Construction and Building Materials 119 (2016) 107–112

Contents lists available at ScienceDirect

Construction and Building Materials

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

Effects of graphene oxide on the properties and microstructures of the magnesium potassium phosphate cement paste

Zeyu Lu [a], Dongshuai Hou [b,*], Hongyan Ma [c], Tianyuan Fan [a], Zongjin Li [a]

[a] Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Hong Kong, China
[b] Department of Civil Engineering, Qingdao Technological University (Cooperative Innovation Center of Engineering Construction and Safety in Shandong Blue Economic Zone), Qingdao, China
[c] Department of Civil, Architectural and Environmental Engineering, Missouri University of Science and Technology, Rolla, MO, USA

HIGHLIGHTS

- The addition of GO decreases the final setting time and fluidity of MKPC paste.
- The mechanical behavior of MKPC paste can be enhanced by GO addition.
- GO addition accelerates hydration degree and lowers porosity of MKPC paste.

ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form 13 April 2016
Accepted 6 May 2016
Available online 13 May 2016

Keywords:
Graphene oxide
Magnesium potassium phosphate cement
Mechanical behavior
Microstructures

ABSTRACT

This paper presents the effect of graphene oxide (GO) on the properties and microstructures of the magnesium potassium phosphate cement (MKPC) paste with a lower water to solid ratio (w/s) of 0.15. The influence of GO on the workability, hydration degree, mechanical behavior and microstructures of the MKPC paste is systematically investigated. The experimental results showed that the addition of GO shorted the final setting time and decreased the workability of the MKPC paste, but the compressive and flexural strength of the MKPC paste were improved by a moderate addition of GO. It was clearly indicated that compared with the fresh MKPC paste, the addition of 0.05 wt.% GO can improve the compressive and flexural strength of the MKPC paste by 6.8% and 8.3%, respectively. The improved mechanical strength is not only attributed to the excellent mechanical properties of GO itself, but also the higher hydration degree and lower porosity of the MKPC paste by the GO addition. The microstructures of the MKPC paste with GO addition of 0.05 wt.% become much denser and better crystallization of the hydration products can be achieved, compared with the fresh MKPC paste. However, more GO addition 0.10 wt.% has a negative effect on the crystallization of the hydration products and mechanical behavior of the MKPC paste. Finally, the FTIR spectra indicated that there was no chemical bonding between the hydration products of the MKPC paste and GO. It is concluded that GO, as a promising nanofiller, has a great potential for reinforcing the MKPC paste.

1. Introduction

Magnesium phosphate cement (MPC) is a type of binary chemically bonded ceramic which is usually formed by through-solution acid-base reaction between dead burned magnesia and phosphate, such as ammonium phosphate and potassium dihydrogen phosphate [1–3]. It has been regarded as a good candidate to replace Portland cement and widely investigated in recent years due to its many advantages, such as rapid setting time, higher mechanical behavior and lower drying shrinkage [4–6]. In terms of civil engineering, MPC cement has widely been used as a repair material for many years, such as damaged runway and bridge piers, because it set rapidly with high early strength, low permeability and good durability. Most recently, MPC is also proved to be a good candidate for the 3D printing materials for biomedical implants or even complicated structures of buildings [7,8].

Traditionally, ammonium phosphate was used one of the raw materials producing MPC cement, but an unpleasant odor was released during the hydration of the MPC cement. Therefore, magnesium potassium phosphate cement (MKPC), a new MPC system, consists of dead-burned MgO (D-MgO) and potassium dihydrogen phosphate (KDP), is regarded as a better and more suitable

* Corresponding author.
E-mail addresses: zluaa@ust.hk (Z. Lu), dshou@outlook.com (D. Hou), mahon@mst.edu (H. Ma), tfanaa@ust.hk (T. Fan), zongjin@ust.hk (Z. Li).

http://dx.doi.org/10.1016/j.conbuildmat.2016.05.060

phosphate for MKPC fabrication [9,10]. The major hydration product of the MKPC cement is struvite-K ($MgKPO_4{\cdot}6H_2O$), which is formed from the dissolution of MgO and KH_2PO_4 reacting in a solution, as expressed as following:

$$MgO + KH_2PO_4 + 5H_2O = MgKPO_4 \cdot 6H_2O \ (MKP)$$

The mechanical properties of the MKPC greatly depend on the molar ratio of magnesia to phosphate (M/P), water to cement ratio (W/C) and the addition of supplementary materials. Many researchers investigated the effects of different supplementary cementitious materials on the mechanical properties of the MKPC paste. Li et al. [11] demonstrated that 50 wt.% fly ash (FA) led to 7.6% increase in compressive strength of the MKPC paste at 28 days. Li et al. [12] also indicated that the addition of FA has a positive effect on the compressive strength but a negative effect on the flexural strength and tensile strength of the MKPC paste. Zheng et al. [13] demonstrated that the combination of 15 wt.% FA and 10 wt.% silica fumes led to a higher density and large-age compressive strength of the MKPC paste. In addition, Chen et al. [14] indicated that the addition of 50% FA, 10% silica fume and 2% re-dispersible latex powder could significantly improve the mechanical strength and water resistance of the MKPC paste. Gardner et al. [15] showed that granulated blast furnace slag (GBFS) is more effective on reinforcing MKPC than FA, and 60 wt.% GBFS led to 94.4% increase in compressive strength of the MKPC paste at 28 days. However, few publications reported the effects of nanomaterials on the properties of the MKPC paste, such as nano-TiO_2, nano-silica, carbon nanotube and graphene oxide (GO).

