Preparation of Portland cement with high compressive and tensile strength by the synergistic effect between micron-size green silicon carbide and micro steel fiber

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ABSTRACT. A composite material was prepared with high compressive and tensile strength, which was composed primarily of Class G oil well cement, superfine cement, and microfine cement, using a simple mixing method. The compressive strength of the material was maintained by the micron-size green silicon carbide, and the tensile strength was enhanced by the micro steel fiber. The strength test results on day 28 showed that the compressive and tensile strength of the material increased from 44 MPa to 74 MPa and from 3.6 MPa to 18.3 MPa compared with the material without the addition of micron-size green silicon carbide. In addition, the composite material was characterized by various techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric (TG) analysis, and measurement of physical adsorption porosity and specific surface area. We also analyzed the sliding contact angle and the work of adhesion of the material. We found that the micron-size green silicon carbide was adsorbed to the surface of calcium hydroxide (the hydration product of cement) by intermolecular forces. The hydration of cement in the later stage and the hardened structure of the cement were improved, thus increasing the strength of the cement.

1. Introduction
Cement materials have high compressive strength and low tensile strength. To solve this problem, fiber materials such as carbon fiber and steel fiber usually are added to the cement matrix materials. In this case, however, the tensile strength will be decreased. Nanomaterials were applied to cement matrix materials beginning in the 1990s, and soon became an emerging research field. The incorporation of nanoparticles into concrete can make the cement material more compact, improve early strength, increase tensile strength, and significantly improve the durability of the material. Research has been conducted on incorporating nano-silica (nano-SiO$_2$) [1-9], nano-titanium dioxide (nano-TiO$_2$) [5,10], nano-iron (nano-Fe$_3$O$_3$) [4], nano-alumina (nano-Al$_2$O$_3$) [11], and nano-clay particles [12,13] into cement. The compatibility and dispersibility of nanomaterials with cement, however, have always been important issues in the application of nanomaterials to cement. For example, (Feng 2018) et al. investigated the incorporation of micro steel fiber (0.8–1.6%) into cement materials and found that cement material containing 1.6% micro steel fiber had the highest flexural strength compared with those
doped by other percentages of micro steel fiber[17]. In the present study, the micron-size green silicon carbide and micro steel fiber were mixed into a composite material, which was composed primarily of Class G oil well cement, superfine cement, and microfine cement. Although the micro steel fiber enhanced the tensile strength of the composite, the micron-size green silicon carbide maintained its compressive strength.

The synergistic effect between micron-size green silicon carbide and micro steel fiber was utilized to modify the composite material. Factors affecting the change in strength were investigated. Changes after 28 days in compressive and tensile strength with variations in the composition of micron-size green silicon carbide were studied. The composite material was characterized by various techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetric (TG) measurement of physical adsorption porosity and specific surface area. Also, the sliding contact angle and the work of adhesion were analysed. The micron-size silicon carbide(Bjornstrom J, Martinelli A, Matic A et al, 2004; Khooshechin M and Tanzadeh J, 2018) adsorbing on the surface of calcium hydroxide by intermolecular forces improved the hydration of the cement in the later stage, optimized the structure of hardened cement, and increased the strength of cement.

2. Materials and Methods

2.1. Materials

The green silicon carbide, with an average particle size of 1 μm, was produced by Yuanfa Abrasives Trading Company (Yancheng, Jiangsu, China). The micro steel fibers, which were produced by a subcontractor, ranged in length from 10 to 15 mm and had a diameter of 0.22 mm. The Class G cement, superfine cement, and microfine cement were produced by Yaobai Group (Xi’an, Shaanxi, China). The mortar defoamer was purchased from Jingqi Chemical Technology (Foshan, Guangdong, China). The polycarboxylic acid water reducer was purchased from Qinfen Building Materials (Shaanxi, China). The tap water was used as fresh water. Table 1 lists the content of each component. All materials were added to a JSF-550 mixer produced by Shunuo Instrument (Kunshan, Jiangsu, China) at a speed of 800 r/min and for 20 min. The paste was taken out after evenly mixed, and then was put into molds (40 mm × 40 mm × 160 mm), which were then transferred to a chamber with a constant temperature of 25°C and a constant humidity of 98% for 28 days.

