Construction and Building Materials 96 (2015) 20–28

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effect of graphene oxide on the rheological properties of cement pastes

Yu Shang, Dong Zhang *, Chao Yang, Yanyun Liu, Yong Liu

Key Laboratory of Advanced Civil Engineering Materials, Ministry of Education, School of Materials Science and Engineering, Tongji University, Caoan Road 4800, Shanghai 201804, People's Republic of China

HIGHLIGHTS

- The addition of GO into the cement caused a noticeable reduction in fluidity and increased rheological parameters.
- GO encapsulated silica fume (GOSF) was prepared. Compared with SF pastes, GOSF pastes had better rheological properties, indicating the addition of GO improved rheological properties.
- A possible mechanism was proposed to explain the different effects of GO on the rheological properties of cement pastes.
- The research provides a pathway to utilizing GO in cement based materials.

ARTICLE INFO

Article history:
Received 26 March 2015
Received in revised form 22 July 2015
Accepted 27 July 2015
Available online 4 August 2015

Keywords:
Graphene oxide
Graphene oxide encapsulated silica fume
Cement
Rheological properties

ABSTRACT

The effects of graphene oxide (GO), silica fume (SF) and graphene oxide encapsulated silica fume (GOSF) on the rheological properties of cement pastes were investigated. It was found that the addition of GO into the cement caused a noticeable reduction in fluidity and increased rheological parameters. However, GOSF pastes had better fluidity and lower rheological parameters at a same dosage of SF, indicating that the addition of GO lowers the rheological parameters. A possible mechanism was proposed to explain the different effects of GO on cement pastes. The research provides a pathway to utilizing GO in cement based materials.

1. Introduction

Cement is the key component of concrete and mortar, which is one of the most important and widely used building materials. The incorporation of admixtures [1–3] and fibers [4–6] is now an important technique in improving the properties of cement composites, such as rheological properties, strength, durability, etc. Recently, the development of nanomaterials, such as carbon nanotubes (CNTs) and graphene, has provide opportunities to improving the performance of cement pastes [7,8]. Many studies have been carried on the effect of CNTs on the cement hydration and mechanical properties of cement composites [7,9–12]. With the addition of small amounts of CNTs, the compressive and flexural strengths of cement composites were improved [13–15].

As a graphene derivative, two-dimensional graphene oxide (GO) has several oxygen-containing functional groups such as hydroxyl, carbonyl, epoxy groups and carboxylic groups, rendering GO sheets hydrophilic. GO has a large surface area and good mechanical properties [16,17]. Consequently, GO shows a better gain in compressive strength at a lower concentration when compared to CNT reinforced cement [12]. The introduction of GO in cement not only can regulate hydration but also improve the tensile, flexural and compressive strengths of the cement paste [8,18–22]. Lv et al. [19] discovered that when the content of GO was 0.03%, the cement composites exhibited remarkable increase in tensile strength (78.6%), flexural strength (60.7%) and compressive strength (38.9%).

However, similar to the other nanomaterials such as nanosilica and CNTs, the addition of GO into the cement affects the fluidity and increased rheological parameters [8,21–23]. Pan et al. [22] noted the reduction in workability was about 42% via a mini-slump test with the incorporation of 0.05 wt.% GO. Gong et al. [23] examined the rheological behaviors of GO reinforced cement composite with the aid of the conventional mini-slump test accompanied by the rheological studies. It was found that small proportions of GO increased both the viscosity and yield stress of fresh cement paste. Moreover, the viscosity increased with the size of GO, confirming the influence of geometry on the workability. These studies infer an inverse correlation between

---

* Corresponding author.
E-mail address: zhangdng@tongji.edu.cn (D. Zhang).

http://dx.doi.org/10.1016/j.conbuildmat.2015.07.181

the concentration of GO and workability. It is widely accepted that the large surface area of nanomaterials demands more water to wet their surface, thereby reducing the free water content required for lubrication. Moreover, large scale agglomerates of nanomaterials in cement matrix lead to lower fluidity. However, the work on the influence of GO on the rheological properties of cements is still scarce.

In this paper, the effects of GO on the rheological properties of cement pastes was investigated. It was found that the addition of GO into the cement caused a noticeable reduction in fluidity and increased rheological parameters. Then GO was modified onto the surface of silica fume (SF) to prepare graphene oxide encapsulated silica fume (GOSF). It is expected that GOSF will achieve a good dispersion of GO and SF in the cement matrix by the synergetic effect of the surface activity of GO and the shape effect of SF. Compared with cement pastes with SF, GOSF pastes had higher fluidity and lower rheological parameters, indicating the addition of GO improved rheological properties. Combined with the results of reduced graphene oxide, the possible mechanism was discussed to explain the different effects of GO on cement pastes in the paper. The research provides a pathway to utilizing GO in cement based materials.

2. Materials and methods

2.1. Materials

Ordinary Portland cement type 42.5R was main materials used in this research. SF was used as the cementitious material. The chemical compositions of the cement and SF are shown in Table 1. Table 2 shows the physical properties of SF and GOSF. Graphite oxide was purchased from the Sixth Element Ltd. The suspension of graphene oxide (GO, 4 mg/mL) was prepared by dispersing the graphite oxide powder into water with the help of ultrasonication for 2 h. The chemical compositions of GO measured by XPS is shown in Table 3. GO is composed of C and O. The C/O ratio is 2.29.

