Characterization of Cement-Based Materials Modified with Graphene-Oxide

Ye Qian, Maika Yzabelle Abdallah, and Shiho Kawashima

Abstract For applications in cement and concrete, studies on carbon-based nanomaterials have been almost exclusively on carbon nanotubes, even constituting a large portion of studies on nanomaterials of any type. Although a promising approach, economic and dispersion issues continue to limit industry acceptance. Graphene oxide (GO), derived cost-effectively from graphite, shows good dispersion in water. In this paper, preliminary results showing the beneficial effects of graphene oxide on the hardening and mechanical properties of cement-based materials are presented.

Keywords Graphene-oxide • Nanomaterials • Cement

1 Introduction

The potential of the use of carbon nanotubes/nanofibers (CNTs/CNFs) to enhance the mechanical properties of cement-based materials has been demonstrated in a number of studies [1–4]. However, as is the case when incorporating any additive or fiber in a cement matrix, achieving effective dispersion is a challenge [5]. And the difficulty increases with decrease in size, where specific surface area increases exponentially as dimensions fall below 100 nm. The use of graphene oxide in cement-based materials has not been widely explored [6–8]. Graphene, the 2D counterpart to CNT, and its oxidized form graphene oxide, has superior elastic modulus and tensile strength. Compared with graphene and CNT, graphene oxide (GO) is readily dispersible in water, requiring only moderate sonication [9–11]. Due to its high specific surface area and 2D feature, it exhibits a very low percolation threshold, which can significantly limit the addition level required.

In this paper, the preliminary results of a study on graphene oxide-reinforced cement paste and mortar are presented. The influence of very small amounts (less than 0.05 % by mass of cement) of GO on rate of hydration heat of cement paste and flexural strength and modulus of mortar are presented.

Y. Qian (✉) • M.Y. Abdallah • S. Kawashima
Department of Civil Engineering and Engineering Mechanics, Columbia University, New York, NY, USA
e-mail: yq2157@columbia.edu; mya2109@columbia.edu; sk2294@columbia.edu
http://www.columbia.edu/~sk2294

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2 Experimental Methods and Procedures

2.1 Materials

Graphene oxide is in aqueous suspension form in deionized water with a concentration of 2 mg/mL. No superplasticizer is added. The stability of the suspension is evaluated through absorbance spectra. Suspensions are diluted with deionized water by a factor of 5 by volume, then centrifuged at 5,000 rpm for 5 min. The absorbance spectra (190–1,100 nm) of the supernatant of samples before and after centrifugation are measured with a spectrophotometer. The absorbance values at 550 nm are 0.98 and 0.96 before and after centrifugation, respectively. This indicates 98.3 % is retained in suspension, therefore highly stable.

Type I Portland cement and deionized water are used in all mixtures. And oven-dried sand passing through sieve #16 (diameter smaller than 1.19 mm) is used in all mortar mixtures. All mixtures have a water-to-cement ratio (W/C) of 0.43 by mass. Mortar has a sand-to-cement ratio (S/C) of 2:1 by mass.

Graphene oxide is added at levels of 0, 0.01, 0.03 and 0.05 % by mass of cement in paste and mortar mixtures. Cement paste samples are denoted as CP, GO.01, GO.03 and GO.05, respectively. Mortar samples are denoted as M, MG1, MG3 and MG5, respectively. The water in the GO suspension and sand absorption are considered when proportioning to achieve the desired W/C.

2.2 Methods

The rate of heat of hydration of cement pastes is measured using a TAM Air isothermal calorimeter. The temperature is set at 25 °C and the heat of hydration is recorded up to 80 h. Cement paste samples are prepared by hand-stirring for 4 min.

Mortar samples are tested for flexural strength. After 10 min mixing of cement, water, sand and GO suspension, the mortar is cast in 25.4×25.4×304.8 mm prism molds in two layers, consolidating on a vibration table in between. They are demolded after 1 day and cured in water at room temperature for 7 and 28 days. Prisms are cut into 25.4×25.4×76.2 mm samples. Four point bending test are performed on an Instron 5984 Universal Testing Machine with a 151 kN capacity. Loading is force controlled at a rate of 1.1 MPa/min.

3 Results

3.1 Rate of Hydration

The normalized heat flow and normalized heat of hydration curves for pastes with 0, 0.01, 0.03 and 0.05 % GO addition are shown in Fig. 1. From Fig. 1a, all curves exhibit two shoulders – the first is due to silicate reaction and the second is due to

