THE EFFECT OF GRAPHENE OXIDE COATING ON THE PERFORMANCE OF SHCC

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Abstract: This study develops a novel graphene oxide (GO) coated polyethylene (PE) fiber which can be used to fabricate Strain-Hardening Cementitious Composites (SHCC). PE fiber can be covered by the GO due to the different thermal expansion behavior. This layer of GO coating would increase the fiber surface wettability and roughness, and also chemically improves the functionality and reactivity of PE fiber. Therefore, the interfacial bond between fiber and matrix can be improved. Since the bond between pristine PE fiber and cementitious matrix is usually too weak, theoretically the tensile performance of PE-SHCC after GO coating on the PE fiber (GO/PE-SHCC) can be improved if the fiber/matrix bond is strengthened. From the experimental results, it indicates that the tensile strain capacity of SHCC using 2 vol.% GO/PE fiber can be improved by 96.62 % (from 3.5% to 6.4%), compared to pristine PE-SHCC. The enhanced interfacial bond between fiber and matrix after GO coating is also confirmed by conducting the single fiber pullout test, which indicates that the peak pullout load can be improved by 45.16% (from 0.62N to 0.90N). These single fiber pullout results are further input into a micromechanical based model to generate the single crack fiber bridging law, and the potential of multiple cracking and robustness of strain-hardening behavior is then evaluated by the model, which predicts GO/PE-SHCC should have better performance than pristine PE-SHCC. In conclusion, the research outcomes provide an effective strategy to strengthen the interfacial bond between PE fiber and matrix through GO coating, leading to the development of a novel SHCC with the strain up to 6 %.

1 INTRODUCTION

By the incorporation of suitable fibers and proper engineering of interfacial properties, composites made with brittle cementitious matrix can achieve pseudo-ductility, high energy absorption capacity as well as excellent durability. The resulting material, known as Strain-Hardening Cementitious Composites (SHCC), is distinguished by its tensile strain hardening behavior up to several percent strain. Various fibers can be used in SHCC to reinforce the matrix, for example, polyvinyl alcohol (PVA) fiber [1], polyethylene (PE) fiber [2], polypropylene (PP) fiber [3], etc. This study focuses on the PE-SHCC.

PE fiber has excellent tensile strength (3GPa), however, due to the weak bond between fiber and cementitious matrix, most

individual fibers are still under the low stress level when the PE-SHCC reaches the tensile strain capacity. Thus, the advantage of high tensile strength of PE fiber cannot be fully utilized. The reason for the weak bond is because PE fiber has inert surface with low surface free energy, which is undesirable to make a good adhesion between fiber and matrix. As a result, a variety of techniques have been used to modify the surface properties of PE fiber and to make it more chemically reactive or physically rougher, such as flame treatment, ion/plasma beams and surface coating.

Recently, carbon nanomaterials (CN), such as carbon nanotubes (CNT), carbon nanofibers (CNF) and graphene derivatives, have drawn much attention due to their superior properties, including high modulus (~1100 GPa), excellent fracture strength (~130 GPa) and large specific surface area (~2630 m2/g) [4], [5], which can be used to reinforce cementitious composites or as a novel coating material for fiber with low surface free energy. One example of using CN to treat the PE fiber can be found in [6]. He et al. coated CNFs on the surface of PE fiber through hydrophobic interactions, and indicated that the interface transition zone between the PE fiber and cementitious matrix can be strengthened by filling nano-pores and cross-linking nano-cracks, which led to 15.0 % and 20.0 % improvement in the ultimate tensile strength and strain capacity of PE-SHCC, respectively. However, there are still some issues that need to be further investigated: (1) although it was claimed that the hydrophobic force could drive the CNFs to cover the whole surface of PE fiber, it is difficult to avoid the aggregation of CNFs on the surface of PE fiber due to the intrinsic poor dispersion of CNFs without treatment. The aggregated CNFs can act like defects between the PE fiber and matrix, and therefore reduces the efficiency of fiber treatment; (2) shape similarity of CNFs and PE fiber reduces the efficiency of GO coating, because a full cover of CNFs on PE fibers is hardly to be achieved as both of CNFs and PE fibers are one dimensional in nature.

Graphene oxide (GO), as one of the most popular CN, it can be easily dispersed in aqueous solution due to the existence of negative charged oxygen functional groups grafted on the edges and basal planes of GO sheets, including hydroxyl, carbonyl and carboxyl groups. On the other hand, these functional groups can chemically interact with cement hydrates by covalent bonds. Due to the easy dispersion in aqueous solution as well as many functional groups with high free energy, GO shows very good potential for being a coating material in the PE fiber treatment.