| Component       | Class G cement | Superfine cement | Microfine cement | Freshwater | Water reducer | Steel fiber | Defoamer | Green silicon carbide |
|-----------------|----------------|------------------|------------------|------------|---------------|-------------|----------|-----------------------|
| Content         | 38.6%          | 10%              | 10%              | 25%        | 0.2%          | 8%          | 0.2%     | 8%                    |

2.2. Analytical methods

The cement material was tested after 28 days of curing using the TYE-300D tensile and compression testing machine produced by Jianyi Instrument Machinery (Wuxi, China). A Bruker Vertex 70 FTIR spectrophotometer (Billerica, MA, USA) with a wavenumber range of 400 cm⁻¹ to 4000 cm⁻¹ and a resolution of 0.1 cm⁻¹ was used to collect the FTIR spectra. The material (1 mg) was mixed with KBr (100 mg) forming a pellet for the measurement. The crystal phases were analysed by a Bruker D8 Advance X-ray diffractometer with a scan range of 5° to 90°, a step size of 5°, and a scan speed of 0.25 sec/step. FEI Verios 460 was used for SEM analysis: 10 mg of the powder sample was sprayed with gold, followed by morphology and line sweep analysis. FEI Tecnai G2 F20 was used for TEM analysis: 10 mg of the powder was dispersed in ethanol, and ultrasound was used to prevent sample agglomeration. The sample was then dripped onto a copper mesh and then baked under a lamp. The solvent was allowed to evaporate to let the sample solidify. Appearance was assessed and line sweep analysis was performed. Analyses of the thermal behaviors of the materials with and without the addition of green silicon carbide were conducted using a TGA5500 instrument. The sample (50 mg) was heated with a heating rate of
10°C/min and a temperature range of 0–800°C in N2 (100 cm³). The Brunauer–Emmett–Teller (BET) test was carried out using a micromeritics 2460 instrument. The surface energy of green silicon carbide was measured using a DSA100 instrument.

3. Results and Discussion

3.1. Analysis of the mechanical properties

After the material was doped with micron-size green silicon carbide, compressive strength increased from 44 MPa to 74 MPa and the tensile strength increased from 3.6 MPa to 18.3 MPa. The addition of silicon carbide markedly improved the compressive tensile strength (Figure 1).

3.2. Analysis of FTIR and XRD results

Figure 2a shows that no obvious new characteristic peaks appeared after the addition of micron-size green silicon carbide, indicating that no new chemicals were generated from the hydration of the cement after the addition of micron-size green silicon carbide. The XRD patterns in Figure 2b show that there was no crystal phase of silicon carbide in the original material, although we observed clear peaks (101, 110, 103, 112 cards of PDF #29-1126) for the crystal phase of silicon carbide for the material with the addition of micron-size green silicon carbide. In addition, the peak for the crystal phase of calcium hydroxide (001 card of PDF #04-0733) was significantly reduced, indicating that calcium hydroxide was covered by silicon carbide and thus revealed lower peaks. In the FTIR spectrum, the peak value of the Si-O vibration absorption peak at 922 cm⁻¹ migrates from a low wave number to a high wave number. This reflects the polymerization of the silicon tetrahedron in the C-S-H gel. The hydration reaction rate of the cement slurry at this stage is accelerated by the addition of silicon carbide.

![Fig. 1. Analysis of mechanical properties.](image1)

![Fig. 2. (a)FTIR spectra (b)XRD patterns.](image2)
3.3. Analysis of SEM and TEM results
The SEM spectral linear scanning images in Figure 3b show the areas where the surface of calcium hydroxide was not covered by green silicon carbide in relation to the areas where the surface of calcium hydroxide was covered by green silicon carbide. The content of silicon content increased as the content of calcium increased, confirming that the silicon carbide covered the surface of the calcium hydroxide by intermolecular forces. Figure 3a shows the SEM image of the material without the addition of silicon carbide. Regular sheets of calcium hydroxide were distributed uniformly in substantial amount and with large voids between particles. Figure 3b shows the SEM image of the composite material after the addition of silicon carbide. No regularly shaped flaky calcium hydroxide was observed, although we did find uniformly distributed paste-like agglomerates (calcium hydroxide covered by silicon carbide), and the voids between particles were reduced.

