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Effect of graphene oxide on the mechanical behavior of strain hardening cementitious composites

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HIGHLIGHTS

- The bonding between PVA fiber and cement can be improved by GO addition.
- Mechanical behavior of SHCCs can be improved by a moderate amount of GO.
- Excessive GO addition has a negative effect on the mechanical behavior of SHCCs.

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ABSTRACT

Graphene oxide (GO) is an attractive nanomaterial in reinforcing cementitious materials due to the excellent mechanical properties. This paper presents the effect of GO on the mechanical behavior of Strain Hardening Cementitious Composites (SHCCs), including mechanical performance under compression, tension and flexure. In this study, GO was firstly synthetized by the modified Hummers' method, and then the SHCCs with different GO content of 0.05 wt%, 0.08 wt% and 0.12 wt% were fabricated. It was found that compared with normal SHCC, the GO reinforced SHCCs show an obvious improvement in mechanical behavior. The addition of 0.08 wt% GO leads to 24.8% increase in compressive strength, 37.7% increase in tensile strength, 80.6% increase in flexural strength and 105% increase in flexural toughness, respectively. The improved mechanical behavior of the GO reinforced SHCCs is attributed to the enhanced matrix strength as well as the chemical bonding between the polyvinyl alcohol (PVA fiber) and the cement matrix by GO addition. However, too much GO will cause PVA fiber rupture before being pulled-out from the matrix and should be avoided in the material design.

1. Introduction

As one of the most commonly used construction materials in civil engineering, the potential of cementitious composites is greatly limited by two main drawbacks in terms of mechanical properties: (1) low tensile strength and; (2) low fracture toughness. Although cementitious composites are capable of adequate compressive strength for normal civil structures, the tensile strength has been found to be only around one tenth of the compressive strength, which accounts for the fact that structures can barely stand load inducing tension without the help of steel reinforcement. Apart from the low tensile strength, being quasi-brittle materials, the low fracture toughness of the cementitious composites risks sudden failure accompanied with a large localized crack [1,2]. Even with the reinforcement of steel bars, the low resistance to cracking still makes cementitious members vulnerable to water penetration and therefore subject to durability issues. All in all, enhancing the tensile strength and fracture toughness of the cementitious composite has become an important task in the current research.

A variety of methods have been developed to address above shortcomes [3,4], among which a common practice to improve the tensile strength and toughness of the cementitious composite is by adding fibers, such as polyvinyl alcohol (PVA) fibers, steel fibers and carbon fibers [5]. In particular, Strain Hardening Cementitious Composites (SHCC) have been developed with PVA fibers being incorporated, which is also referred to as Engineered Cementitious Composites (ECCs) in the literature [4]. Based on micromechanical models that provide guidelines for selecting the properties of the fiber, matrix and fiber/matrix interface [1,6,7], high tensile ductility of the SHCCs can be achieved with the sequential formation of multiple cracking [8]. Experimental results in Fig. 1 by SHCC researchers [9] have demonstrated that the

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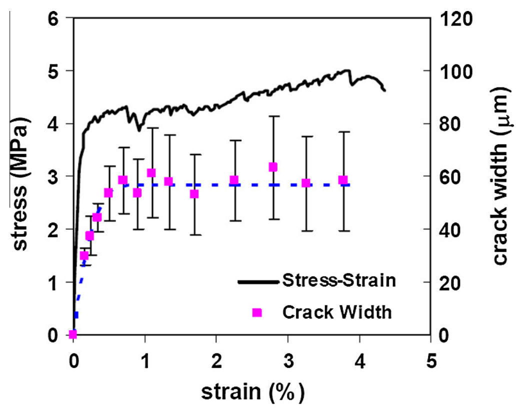

Fig. 1. Typical tensile stress-strain-crack width relationships of the PVA-SHCC [9].

ultimate tensile strain for the SHCC can reach 4% with the addition of 2 vol.% PVA fibers, while the crack width is typically controlled under 80 micros, which is preferable for designing durable structures.

Moreover, carbon nanomaterials, such as carbon nanotubes (CNTs) [10–12], graphene and graphene oxide (GO) [13–15], have been widely investigated for reinforcing the cementitious composite due to its excellent elastic modulus and tensile strength. Differing from hydrophobic CNTs and graphene, GO is an excellent hydrophilic material by introducing oxygen-containing groups, such as hydroxyl, carbonyl and carboxyl [16,17]. The calcium silicate hydrate, the main product of cementitious materials, has silicate hydroxyl and calcium hydroxyl groups near the surface, it can form stable H-bonds connection with GO [18,19]. Therefore, the dispersion of GO in water is excellent and is much easier to mix with cementitious composites [20,21]. Pan et al. [13] found that the introduction of 0.03 wt% GO sheets increased the compressive strength and tensile strength of the cement composite by more than 40% due to the reduction of the pore structure. Lu et al. [22] demonstrated that 0.05 wt% GO led to 11.1% and 16.2% increases in the compressive and flexural strength of the cement paste. Saafi et al. [23] also indicated that the addition of 0.35 wt% GO improved the flexural strength, Young's modulus and flexural toughness of geopolymeric cement by 134%, 376% and 56%, respectively. Lv et al. [14] demonstrated that cement paste with 0.03 wt% GO exhibited remarkable increases in tensile strength (78.6%), flexural strength (60.7%) and compressive strength (38.9%). To conclude, GO has become a great potential nanomaterial for reinforcing cementitious materials.

