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Mechanical behavior and toughening mechanism of polycarboxylate superplasticizer modified graphene oxide reinforced cement composites

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ABSTRACT

Graphene oxide (GO) has attracted increasing interests for the use as nano-reinforcement in cement composites. However, the dispersion problem of GO nanosheets in alkaline cement matrix has been restricting its real application. In this paper, polycarboxylate superplasticizer (PC) modified GO (PC@GO)[1] was used to improve the dispersion of GO and the mechanical behavior of cement composites. The results show that PC@GO disperses uniformly in alkaline cement matrix and exhibits reinforcing effects on mechanical behavior of cement composites. With the addition of ~0.242 wt% PC@GO (PC 0.22 wt%, GO 0.022 wt%) of cement, the compressive strength, flexural strength, Young's modulus and flexural toughness can be increased to 34.10%, 30.37%, 32.37% and 33%, respectively at early days. The toughening mechanism of PC@GO is attributed to its resistance to the formation and growth of cracks based on the characterization of cracks in scanning electron microscope images. This work has opened an effective way to use GO as a nano-reinforcing material for cement composites.

1. Introduction

Cement based composites have been extensively used in building and construction for many decades. However, the inherent brittle nature of cement composites makes crack development easy under mechanical and environmental loads [1–3].

Many attempts have been directed at enhancing the performance of cement composites by incorporation of fibers with different shapes, such as steel fibers, glass fibers, carbon fibers and polymeric fibers [4–10]. It has been demonstrated that fiber-reinforced-cement can effectively strengthen and toughen cement composites by controlling the cracks either at micro-level or at macro-lever. But the fibers fail to stop the initiation of cracks at nanoscale [11]. Moreover, the fibers do not participate in cement hydration, the loosely stacked cement hydrates which are responsible for the brittle nature of cement composites remain unchanged [12].

The recent progress in the field of nanomaterials has provided an invaluable possibility to further improve the performance of cement composites. Nanosilica with high specific surface area and pozzolanic activity can promote cement hydration and consume lime quickly, which is beneficial for densifying the microstructure [13,14]. On top of the nucleating effect, 1D CNTs with large aspect ratio also exhibit the ability of bridging cracks at nanoscale [15]. However, the poor dispersion properties of nanosilica and CNTs coupled with their high cost are the potential obstacles for their widely application in civil infrastructure.

It is urgent to find a nanomaterial with good dispersion property to reinforce cement composites. The recent emergence of graphene oxide (GO) with high specific surface area and excellent mechanical nature is a potential candidate for the use as nano-reinforcer in cement composites. As a graphene derivative, GO can be viewed as a two-dimensional honeycomb lattice with many oxygen-containing functional groups that make GO easily dispersed in water [16]. Another appealing advantage of GO is the low cost, which can be easily acquired from nature graphite flakes by oxidation.

It is reported that GO can accelerate the degree of cement hydration, regulate the formation of hydration crystals and

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[1] PC@GO is short for polycarboxylate superplasticizer (PC) modified GO.

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remarkably improve the mechanical strength of cement composites [12,17]. Although GO can be well-dispersed in water, it is difficult to disperse in alkaline cement matrix due to the electrostatic interaction with charged ions in cement pore solution. Thus extra attention should be paid towards dispersing GO in cement paste/mortar with high PH-value [18]. In some researches, the dosage of water reducing agent was incorporated at a constant amount for plain cement mix and mixes with different GO concentration levels [19,20]. Concerns are raised regarding the negative effect of GO on the fluidity of fresh cement pastes. Large surface areas of GO nanosheets demand more water to wet their surface and reduce the free water content required for lubrication. It has been reported that the tensile strength of cement composite is increased about 48% by adding 1.5 wt% of GO in cement matrix [21]. The compressive strength of cement composites is increased about 63% and 85% by adding 1 wt% of as-synthesized GO and 1 wt% of size-reduced GO in cement matrix, respectively [22]. However, there are few reports on the reinforcing effects and mechanisms of modified GO in cement composites.

In this research, PC (a new-generation water reducing agent providing steric hindrance effect) is used as the modifier of GO to achieve better dispersion in alkaline cement matrix and required fluidity. The effectiveness of PC@GO at different dosages on the mechanical properties of cement composites has been evaluated. The results show that the addition of PC@GO exhibits significant reinforcing effects on mechanical properties of cement composites. With the addition of PC@GO up to ~0.242 wt% (PC 0.22 wt%, GO 0.022 wt%) of cement, the compressive strength, flexural strength, Young's modulus and flexural toughness of the cement composites can be increased by 34.10%, 30.37%, 32.37% and 33%, respectively at early days. The toughening mechanism of PC@GO is attributed to its resistance to the formation and growth of cracks in cement composites based on the characterization of cracks in scanning electron microscope (SEM) images. This work has opened an effective way to use GO as a nano-reinforcing material for cement composites.