Graphene is composed of sp^2-bonded carbon atoms and possesses excellent mechanical properties, good thermals and electrical conductivities. In addition, GO is an excellent hydrophilic materials by introducing oxygen-containing groups into the graphene, such as hydroxyl, carbonyl and carboxyl. Due to its good dispersity in water, high aspect ratio and satisfied mechanical properties, GO has become a good candidate to reinforce cementitious materials. Lu et al. [16] demonstrated that 0.05 wt.% GO led to 11.1% and 16.2% increase in compressive strength and flexural strength of the cement paste. Duan et al. [17] found that 0.03 wt.% GO sheets improved the compressive strength and tensile strength of the Portland cement composite by more than 40% due to the reduction of the pore structure. However, few studies investigated the effect of GO on the properties of the MKPC paste. The reinforcing effect of GO on the MKPC paste is still not clear. The aim of this paper is to investigate the properties of the GO modified MKPC paste, including the workability, hydration degree, mechanical behavior and microstructures.

2. Experimental

2.1. Materials

The D-MgO powder with a purity of 95.05% and calcination of 1200 °C for 5 h was purchased from Jinan Magnesia-Carbon Brick Plant Co. Ltd., Shandong, China. The KDP powder and borax were supplied by Guangzhou Chemical Reagent Factory, Guangdong, China. The particle size distributions of the D-MgO and KDP are shown in Fig. 1. Chemical composition of the D-MgO was determined by X-ray fluorescence spectrometry (XRF, JEOL, JSX-3201Z) and shown in Table 1. The GO was synthesized from graphite (Alfa Aesar, 200 mesh, metal basis) by using a modified Hummer's methods [18]. The oxidation degree and morphologies of GO was characterized by the X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Fig. 2 shows four types of carbon bonds in GO, including the C-C at 284.4 eV, C—O at 286.4 eV, C=O 288.3 at eV and –COOH at 289.0 eV. The elemental analysis of the XPS results indicate that the C/O ratio and oxygen content of the GO are 3.0 and 30.7%, respectively. Fig. 3 shows the TEM image of the GO. It is clear to see that the GO is a wrinkled layer due to intercalating the oxygen-containing functional groups.

Table 1
Chemical composition of the D-MgO.

MgO	SiO_2	CaO	Fe_2O_3	MnO
95.05	3.68	0.80	0.30	0.17

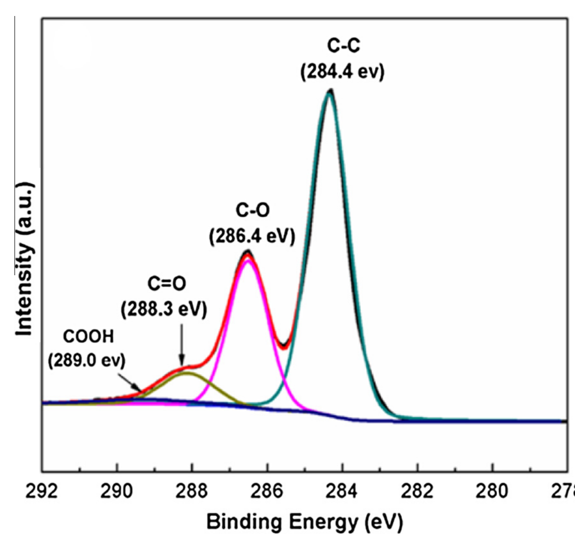

Fig. 2. XPS spectra of the GO.

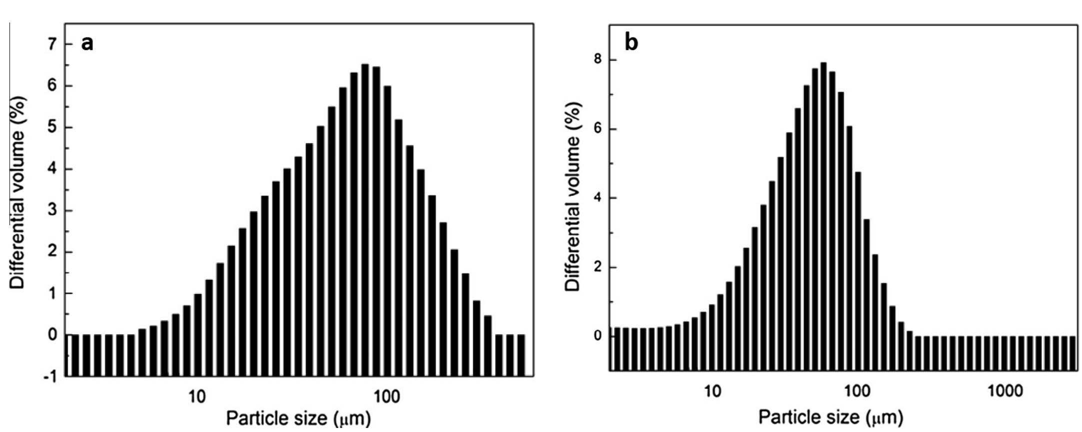

Fig. 1. Paticle size distribution of (a) D-MgO and (b) KDP.