Cement and Concrete Composites 66 (2016) 1–9

Contents lists available at ScienceDirect

Cement and Concrete Composites

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

Fabrication of polycarboxylate/graphene oxide nanosheet composites by copolymerization for reinforcing and toughening cement composites

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ARTICLE INFO

Article history:
Received 10 February 2015
Received in revised form
6 October 2015
Accepted 11 November 2015
Available online 24 November 2015

Keywords:
Graphene oxide nanosheets
Copolymeric composite
Self-repairing effects
Reinforcing
Toughening

ABSTRACT

Polycarboxylate (PC)/graphene oxide nanosheet (GON) composites are prepared by copolymerization of graphene oxide nanosheets (GONs) and PC's monomers of methacrylic acid, sodium allyl sulfonate and methacrylate polyoxyethylene ether. The test results indicate that GONs in the PC/GON copolymeric composites have smaller size and uniformly dispersed. Using of PC/GON composites in cement paste can achieve uniformly disperse GONs and eliminate the effects of GONs on the cement paste fluidity. The GONs from the composites can regulate the cement hydration products to form ordered microstructure and have significantly reinforcing and toughening effects. Meanwhile, the results research indicate that GONs have self-repairing effects for the holes and cracks for cement composites. The results have a very positive to application of GONs for improving the strength/toughness and extensing the service life of cement composites.

1. Introduction

Cement composites, mainly concrete and mortar, are still the most important and widely used building materials worldwide [1]. The trend in the development of cement composites is toward high strength, long service life and greenization [2]. For commonly used concrete, the compressive and flexural strengths are in the ranges 30–80 and 3–8 MPa, respectively, and its service life is in the range 30–70 years. This show that concrete has high compressive strength and comparatively low flexural strength, and means concrete is a brittleness materials and is prone to crack [3,4]. Moreover, its really service life is also far from the theoretical service life of 500 years [5]. Therefore, to reduce the cracks and improve the strength especially the flexural strength is an inevitable and essential requirement for the realization of long service life [6].

Cement composites such as concrete is composed of hardened cement paste, sands and stones. Of these components, it is only in the cement paste that cracks and holes can produce in the hydration process [7–10]. The main reason is that the cement paste consist of cement hydration products of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, AFt), monosulfate ($Ca_4Al_2(OH)_2\cdot SO_4\cdot H_2O$, AFm), calcium hydroxide ($Ca(OH)_2$, CH), and calcium silicate hydrate ($3CaO\cdot 2SiO_2\cdot 4H_2O$, C–S–H) gel [11]. These hydration products were produced by hydration reaction of the cement principal components of tricalcium silicate (C_3S, Ca_3SiO_5), dicalcium silicate (C_2S, Ca_2SiO_4), tricalcium aluminate (C_3A, $Ca_3Al_2O_6$), tetracalcium aluminoferrite C_4AF ($Ca_4Al_nFe_{2-n}O_7$), and gypsum ($CaSO_4\cdot 2H_2O$) with water, which have irregular shape and randomly agglomeration. So the cracks and holes as well as leaks are usually exist in cement paste [12–14]. Therefore, regulating the shape and aggregating way of hydration products to form regular microstructure should have a significantly influence on reducing cracks and improve the flexural strength of cement composites. We practice the ideal earliest and had firstly found that graphene oxide nanosheets (GONs) can control the cement hydration reaction to form regular microstructure assembled flower-like, polyhedral and sheet-like crystals. The corresponding cement composite has less cracks/holes and exhibit a significant increase in compressive and especially flexural strength [15,16]. Though, some researchers also begin studying on the effects of GONs on mechanical properties of cement composites, but they do not found the regulation of GONs on cement hydration products and microstructure [17–21].

In the previous research, we also found some problems, such as GONs would dramatically decrease the fluidity of cement

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http://dx.doi.org/10.1016/j.cemconcomp.2015.11.007
0958-9465/

composites and GONs can not evenly disperse in cement composites. These problems will affect the reinforcing and toughening effects of GONs for cement composites. In this paper, a polycarboxylate (PC)/GON composite is prepared by copolymerization of GONs with the PC's monomers such as methacrylic acid (MAA), sodium allyl sulfonate (SAS), and methacrylate polyoxyethylene ether (MPE). The aim is to improve the compatibility of GONs and polycarboxylate superplasticizer (PCs) and achieve evenly disperse GONs in cement paste. The results will be useful in the application of GONs to reinforce and toughen cement-based composites.

2. Experimental

2.1. Materials and chemicals

The major materials used were powdered graphite, polycarboxylate superplasticizer (PCs), and Portland cement. PCs was supplied by Xi'an Daliang Concrete Additive Co. Ltd (Xi'an, China), and prepared by copolymerization of MPE, MAA, and SAS. The Portland cement (42.5R) was composed of 55.8% C_3S, 21.6% C_2S, 8.92% C_3A, 8.5% C_4AF, and 4.5% gypsum. The mainly chemicals used were concentrated H_2SO_4 (98%), $KMnO_4$, $NaNO_3$, H_2O_2 (30%), MAA, SAS, MPE ($M_n = 2250$), $(NH_4)_2S_2O_8$ (APS), $NaHSO_3$, and NaOH. All of chemical are reagent purity.