Although many researchers focused on the mechanical behavior of cementitious materials reinforced by GO, no investigations on the combination of GO and SHCCs have been reported in the literature. In this research, experimental studies on the GO reinforced SHCCs were carried out with the following aims: being nano fillers, GO interacting with the surrounding matrix can significantly influence the micromechanical properties of the SHCCs matrix, which can help to improve the compressive strength of the SHCCs. Moreover, the interface bonding between the fibers and matrix is expected to be modified by GO addition to improve the post-crack behavior of the SHCCs. Since the SHCC is one type of engineered material based on micromechanical mechanics [4], this study explores the potential of incorporating GO into the SHCCs for tailoring the micromechanical parameters and therefore achieve the optimized mechanical performance.

In this study, the GO reinforced SHCCs were firstly characterized by Raman, Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) techniques to investigate the interactions between the GO and the PVA fibers. Secondly, the effects of GO on mechanical properties of the SHCCs, including the compressive behavior, tensile behavior and flexural behavior, were investigated systematically. Finally, the mechanism of the improved mechanical properties of the GO reinforced SHCC was proposed.

2. Materials and experimental methods

2.1. Preparation of GO

GO was prepared from graphite powder (Alfa-Aesar, 200 mesh) according to the modified Hummers' method [24]. Graphite powder (3 g) was added to a solution containing $K_2S_2O_8$ (2 g), P_2O_5 (2 g) and concentrated H_2SO_4 (40 mL, 98 wt%) for 6 h of mixing at 80 °C. The resulting mixture was then diluted with distilled water, filtered and washed until the pH value of the rinse water became neutral. The dried graphite oxide was re-dispersed into concentrated H_2SO_4 (100 mL, 98 wt%) in an ice bath. $KMnO_4$ (15 g) was gradually added and stirred for 2 h. The mixture was then stirred and mixed at 35 °C for another 2 h, followed by the addition of 230 mL of distilled water. The resultant bright yellow solution was terminated by adding 700 mL of distilled water and 15 mL 30% H_2O_2, and then subjected to centrifugation and careful washing by 37% HCl and distilled water. After immersing the as-prepared suspension in dialysis tubing cellulose membranes for 7 days, it was finally centrifuged and collected for preparing different concentrations of the GO solution. In this study, the concentrations of the GO solution used for SHCCs were 1.0, 1.5 and 2.0 mg/mL.

2.2. Preparation of SHCCs

The binder consists of cement, silica fume and a high-volume fly ash (80 wt%). Based on previous experience, a good ductility with more than 3% strain at failure of the SHCCs can be obtained with this mix proportion. To make the comparison, SHCCs with different content of PVA fibers and GO were fabricated, as shown in Table 1. Note that in all five mix proportions, 0.2 wt% superplasticizer were used.

To achieve better dispersed PVA fibers in the SHCCs matrix, the mixing procedures were conducted as follows:

(1) Solid materials were mixed first at low speed for 1 min.
(2) GO was mixed with water and superplasticizer, and then added into the mixing batch at high speed for 5 min until the desired flowability was achieved.
(3) PVA fibers were added and mixed at low speed for 3 min.
(4) Fresh SHCCs were cast into moulds.

The cast samples were cured for 1 day at room temperature and then demolded and cured in a curing room, with a relative humidity of 95 ± 5% and temperature of 23 ± 2 °C, for 7 days.

2.3. Characterization methods

The morphology of the GO/PVA fiber composite was characterized by SEM (JEM-6390). The morphologies of GO was characterized by the transmission electron microscopy (TEM). Raman scattering was conducted on a Renishaw RM 3000 Micro-Raman system using a 633 nm laser source. X-ray Photoelectron Spectroscopy (XPS) was performed with a Physical Electronics 5600 multi-technique system to investigate the carbon status of the GO reinforced SHCCs. The chemical bonding between the PVA fiber and GO was measured by using FTIR (Bio-Rad FTS 6000).

2.4. Testing methods

To assess the mechanical behavior of the SHCCs with different content of PVA fibers and GO, three mechanical tests, a compressive test, uniaxial tensile test and flexural test, were conducted by using a Materials Testing System (MTS 2000). Three specimens of each mix proportions were tested for obtaining the mean mechanical strength value.

Table 1
Mix proportions of the GO reinforced SHCCs.

Mixture	Binder (wt%)			Aggregate (wt%)	Fiber (vol.%)	w/c	GO (wt%)
	Cement	FA	SF	Sand			
Mortar	0.18	0.8	0.02	0.2	0%	0.2	
SHCCs	0.18	0.8	0.02	0.2	2%	0.2	
SHCC-GO0.05	0.18	0.8	0.02	0.2	2%	0.2	0.05
SHCC-GO0.08	0.18	0.8	0.02	0.2	2%	0.2	0.08
SHCC-GO0.12	0.18	0.8	0.02	0.2	2%	0.2	0.12

Note: (a) FA is short for fly ash and SF is short for silica fume; (b) GO is by weight of cement.