2. Experimental

2.1. Materials

GO aqueous solution with the concentration of 5 mg/ml was prepared based on the modified Hummer's method, the details of which are described in our earlier work [23]. The chemical compositions of type P.I. 52.5R Portland cement and the gradation of standard sand used in this research are listed in Ref. [23]. PC with solid content of 40% was used as the modifier of GO.

2.2. Modification of GO

Agglomeration of GO sheets hinders their potential to reinforce cement composites. Therefore, it is necessary to develop an effective dispersion method of GO nanosheets. Compared with dispersion in water, the dispersion of GO nanosheets in cement pore solution proves to be a challenge due to the presence of charged ions. The combination of ultra-sonication and surface modification appears as the most feasible method.

In this study, PC was served as the modifier of GO. The diluted PC was gradually added to GO solution at 60 °C with continuous stirring for 10–20 min. Then the mixture was subjected to ultrasonic vibration for 30 min. It was recommended dripping drops of PC@GO in mixed solution of $Ca(OH)_2$, NaOH and KOH ($PH = 13.5$) prior to mixing with cement to examine the dispersive feature. The amount of PC was kept for ten times of the weight of GO in this study to ensure good dispersion of GO.

2.3. Fabrication of cement composites

There is a plain-cement sample without any GO serving as the reference sample. The others are GO-cement samples at GO concentration levels of 0.011 wt%, 0.022 wt%, 0.044 wt% and 0.066 wt% of cement, which are labeled as 0.011% GO-cement, 0.022% GO-cement, 0.044% GO-cement and 0.066% GO-cement, respectively. In these samples, the amount of PC for the modification of GO nanosheets is 0.11 wt%, 0.22 wt%, 0.44 wt% and 0.66 wt% of cement, respectively. For each mix, the exact volume of PC@GO solution was calculated based on the solution concentration. Then exact amount of water was mixed thoroughly with the prepared PC@GO solution to keep the amount of total water in the diluted solution constant. Therefore, the water to cement ratio for all samples was maintained consistent. Mixing procedures were adopted according to ASTM C305-14 [24]. After mixing, a portion of the mixture was used for fluidity test according to ASTM C1437-13 [25], the rest of the mixture was cast into a rectangle mold (40 mm × 40 mm × 160 mm), then it was vibrated to ensure good compaction. After 24 h, the samples were demolded and cured in a standard room (20 ± 2 °C, 95% relative humidity). The details of the mix design and the fluidity results are shown in Table 1.

2.4. Characterization

The crystallinities of GO and PC@GO were analyzed by X-ray diffraction (XRD). The functional groups grafted on the GO nanosheets were probed by an X-ray photoelectron spectroscope (XPS). The aqueous solution was dropped on a silica substrate and then dried in a vacuum dry box at 60 °C for 10 h. The transmission electron microscope (TEM) were used to observe the morphologies of GO and PC@GO, respectively. To prepare the sample, a drop of diluted solution was dipped on copper grids and then dried at room temperature to remove the moisture.

Heat of hydration measurements were carried out using TAM-AIR isothermal conduction calorimeter instrument at a bath temperature of 23 °C for 72 h. After curing for specific time, the samples were subjected to three-point flexural tests according to ASTM C348-02 with the pressure increasing ratio of 50 ± 10 N/s [26]. Compressive strength is determined according to ASTM C349-14 with the pressure increasing ratio of 2400 ± 200 N/s [27]. The flexural "load-displacement" curves were obtained by using an electronic universal testing machine with a capacity of 100 KN and a load rate of 500 N/s. SEM images were obtained to characterize the cracks of cement composites.

3. Results and discussion

3.1. Characterization of GO and PC@GO

The XPS spectra of GO are showed in Fig. 1. The peaks indicate the existence of following functional groups: graphitic carbon C=C (284.81eV), epoxy/hydroxyls C-O (286.14 eV), ketone/quinone C=O

Table 1
Mix design and fluidity results of the test samples.

Sample	Ingredient (g)					Fluidity (mm)
	Cement	Water	Sand	GO	PC	
Plain-cement	450	188	1350	–	–	145
0.011% GO-cement	450	188	1350	0.05	0.5	162
0.022% GO-cement	450	188	1350	0.1	1.0	165
0.044% GO-cement	450	188	1350	0.2	2.0	173
0.066% GO-cement	450	188	1350	0.3	3.0	184