2.2. Preparation of PC/GON composites

2.2.1. Preparation of GONs

A three-necked flask was placed in an ice bath (5 °C), and 3 g powered graphite, 60 g concentrated H_2SO_4, and 3 g $NaNO_3$ were added and mixed well. Then, 12 g $KMnO_4$ was slowly added to the flask over 15 min under stirring. The reaction temperature was kept at 5 °C for 1 h, then at 35 °C for 6 h. Then 200 mL deionized water was put to the flask and heated to 70 °C, following which 30 g H_2O_2 was dripped into the flask over 60 min. The final product was purified by centrifugation precipitation and washing repeatedly with deionized water until the washing water had a pH of 7.0. Then ultrasonic processing graphite oxide aqueous may obtain graphene oxide nanosheets (GONs).

2.2.2. Fabrication of PC/GON copolymeric composites

A monomers solution was obtained by mixing 17 g MPE, 2 g MAA, 1 g SAS, and 20 g deionized water in a dropping funnel. An initiator solution (I) was prepared by dissolving 0.3 g APS in 15 g deionized water in another dropping funnel, and an initiator solution (II) was obtained by dissolving 0.3 g $NaHSO_3$ in 15 g deionized water in the third dropping funnel. The monomers solution and the initiator solutions (I) and (II) were then simultaneously added dropwise to a three-necked flask with GONs suspension solution at 50 °C over 1 h. The copolymerization was then allowed to proceed at 50 °C for 2 h. Finally, the temperature of the reaction product was reduced to 30 °C and its pH was adjusted to 7.0 with NaOH solution. The content of PC and GON in PC/GON composites was controlled as 13% and 2%, respectively.

2.3. Preparation of cement composites

The cement composites were prepared by mixing cement, water, PCs and GONs or PC/GON composites. The weight ratio of water and cement is 29:100 (w/c = 0.29). All dosages were solid dosages and calculated by weight of cement (bwoc). The sample size was 40 mm × 40 mm × 160 mm. The samples were cured at 20 °C and 90% relative humidity until testing.

2.4. Test methods

The chemical structures of the GONs and the PC/GON composites were characterized by Fourier-transform infrared spectroscopy (FTIR, EQUINOX-55, Bruker, Germany).

The M_n, M_w, and polydispersity index (PDI) of PCs and PC/GON composites were determined using a Waters 575–2414 GPC instrument (Massachusetts, USA) at 40 °C.

The size distribution of the GONs was measured using a Zetasizer NANO-ZS90 laser particle analyzer (Malvern, UK). The average size of GONs was determined using an atomic force microscope (AFM) (SPI3800N/SPA400, Seiko, Japan). The average thickness and size were obtained from the AFM images by statistical analysis.

The flexural strength of hardened cement paste was determined using a DKZ-500 concrete three-point flexural strength tester (Wuxi, China), and the compressive strength was tested on a JES-300 compressive strength tester (Wuxi, China) according to GB/8076-2008. Each sample was tested three times and the results averaged.

The microstructure of hardened cement paste was examined using a field-emission scanning electron microscope (SEM) (S-4800, Hitachi, Japan).

The pore structure of the hardened paste was tested using an Autopore® IV9500 automatic mercury porosimeter (Micromeritics Co., USA). The dry samples were weighed accurately, placed in an expansion joint and sealed, subjected to low pressure (0–30 MPa), and then reweighed, further tested at high pressure (30–400 MPa).

3. Results and discussion

3.1. Structural characterization of PC/GON composites

FTIR spectra of graphite, GONs, and PC/GON composites are shown in Fig. 1. The graphite spectrum has an obvious absorption peak at 1620 cm^{-1} due to the C=C double bond. The GONs spectrum shows absorption peaks due to the hydroxyl group (−OH) at 3350 cm^{-1} and the carbonyl group (−C=O) at 1690 cm^{-1}, as well as the ether bond (−C−O−C−) at 1360, 1260 and 1100 cm^{-1}, indicating that the functional groups −OH, −C=O, and −C−O−C− are present in GONs. The spectrum of PC/GON composites shows absorption peaks due to the methyl and methylene groups ($-CH_3$ and $-CH_2-$) at 2950, 2920 and 2850 cm^{-1}, the carboxyl carbonyl group at 1730 cm^{-1}, the carbonyl bond at 1460 cm^{-1}, and the ether bond at and 1370, 1230, 115, 1108 cm^{-1}. The results indicate that graphite has become GON and PC/GON copolymeric copolymer by

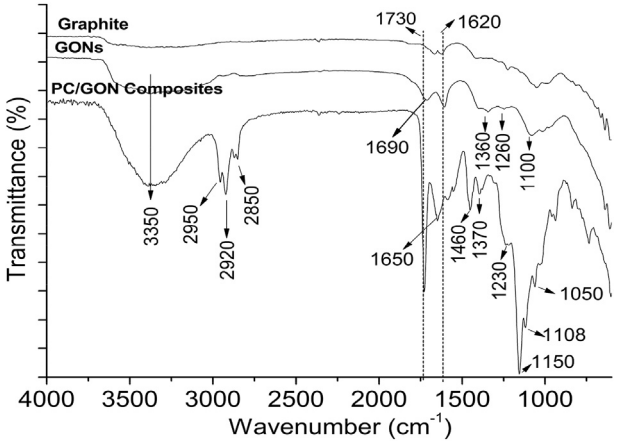

Fig. 1. FTIR spectra of graphite, GONs, and PC/GON composite.