The morphology of GO is a 2D wrinkle-like sheet, so compared with 1D fiber-like CNFs or CNTs, GO with 2D structure should play a better role in enhancing the microstructures of the interface and also controlling the growth and propagation of cracks at the nanoscale level. More importantly, due to the hydrophilic properties of GO, the surface free energy and wettability of GO coated PE fiber (GO/PE fiber) can be increased and lead to a strengthened bond with the matrix. Therefore, a better performance of SHCC by using the GO/PE fiber can be expected.

In summary, the aim of this study is to use GO as a coating material to modify the surface properties of PE fiber, and then develop a novel SHCC with improved strain hardening performance by using the treated GO/PE fiber.

2 MATERIALS AND PREPERATION

2.1 Fiber treatment

Table 1: Physical properties of pristine PE fiber

Length (mm)	Diameter (μm)	Tensile strength (MPa)	Elastic Modulus (GPa)	Density (g/cm^3)
12	24	3000	100	0.97

The physical properties of the pristine PE fiber used in this study are listed in Table 1, and the schematic diagram of the fabrication setup is shown in Fig.1. For each test, 8 mL of GO (4 mg/mL) and 0.5 mL polycarboxylate-based surfactant were first mixed in 800 mL of pure water and subjected to ultrasonication by a Sonics Vibra-Cell vcx-500 ultrasonic processor (750 W, Vibra-Cell-Sonics &

Materials, Inc.) at the amplitude of 30 % for 10 mins. Then, 18.0 g of PE fiber was added into the suspension above with an ultrasonic and mechanical stirring (150/rpm, 80W), under a water bath with a time-dependent temperature, as shown in Fig. 1. The temperature of water bath was increased from 25°C to 80°C in 4 hours and then kept at 80°C for another 2 hours, to enable full deposition of GO on the surface of PE fiber. The final GO/PE fiber was washed by DI water to remove the excess GO attached on the surface of fiber and then vacuum dried at 80°C for 2 days. Uniform deposition of GO on the surface of PE fiber can be observed at the micro-scale level through the optical microscopic.
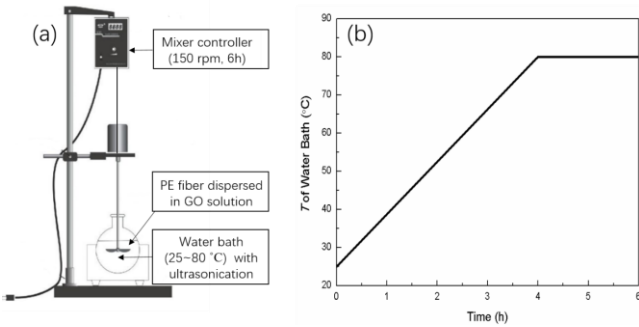

Figure 1: Schematic diagram of the setup for fiber treatment.

2.2 SHCC samples

Table 2: Mix Proportions for the SHCC

Specimen	PE-SHCC	GO/PE-SHCC
Cement	0.8	0.8
Silica Fume	0.2	0.2
Sand	0.3	0.3
Water	0.2	0.2
SP	0.025	0.025
PE (vol.%)	2.0	-
GO/PE (vol.%)	-	2.0

Portland cement fulfilling the requirement of type 52.5R (Green Island, HK) and silica fume (SF, Elkem Co., Ltd, Norway) were used as the binder to fabricate the SHCC. Silica sand with a mean size of 150μm was used as the fine aggregate. A polycarboxylate ether (PCE) superplasticizer was employed to achieve an extremely low water/binder ratio

(0.2) for high matrix strength. 2.0 vol. % PE fiber was added in all mixes. The mix proportions in this test are listed in Table. 2.

In order to achieve good dispersion of fibers in the cementitious matrix, the mixing procedures were as follows. Firstly, all the dry ingredients, including cement, SF and silica sand were mixed at a low speed for 3 mins in a Hobart® mixer with the capacity of 12 L. Water and PCE superplasticizer were then added into the mixing batch. Mixing was conducted at a low speed for 1 min and then turned to high speed for 10 mins until the desired flowability was achieved. After that, PE or GO/PE fibers was added and mixed at a medium speed for another 5 mins. Finally, the fresh SHCC were cast into molds and cured for 24 hours at room temperature before the specimens were demolded and transferred to a curing room (with relative humidity of 95±5 % and temperature of 23±2 °C). Before testing, the specimens were cured for another 13 days.

