Construction and Building Materials 145 (2017) 402–410

Contents lists available at ScienceDirect

Construction and Building Materials

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

Effects of graphene oxide agglomerates on workability, hydration, microstructure and compressive strength of cement paste

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HIGHLIGHTS

- Workability of cement paste was reduced due to water trapped in GO agglomerates.
- Hydration of cement paste was not improved significantly since GO was agglomerated.
- The porosity of cement paste was not densified notably due to GO agglomeration.
- Compressive strength was improved due to effects of GO on pore, hydration, and crack-bridging.

ARTICLE INFO

Article history:
Received 23 August 2016
Received in revised form 7 April 2017
Accepted 8 April 2017

Keywords:
Graphene oxide
Cement paste
Agglomerates
Hydration
Microstructure
Mechanical properties

ABSTRACT

In this study, the effects of graphene oxide (GO) agglomerates on the workability, hydration, microstructure, and compressive strength of cement paste were addressed. The workability of cement paste was reduced because of the presence of GO agglomerates, which entrap a large amount of water. The mini-slump diameter was reduced by 21% with the incorporation of 0.03% by weight GO in cement paste. Hydration of the cement paste was accelerated due to nucleation sites provided by GO agglomerates serving as seeding material in the cement paste. The incorporation of GO refined the pore structure of the cement paste. The incorporation of GO was found to have much greater impact on macropores than on large and small mesopores. At 28 days, the incorporation of 0.04% by weight GO produced a 14% improvement in the compressive strength of cement paste. Below 0.03%, the incorporation of GO had no positive effects on compressive strength.

1. Introduction

Cement is the principal binder material in the production of concrete, which is the world's most widely used construction material. However, the major limitation of concrete and cement-based materials is their quasi-brittle nature [1], which results in poor resistance to crack formation and low tensile strength and strain capacities. Thus, the use of reinforcement materials has become increasingly important for improving the properties of concrete and cement-based materials. Recently, nanomaterials including 0D nanoparticles, 1D nanofibres and 2D nanosheets have received considerable attention and are in use as reinforcements to improve the properties of cement-based materials.

Nano-SiO_2 particles have been widely used to improve concrete workability and strength, to increase resistance to water penetration, and to help control the leaching of calcium, features that are closely associated to various concrete durability issues [2]. The enhancements can be attributed to chemical pozzolanic activity and nucleation effects as well as pore filling of the concrete. Obviously, there is no crack-bridging effect for 0D nanoparticles in cement matrix due to their spherical shape. Recently, it was shown that the incorporation of a very small amount of 1D carbon nanotubes (CNTs) substantially enhanced the mechanical properties of cement paste [3,4] and cement mortars [5]. By incorporation of CNTs, mechanical and electrical properties of fly ash-based geopolymers were also greatly enhanced [6]. The main mechanisms involving CNTs in cement matrix are the filling of nano-sized gel pores, the nucleation effect, and bridging of micro-sized capillary pores [3]. However, CNTs tend to form CNT bundles [7,8] since they have high aspect ratios and strong van der Waals

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http://dx.doi.org/10.1016/j.conbuildmat.2017.04.058

attraction between nanotubes. It has also been reported that sliding of CNTs from the cementitious matrix in tension indicates weak bonding with the matrix [9]. Thus, the effects of CNTs on the properties of cementitious materials have been limited due to poor dispersion and weak bonding between CNTs and the cementitious matrix.

Graphene oxide (GO) is a layered nanomaterial consisting of hydrophilic oxygenated graphene sheets bearing hydroxyl and epoxide functional groups on their basal planes, in incorporation to carbonyl and carboxyl groups located at the sheet edges [10]. As such, GO has attracted much attention in various applications [11–13]. Unlike CNTs, GO can readily yield stable dispersions in water consisting mostly of 1-nm-thick sheets [14], due to the presence of these oxygen-containing functional groups. In terms of mechanical properties, the elastic modulus and tensile strength of GO are around 32 GPa and 130 MPa [13,15], respectively, levels which are superior to those of cementitious materials. Most importantly, GO can be synthesized in large quantities from inexpensive graphite powder. This makes GO potentially more favourable than 0D nanoparticles and 1D nanotubes for altering various matrix properties such as mechanical, rheological and permeability properties, whereby GO provides an extra dimension of interaction with cement and concrete matrix [16].