Figure 3c shows the TEM image of calcium hydroxide without the addition of green silicon carbide. Flaky calcium hydroxide particles with a dispersed distribution and large voids were observed. As shown in Figure 3d, however, the calcium hydroxide with the addition of green silicon carbide had a uniform distribution and small voids between the particles. These results indicated that the addition of green silicon carbide not only filled the voids between the calcium hydroxide particles but also covered the surface of calcium hydroxide particles, which improved the strength of the cement material.

3.4. Analysis of TG results
The results are shown in Figure 4. As indicated by the endothermic peaks, at 97°C, the total water content in the C-S-H gel remained similar for samples with and without silicon carbide (Figure 4b and c). The endothermic peak at 445°C, however, indicated that the content of calcium hydroxide loss in the
material with the addition of silicon carbide was about 1.8% lower than that in the material without the addition of silicon carbide, which suggested that silicon carbide had already adsorbed on the surface of calcium hydroxide, resulting in a decrease in the thermal decomposition of calcium hydroxide. The endothermic peak at about 700°C showed the content of the gas released from calcination and decomposition of the material. A 3.5% decrease was observed for the material with the addition of silicon carbide compared with the original material, indicating that the addition of green silicon carbide enhanced the heat resistance of the cement material.

![Graph showing TG analysis](image)

3.5. Brunauer–Emmett–Teller porosity and specific surface area analysis
The sample (400 mg) was dried and added to the sample tube, and it was degassed for 4 hours. The dewar was placed on the stage, the bottle mouth was aligned with the sample tube, and the test was conducted for 3 hours. The results were obtained through the ASAP2460 software (see Figure 5). The maximum pore size of the material with the addition of green silicon carbide was 5.2916 nm, and the specific surface area was 194.4775 m²/g, and the maximum pore size of the material without the addition of silicon carbide was 9.5891 nm and the surface area was 123.3535 m²/g. Therefore, with the addition of silicon carbide, the porosity of the cement material was reduced, whereas the specific surface area was increased. The main factor affecting the porosity and strength of the material was the content of calcium hydroxide; therefore, the results showed that the green silicon carbide was adsorbed on the surface of calcium hydroxide, thus improving the strength of the material (Figure 5).
3.6. Analysis of surface energy and work of adhesion

The surface energy was $\gamma_A = 67.52 \text{ mN/m}^2$ and the contact angle was $0^\circ$, indicating a complete wetting situation. Therefore, we obtained the following: $\gamma_A^d = 67.52 \text{ mN/m}^2$, $\gamma_A^p = 67.52 \text{ mN/m}^2$. The surface energy of the cement material with the addition of silicon carbide was $\gamma_B = 71.34 \text{ mN/m}^2$ and the contact angle was $32^\circ$. Therefore, we obtained the following: $\gamma_B^d = 63.56 \text{ mN/m}^2$, $\gamma_B^p = 7.78 \text{ mN/m}^2$. Based on the equation $W_{AB} = \gamma_A + \gamma_B - \gamma_{AB}$, we calculated the following:

$$\gamma_{AB} = \sqrt{(\gamma_A^d)^2 - (\gamma_B^d)^2 + (\gamma_A^p)^2 - (\gamma_B^p)^2}. \quad (1)$$

The work of adhesion of the cement material doped with silicon carbide was $175.82 \text{ mJ/m}^2$. These results showed that the addition of silicon carbide greatly enhanced the interaction between the filler and the cement matrix, such that the strength of the cement was increased. Moreover, the strong intermolecular force causes calcium hydroxide and silicon carbide to combine very tightly and not easily disperse.

4. Conclusion

Using a simple mixing method, the compressive and tensile strength of the composite material was improved, which was composed primarily of Class G oil well cement, superfine cement, and microfine cement, through the synergistic effect between micron-size green silicon carbide and micro steel fiber. The day 28 compressive and tensile strength of the material increased from 44 MPa to 74 MPa and from 3.6 MPa to 18.3 MPa, respectively. The micron-size green silicon carbide adsorbed on the surface of calcium hydroxide by intermolecular forces, which improved the hydration of cement in the later stage and optimized the structure of hardened cement, thereby improving the strength of cement. In addition, this composite cement material has many uses in oil well plugging and physical simulation of secondary and tertiary hydraulic fracturing.

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