properties (single-fiber pull-out) of the fibers were tested using a JSF10 high-precision short-cut fiber mechanical properties tester. Details of the single-fiber pull-out test and the process of calculating the parameters of the micromechanical properties, that is, the chemical debonding energy and frictional bond strength at the fiber–matrix interface, are presented in Chen et al [9].

Uniaxial tensile tests. According to the Japan Society of Civil Engineers’ code, “Recommendations for Design and Construction of High Performance Fiber Reinforced Cement Composites with Multiple Fine Cracks,” uniaxial tensile tests were conducted with dumbbell-shaped specimens with a thickness of 13 mm, a parallel portion width of 30 mm, a parallel portion length of 100 mm, and an original reference point distance of 100 mm. Details of the test system and process are provided in Guo et al [10,11].

Thermal analysis experiment. The PVA fiber powder was analyzed according to thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses using a STA449 F3 synchronous thermal analyzer. The temperature range of the instrument was RT ~ 1500 °C, the temperature accuracy was < ±0.1 °C (standard metal), the calorimetric accuracy was < ±1%, and the balance sensitivity was 0.1 µg. The experimental system was set up as follows: from room temperature to 800 °C, the heating rate was 10 °C/min, protected by nitrogen.

3. Results and discussion

3.1. Effect of temperature on the tensile strength of PVA fibers

Photographs of PVA fibers treated at five temperatures for 3 hours are shown in Fig. 1.

(a) −30°C  (a) 0°C  (a) 20°C  (a) 60°C  (a) 180°C

Figure 1. Photographs of PVA fibers after the heat treatment at different temperatures

Fig. 1 shows that the PVA fibers are white at a room temperature of 20 °C. After the constant-temperature heat treatment at different temperatures, the color of the surface of the PVA fibers changed to some extent. In particular, after the constant-temperature heat treatment at −30 °C, 0 °C, and 60 °C, the surface color of the fibers changed from white to beige, and after the constant-temperature heat treatment at 180 °C, it changed to golden yellow. After the heat treatment at different temperatures, the morphology of the fibers remained fascicular and their integrity remained good.
To study the effect of temperature on the tensile strength of short-cut PVA fibers, after the heat treatment at different temperatures, the PVA fibers were tested using a high-precision mechanical property tester, and the variation rule of the tensile strength was obtained (see Fig. 2). Taking the tensile strength at 20 °C as a reference value, the average tensile strength of PVA fibers after the heat treatment at −30 °C, 0 °C, 60 °C, and 180 °C was 86%, 89%, 88%, and 60% of that at 20 °C, respectively. Lin et al. [12] found that after heat treatments at 50 °C and 200 °C for 1 hour each, the tensile strength of PVA fibers after the heat treatment at 50 °C was similar to that at 20 °C, whereas after the heat treatment at 200 °C, the tensile strength was 64% of that at 20 °C. These conclusions are consistent with those of this study: the tensile strength decreases to some extent after the heat treatment, and the tensile strength and temperature are in a piecewise linear correlation.

The change in the physical and mechanical properties of fibers is closely related to the temperature of the heat treatment. The results of DSC-TG analyses of PVA fibers show that the PVA fiber mass gradually reduces with increasing temperature (see Fig. 3). The glass transition temperature of the fibers is 160–180 °C, the decomposition temperature is 294.1 °C, and the fiber mass loss is 94.37% at 500 °C, which mean that the fibers almost completely melted. Therefore, the fibers become brittle at low temperatures, resulting in a decrease of their tensile strength. At high temperatures, the fibers are decomposed, vitrified, lose weight, etc., also resulting in a decrease of their tensile strength.

![Figure 2. Effect of temperature on the PVA fiber tensile strength](image)

**3.2. Effect of temperature on micromechanical properties of the fiber–matrix interface**

The effects of temperature on the chemical debonding energy and frictional bond stress of the fiber–matrix interface are illustrated in Figs. 4 and 5, respectively.

![Figure 3. PVA fiber thermal analysis](image)

![Figure 4. Effect of temperature on the chemical debonding energy](image)

The relationship between the chemical debonding energy of the fiber–matrix interface and temperature vary significantly. Taking the 0.25F80 series as an example, the order of chemical debonding energy at different temperatures is as follows: it is the lowest at 0 °C, followed by those at −30 °C, and 60 °C, a larger value at 20 °C, and the largest at 180 °C. For the 0.25F60, 0.3F60, and 0.3F80 series,
the effect of temperature on the chemical debonding energy is essentially the same as that for the 0.25F80 series. Due to the hydrophilic nature of the PVA fiber surface, the fiber is chemically bonded to the cement-based matrix. Therefore, the surface properties of the fiber are closely related to the chemical debonding energy. After the treatment at −30 °C, 0 °C, and 60 °C, the chemical debonding energy is lower than that at a normal temperature of 20 °C, indicating that the hydrophobicity of the fiber surface can be enhanced by an appropriate heat treatment. After the treatment at 180 °C, due to the glass transition of the fiber, the surface roughness increases, the micro-defects increase, and hydrophilic increases, resulting in increases of the fiber–matrix interface bonding ability, fiber pull-out load, and chemical debonding energy.