2.2. Preparation of GOSF

The SF particles were dispersed into ethanol solution via sonication. After 30 min, 3-Aminopropyltrimethoxysilane (APS) was poured into the above solution and reaction for 24 h to obtain APS-modified silica fume. Then the suspension was washed with ethanol and deionized water.

GOSF was fabricated via the electrostatic interaction between positively charged modified silica fume and negatively charged graphene oxide in aqueous solutions. GO suspension (4 mg mL^{-1}) was added into APS-modified silica fume dispersion under mild magnetic stirring. Almost all the graphene oxide and modified silica nanoparticles coassembled to leave a transparent aqueous solution. The GOSF particles were obtained after centrifugation and kept in a vacuum desiccators at 60 °C for 24 h (see Fig. 1).

2.3. Preparation of cement pastes

The cement paste was prepared by mixing cement, water and GOSF/SF/GO. The water/cement weight ratio remained 0.4. There was a plain cement mix that serves as the reference sample. To investigate the influence of GO, the dosage of GO nanosheets was varied from 0.02% to 0.08% by weight of cement. In other series experiment, the replacement ratio of OPC with GOSF/SF was varied from 2% to 8% by weight (2%, 4%, 6%, 8%). While the cement pastes with the combined addition SF and GO were also prepared (GO + SF).

Mixing procedures similar to GB/T 8077-2000 were adopted. Water was added to a mixing container. The GOSF/SF were then added and stirred for 60 s. Then cement was added and the mixture was stirred at low speed for 120 s. Stop the mixer for 15 s, during which any paste on the sides of the bowl is scraped down into the hatch. Then operate the mixer at high speed for 120 s. After mixing, a portion of the mixtures was used for the mini-slump test.

Table 1
Chemical compositions of cement and SF.

Component	SiO_2	CaO	Al_2O_3	MgO	K_2O	SO_3	Fe_2O_3	Na_2O
Cement (%)	22.7	61.1	6.85	0.95	0.28	3.61	2.86	0.36
SF (%)	91	0.4	1.1	1.0	0.9	0.3	2.0	0.2

Table 2
The physical properties of SF and GOSF.

	Density (g/cm^{-3})	Specific surface area (m^2/g)	Mean particle size (μm)
SF	2.29	13.51	0.1040
GOSF	2.12	14.99	0.1057

Table 3
The chemical compositions of GO measured by XPS.

	C (Atomic %)	O (Atomic %)
GO	68.93	30.15

2.4. Testing methods

2.4.1. Mini-slump tests

In order to evaluate the influence of GO sheets on the fluidity of the cement pastes, mini-slump test was carried out. After mixing, mixtures were poured into a mini-core (top diameter 36 mm, bottom diameter 60 mm, and height 60 mm) immediately. The testing procedures are the same as GB/T 8077-2000 (National Standard of China).

2.4.2. Rheological measurements

The rheological measurements of the pastes were performed by means of a NXS-11 rotary viscometer. The method was based on measuring the shear stress (τ) along complete cycles containing the ascending and descending shear rates; 15 rotating speeds are available. The initial and final speeds were 5.6 and 360 rpm, respectively.

Since cement pastes coincides with Bingham flow, the plastic viscosity (η_p) and the yield stress (τ_0) can be obtained by working out the slope and the intercept of the shear stress–shear rate curve, with the linear regression calculation. The mathematical form of the Bingham equation is as follows:

$$\tau = \tau_0 + \eta_p \gamma \tag{1}$$

where τ is the shear stress (Pa), γ is the shear rate (1/s), η_p is the plastic viscosity (Pa s), and τ_0 is the yield stress (Pa).

2.4.3. Compression tests

In order to examine the influence of GO, SF, GOSF on the mechanical properties of cement pastes, compression tests were conducted on the specimens (2 cm × 2 cm × 2 cm). The specimens were tested at the age 28 days. The loading rate was set to 10 mm/min. At least three samples were repeated for each test.

The morphology of the samples was observed with a field emission scanning electron microscopy (Quanta 200FEG, FEI). Atomic force microscopy (AFM) images were acquired on a scanning probe microscope (NSK, SPA-300HV). The particle size distribution of GO, SF and GOSF was measured by laser particle size analyzer (LS230). X-ray photoelectron spectroscopy (XPS) analysis were performed on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K radiation (*h* = 1253.6 eV). Fourier transform infrared (FTIR) spectra were obtained through a BRUKER EQUINOXSS spectrometer use the attenuated total reflectance.

3. Results and discussion

3.1. Characterization of GO, SF and GOSF

Fig. 2a shows the AFM image of the GO sheets after ultrasonication. It can be found that the average thickness of the GO sheet after ultrasonication is approximately 1 nm, indicating that the GO sheets are exfoliated into monolayer. The size distribution of the GO determined with a help of laser particle size analyzer is shown in Fig. 2(b). The average lateral dimension of GO sheets is approximately 1.12 μm and the size distribution of the GO is found to approximately follow normal distributions after ultrasonication, which is similar to the results of the effect of ultrasonication treatment on the carbon nanotubes [24].

As shown in Fig. 2c, the C1s spectrum of GO consists of four different peaks: C=C in aromatic rings (284.3 eV); C–O (286.3 eV); C=O (287.6 eV); COOH (289.0 eV), indicating the existence of these oxygen-containing functional groups. Fig. 2d shows the FT-IR transmittance spectra of GO. The spectrum of GO illustrates C–O