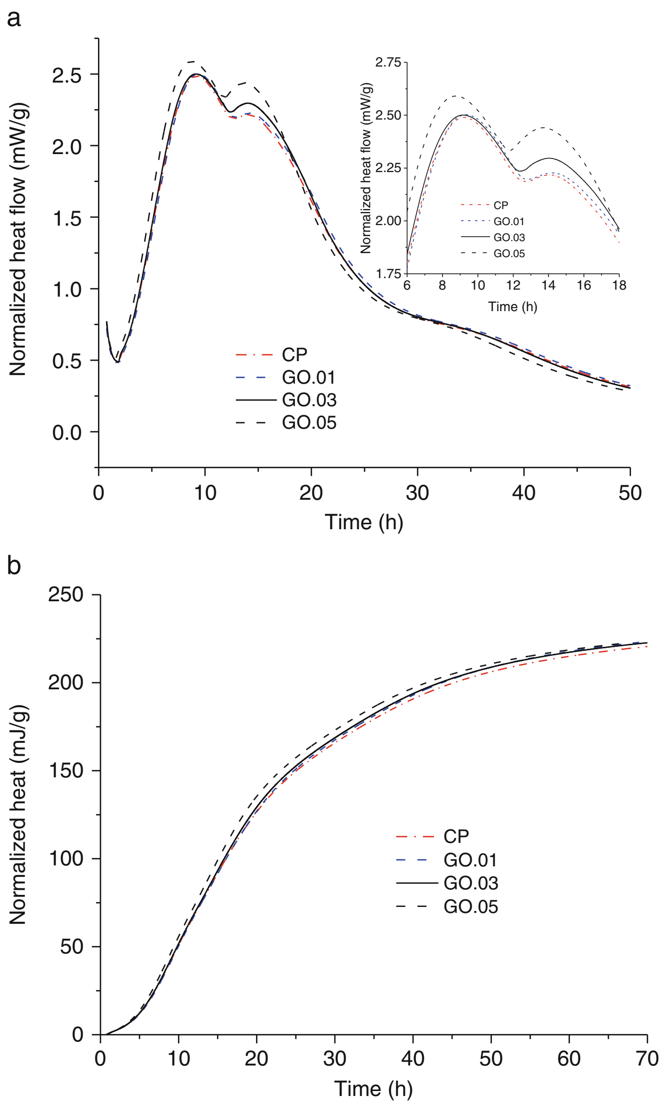

Fig. 1 Normalized (**a**) heat flow and (**b**) cumulative heat generated of cement pastes with 0, 0.01, 0.03 and 0.05 % graphene oxide addition

aluminate reaction. Graphene oxide has a slight accelerating effect on both, where the peaks are shifted up and to the left. Compared with CP, the first and second peak of GO.05 increases 3.6 % and 9.6 %, respectively. This may be attributed to the seeding effect that is often observed in cementitious systems with nanomaterials [12, 13]. While at the deceleration period, GO.05 shows smaller heat flow, rendering almost the same total normalized heat for all samples at 70 h after mixing, as shown in Fig. 1b.

3.2 Four Point Bending Test

The results of the four point bending test are shown in Figs. 2 and 3. Figure 2 shows the relationship between flexural strength of mortar and GO addition at 7 days and 28 days. Even at small additions of graphene oxide, there is an apparent increase in strength. Compared to the neat cement paste, at 0.03 %, graphene oxide increases the flexural strength of mortar by 18.7 % and 13.7 % at 7 days and 28 days, respectively.

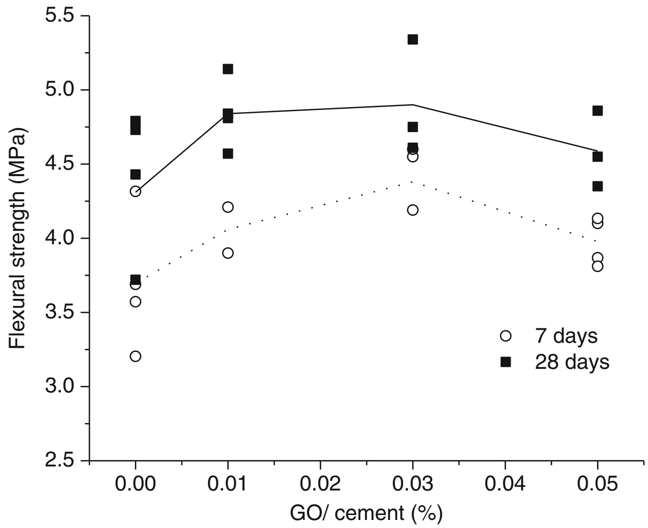

Fig. 2 Flexural strength of mortar with GO addition

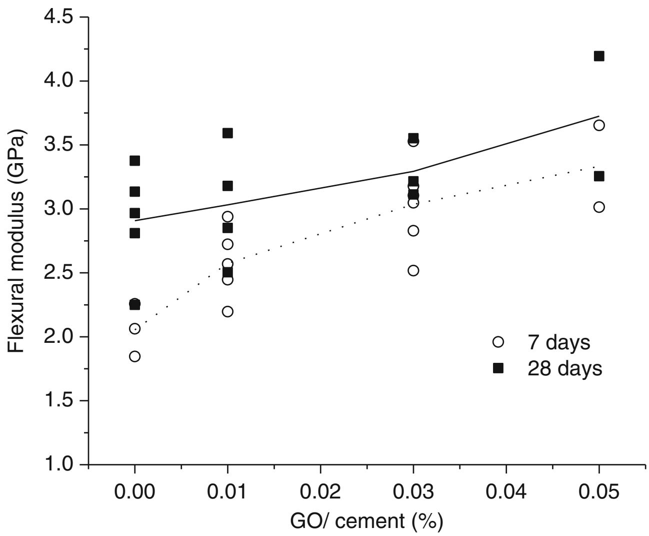

Fig. 3 Flexural modulus of mortar with GO addition

As summarized in Fig. 3, the flexural modulus of mortar samples at 7 and 28 days, with increasing GO addition, the flexural modulus increases. Especially at 7 days, the flexural modulus of GO.05 increases 61.7 % compared to CP. It could be due to bridging and strengthening effect of graphene oxide in the cement matrix, or refined pore structures [3, 14].

4 Conclusions

The preliminary results of a study on graphene oxide-reinforced cement pastes and mortar are presented. Results indicate that at relatively low additions (below 0.05 % by mass of cement), graphene oxide can enhance flexural strength. Work is ongoing on later-age properties, i.e. strength gain and permeability, and microstructural characterization.

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