When the PVA fibers are pulled out from the matrix, they undergo the process of local debonding, total debonding, and pull-out failure; the initial interfacial frictional bond stress occurs during the pull-out process [13]. It can be seen intuitively from Fig. 5 that the friction stress is the smallest at 20 °C, followed by those at 0 °C and 60 °C, and the greatest value at −30 °C. After debonding, the bridge stress of the fibers is mainly borne by the friction stress. Therefore, an increase of the friction stress between the fiber surface and the matrix is conducive to improving the ductility of HDCC. It should be pointed out that the fibers treated at 180 °C were fractured before they were completely debonded. Therefore, the corresponding friction stress has not been detected.

In summary, an appropriate heat treatment can reduce the chemical debonding energy of the fiber–matrix interface and increase the initial interface frictional bond stress.

3.3. Effect of temperature on uniaxial tensile properties of HDCC

Taking the 0.25F80 and 0.3F80 series as examples, the effects of the heat treatment temperature on uniaxial tensile properties of HDCC were studied. The relationships between the uniaxial tension stress and strain of HDCC treated at low temperatures (−30 °C and 0 °C) and high temperatures (60 °C and 180 °C) were compared with that of the HDCC cured at the normal temperature (i.e., 20 °C).

The curves of the uniaxial tension stress vs. the tensile strain for different temperatures are shown in Figs. 6 and 7.
After the PVA fibers were treated at −30 °C, 0 °C, 20 °C, 60 °C, and 180 °C, the ultimate tensile strain values of the 0.25F80 series HDCC specimens were 2.31%, 2.55%, 1.17%, 2.26%, and 0.25 %, respectively. For the 0.3F80 series HDCC specimens, the values were 3.85%, 5.04%, 2.58%, 3.78%, and 0.73%, respectively. The ductility of HDCC decreased sharply after the heat treatment at 180 °C compared to that at 20 °C, which is consistent with the experimental results obtained by Bhat [14]. After analyzing the ductility of the two series HDCC specimens, it was found that the ultimate tensile strain was closely related to the treatment temperature. The strain values were sorted from large to small, with the maximum value observed at 0 °C, followed by those at −30 °C, and 60 °C, a smaller value at 20 °C, and the smallest value at 180 °C. Although a very small amount of hydration products may dehydrate at 180 °C, the HDCC specimens were kept at the constant treatment temperature for only 1 hour, and the effect of the phase change of the hydration products on uniaxial tensile properties of HDCC was very limited.

The effect of temperature on the ultimate tensile strain of HDCC specimens is opposite to that on the chemical debonding energy of the fiber–matrix interface. Comparing the data of the chemical debonding energy of the fiber–matrix interface and the ultimate tensile strain value, a significant negative linear correlation was found between them. The correlation coefficients $R^2$ of the 0.25F80 and 0.3F80 series were 0.9746 and 0.9896, respectively (see Fig. 8). With the increase of the interfacial chemical debonding energy between the fiber and the matrix, the ultimate tensile strain value of HDCC specimens decreased gradually, and the macroscopic ultimate tensile properties of HDCC specimens were determined by the interfacial microchemical debonding energy performance parameters.
3.4. Micromorphology of fibers in HDCC

The typical micromorphology of PVA fibers treated at different temperatures and pulled out or fractured in HDCC specimens which cured at a temperature of (20±3) °C and a relative humidity ≥95% for 28 days is shown in Fig. 9. When the interfacial friction stress is low, the fibers can be pulled out completely from the matrix, leaving a smooth and complete fiber channel in the matrix (see Fig. 9(a)). When the interfacial frictional stress is high, the fibers can still be pulled out from the matrix, but shear friction occurs between the surface of the fibers and the matrix, and obvious fiber debris remains in the matrix (see Fig. 9(b)). For PVA fibers treated at 180 °C, the fibers are fractured before they are completely debonded due to their higher chemical debonding energy and lower tensile strength (see Fig. 9(c)).

![Figure 9. Micromorphology of PVA fibers in HDCC](image)

A test using a scanning electron microscope demonstrated that when the chemical debonding energy between fibers and the matrix is low, the fibers can be pulled out without breaking, and the morphology of the fibers remains intact or partially intact. In this case, HDCC has a higher ultimate tensile strain value and better ductility. When the chemical debonding energy is high, the fibers are fractured. In this case, the ultimate tensile strain value of HDCC is low and ductility is poor. The heat treatment has a significant effect on the micromechanical properties of the fiber–matrix interface. The pictures illustrating the micromorphology vividly explain the effect of the micromechanical properties on the ductility of HDCC.

4. Conclusions

After heat treatment, the tensile strength of the fiber decreases to a certain extent, while the tensile strength and temperature are in a piecewise linear relationship. Heat treatment has a significant effect on the micromechanical properties of the fiber–matrix interface. An appropriate heat treatment can reduce the chemical debonding energy between the fiber and the matrix, as well as increase the initial interfacial frictional bond strength.

The effect of temperature on the ultimate tensile strain of HDCC is opposite to that on the chemical debonding energy of the fiber–matrix interface. There is a negative linear correlation between the chemical debonding energy of the fiber–matrix interface and the ultimate tensile strain of HDCC.

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