A few studies have experimentally investigated the incorporation of GO into cement-based materials, including cement paste and cement mortar. A recent study [17] of the effect of GO on the workability (rheological behaviour) of cement paste found that the fluidity of cement paste was reduced with the incorporation of GO. This reduction was attributed to the formation of agglomerates and flocculation by electrostatic interactions between GO and cement particles. The agglomerates and flocculation were not stable since they could be broken by shear mixing. Investigation of the effect of GO on the mechanical properties of cement-based materials showed that the incorporation of GO increased compressive and flexural strength. The 28-day compressive strength and tensile strength were reported to be increased by over 40% with the incorporation of 0.03% by weight GO [18]. The introduction of as little as 0.05 wt% of GO increased compressive strength by 15–33% and flexural strength by 41–58%, respectively [19]. In another study, Lv et al. [20] reported up to 37.5% increase for compressive strength at 28 days in cement paste containing 0.04% GO. The effect of GO on mechanical properties was hypothesized to correlate with the properties of GO nanosheets such as interlocking facilitated by the wrinkled morphology of GO nanosheets, interaction between cracks and GO nanosheets, and interfacial forces between functional groups and hydration products [19]. In an investigation of the effect of GO on cement microstructure, the incorporation of GO was found to produce a finer pore structure of cement paste [18,19]. In addition, it was found GO nanosheets could regulate to form flower-like, polyhedral and lamellar hydration products which formed denser structures [20,21]. Effects of GO on properties and microstructure of magnesium potassium phosphate cement were also investigated [22]. Saafi et al. [23] reported that the reduced GO sheets significantly reduced the porosity, increased the electrical conductivity and gauge factors under tension and compression of the alkali activated cement matrix. To the best of the authors' knowledge, no study has investigated the effects of the incorporation of GO on the hydration of cement paste.

A recent study [24] involving some of the present authors revealed that GO agglomerates formed immediately when GO nanosheets came into contact with water and cement if no dispersion aid was applied. It is the behaviour of the GO agglomerates, not the GO nanosheets, that influences the properties of cement paste. Therefore, careful investigation is required to correlate the influences on the properties of cement paste with the presence of GO agglomerates, which have been found to have relatively large lateral size and capacity of water retention [24].

The main objectives of this study were to elucidate the mechanisms by which GO agglomerates affect the workability, hydration, microstructure, and compressive strength of cement paste. It should be noted that no superplasticizer or water reducing agent was used for improving the GO dispersion in the matrix. To accomplish the goals, a mini-slump test was carried out to assess workability as a function of GO content; isothermal calorimetry was conducted to study early-age hydration heat development of GO-incorporated cement paste within 72 h; mercury intrusion porosimetry and scanning electron microscopy were carried out to study the pore structure of GO-incorporated cement paste cured for 28 days; the compressive strength of GO-incorporated cement paste was investigated by compression tests at 3, 7 and 28 days.

2. Materials

2.1. GO

GO solution was purchased from Graphenea®. In the solution, GO nanosheets were dispersed in water at the concentration of 4 mg/ml. A scanning electron microscopy (SEM) image of GO nanosheets is shown in Fig. 1. The mean size of the GO nanosheets was around 1 μm. The major functional groups on surface of GO were found to be –OH and –COOH. Elemental analysis of the GO is given in Table 1.

2.2. Cement powder

General-purpose ordinary Portland cement (OPC) conforming to the requirements of Type I – Normal Cement, as defined by ASTM C 150, was used throughout the study. The chemical composition of the cement powder as determined by X-ray fluorescence is shown in Table 2.

2.3. Mixing of cement paste

A high-speed shear mixer (CTE Model 7000) was employed to prepare cement paste incorporating GO. Mixing procedures similar to ASTM C1738-11a were adopted:

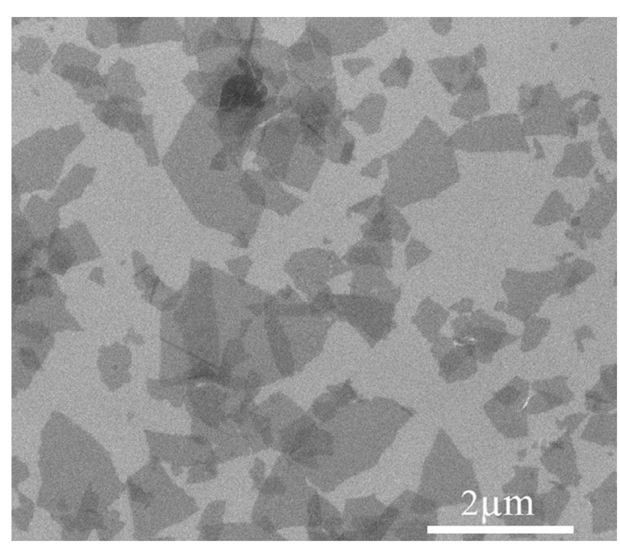

Fig. 1. SEM image of GO.