3   RESULTS AND DISCUSSION
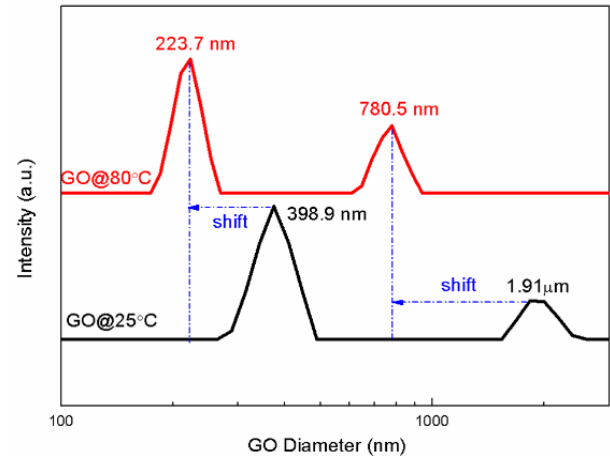
3.1 GO coating on PE fiber

Figure 2 Particle size distribution of GO in water under two different temperatures.

The mechanism that GO can be tightly covered on the surface of PE fiber is based on the fact that GO and PE fiber have an opposite behavior in thermal expansion. It is well known that the thermal expansion coefficient of PE is around $(10-24) \times 10^{-5}$ K, which indicates that PE tends to expand with the increasing temperature [7]. For the thermal

expansion coefficient of GO, it is still unknown due to the variation of numbers of layers and oxygen functional groups. Fig. 2 shows the particle size distribution of GO at the temperature of 25 ˚C and 80 ˚C, respectively. It clearly indicates that with the increasing temperature, the curve shifts to the left-hand side, indicating that the size of GO tends to decrease with increasing temperature. However, this abnormal thermal expansion behavior of GO only occurs in aqueous solution. In dry condition, GO has the same behavior with PE fiber (volume increases with temperature). Based on this phenomenon, GO can be coated on to PE fiber through mixing them and then being vacuum dried at a high temperature. Due to the different behavior of PE fiber (expansion) and GO (shrinkage) with increasing temperature, there must exists some physical interaction forces between the PE fiber and GO, which can be reflected through the Raman spectra, as shown in Fig. 3.
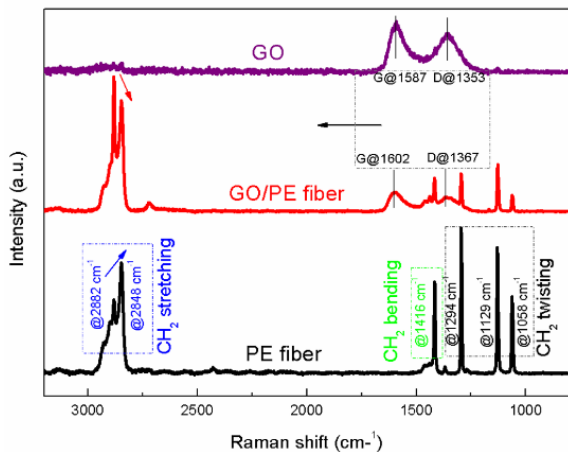

Figure 3 Raman spectra of GO, PE fiber and GO/PE fiber.

The peaks of GO, which are 1587 cm^{-1} (G band) and 1353 cm^{-1} (D band), show a right Raman shift after it is being covered on the surface of PE fiber, with the G band shifting to 1602 cm^{-1} and D band to 1367 cm^{-1}, respectively. This right Raman shift indicates that there exists compressive stress between the GO coating and PE fiber, which makes the coating not easy to spall from the fiber.

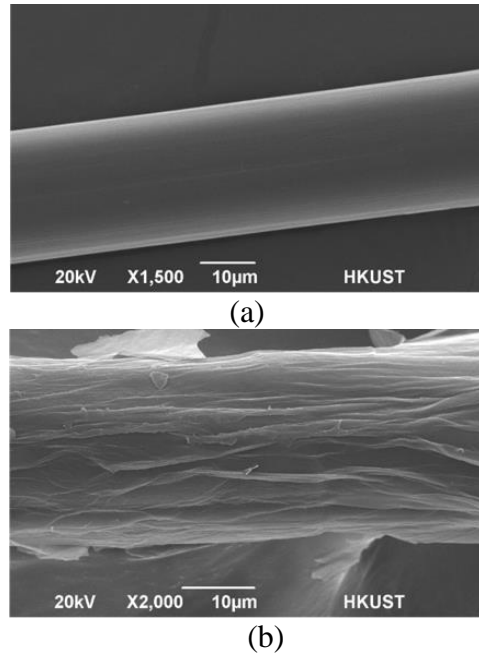In addition, the SEM photos comparing pristine PE fiber and GO coated PE fiber can be found in Fig. 4.

(a)

(b)

Figure 4 SEM of (a) pristine PE fiber; (b) GO coated PE fiber.

3.2 The tensile performance of PE-SHCC and GO/PE-SHCC

In order to test the tensile performance of SHCC with these two different kinds of fibers, the dumbbell specimens, with the dimension shown in Fig. 5, are prepared. Tension tests were performed with a servo-hydraulic machine (MTS), at a loading rate of 0.5 mm/min. For each test, there were at least three samples in order to reduce the stochastic error.
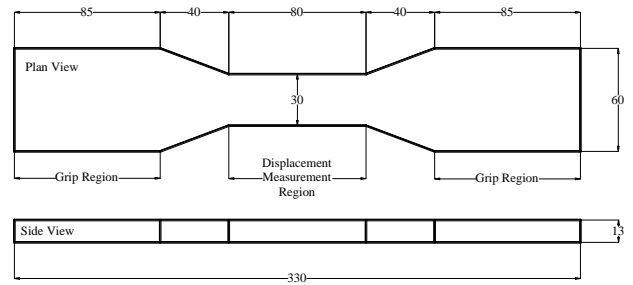

Figure 5 Configuration of the direct tension test sample

The results are shown in Fig. 6. In order to show the results more clearly, only three curves for each group are drawn in the figure. However, the actual tested sample numbers are 8 and 4 for PE-SHCC and GO/PE-SHCC, respectively. For PE-SHCC, the first cracking strength, tensile strength and strain capacity

obtained through averaging the results from all samples are 4.50MPa, 8.80MPa and 3.25%, respectively, while for the GO/PE-SHCC, the corresponding values are 4.95MPa, 10.43MPa and 6.39%, respectively. It can be seen that the first cracking strength of GO/PE-SHCC (4.95 MPa) is slightly higher than the value of PE-SHCC (4.50 MP). Since the first cracking strength is mainly dependent on the property of matrix, and the matrix mix proportion for these two samples are exactly the same, this slight increase can be explained in terms of the matrix enhancement by the dispersed GO.

For the tensile strength, GO/PE-SHCC is 10.43 MPa and PE-SHCC is 8.80 MPa, so there is 18.5 % improvement. This is a direct evidence that GO coating is very efficient in strengthening the bond between PE fiber and matrix, leading to a better utilization of the high strength of PE fiber.

Last but not the least, the strain capacity of GO/PE-SHCC is 6.39 % and PE-SHCC is 3.25 %, so there is 96.62 % improvement which means the ductility of PE-SHCC has been significantly improved through the fiber treatment. In practical engineering applications of SHCC, ductility is a very important property, which is usually related to the crack opening width control, energy absorption capacity, durability, etc.

In conclusion, through the above test, it was found that coating GO on the PE fiber can significantly improve both the tensile strength and ductility of SHCC, which facilitates the potential of applying SHCC in real engineering.
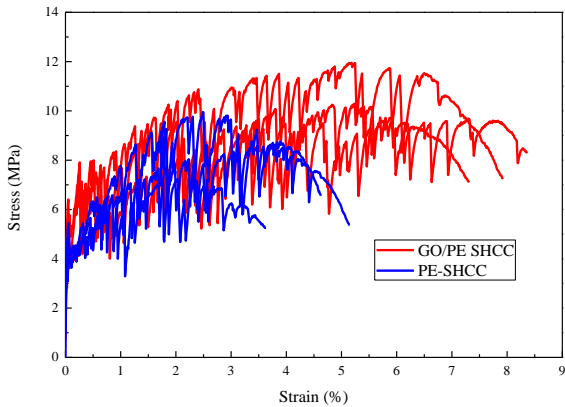

Figure 6 Direct tension test results

3.3 Single fiber pullout test

In order to verify that GO coating can improve the bond between fiber and matrix, single fiber pullout tests were conducted. The matrix mix proportions are the same as Table 2, and the loading rate was chosen to be as same as the one used in direct tension test, i.e. 0.5mm/min. The pullout results are summarized in Table 3. During the pullout process, two phenomena can be observed: (1) the slip hardening effect is not obvious; (2) there is no sudden post-peak drop, so the chemical bond is also not significant. Therefore, the bond between PE fiber and GO/PE fiber can be considered as pure frictional. Maximum pullout force can be used to derive the interfacial friction between PE fiber and matrix based on Eq. (1):

$$\tau \approx \frac{P_{max}}{\pi d_f L_f} \qquad (1)$$

where P_{max} is the maximum pullout force extracted from the testing result, d_f is the fiber diameter and L_f is the fiber embedded length. From the results, the average interfacial friction of GO/PE fiber is 3.99 MPa, 71.2% higher than the value of 2.33MPa for pristine PE fiber.

Table 3: Single fiber pullout test results summary

	Diameter (μm)	Embedded Length (mm)	Maximum Pullout Force (N)	Frictional Stress (MPa)
Pristine PE	24	3	0.55	2.43
			0.70	3.11
			0.58	2.58
			0.64	2.84
			0.58	2.55
			0.64	2.82
Average			0.62	2.33
GO/PE	24	3	0.78	3.44
			1.03	4.56
			0.95	4.18
			1.02	4.52
			0.92	4.06
			0.73	3.22
			0.89	3.95
Average			0.90	3.99

4 MICROMECHANICAL BASED MODEL

For steady-state multiple crack behavior of

SHCC, there are two conditions need to be satisfied [8], [9]:

(1) energy condition:

$$J_{tip} \leq \sigma_0 \delta_0 - \int_0^{\delta_0} \sigma(\delta)d\delta \equiv J_b' \qquad (3)$$

(2) strength condition:

$$\sigma_c \leq \sigma_0 \qquad (4)$$

A micromechanical model developed by Yang et al. [10] was adopted to determine the single crack fiber bridging law (σ-δ). For the two cases (PE-SHCC and GO/PE-SHCC), the only different input parameter is the frictional stress. It has been experimentally determined in Section 3.3, which are 2.33MPa for pristine PE fiber and 3.99MPa for GO/PE fiber. A frictional stress reduction factor 0.4 was applied to account for the decrease of frictional stress with increasing fiber volume content [10]. The simulation results of two σ-δ curves are shown in Fig.7. From the figure, it can be obtained that complimentary energy J_b' was increased from 99.17J/m^2 to 103.84J/m^2 and the maximum bridging stress σ_0 was increased from 10.72 MPa to 13.97 MPa, after the fiber treatment. These increments indicating that both Eq. (3) and Eq. (4) stands more robustly, therefore, it explains why coating GO on PE fiber can improve the strain hardening behavior of SHCC.
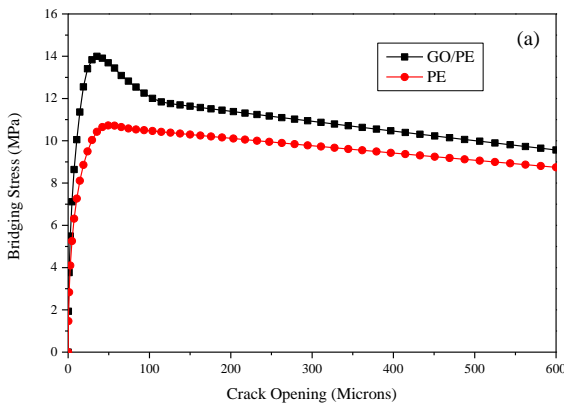

Figure 7 single crack fiber bridging law (σ-δ)

7 CONCLUSIONS

This study developed a novel surface treatment method for the PE fiber, which has inert surface with low free energy and hence has a weak bond with cementitious matrix. The basic idea of this treatment is to add a layer of graphene oxide to the interface between fiber and matrix. The layer of GO can tightly cover on the PE fiber due to the compressive stress generated during the treatment process, and it also has strong connection with the cementitious matrix through covalent bonds. Therefore, the bond between PE fiber and matrix can be improved through this layer of GO coating. Direct tension test results of PE-SHCC and GO/PE-SHCC show that the tensile strength can be improved by 18.5 % and the strain capacity can be improved by 96.62% after fiber treatment. Moreover, single fiber pullout tests directly prove that the interfacial frictional stress can be increased from 2.33 MPa to 3.99 MPa. Finally, a micromechanical model is adopted to explain the mechanism behind the improvement of the strain hardening behavior, which reveals that the increased frictional stress lead to both higher complimentary energy and maximum fiber bridging stress.

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