Construction and Building Materials 64 (2014) 231–239

Contents lists available at ScienceDirect

Construction and Building Materials

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

Effect of GO nanosheets on shapes of cement hydration crystals and their formation process

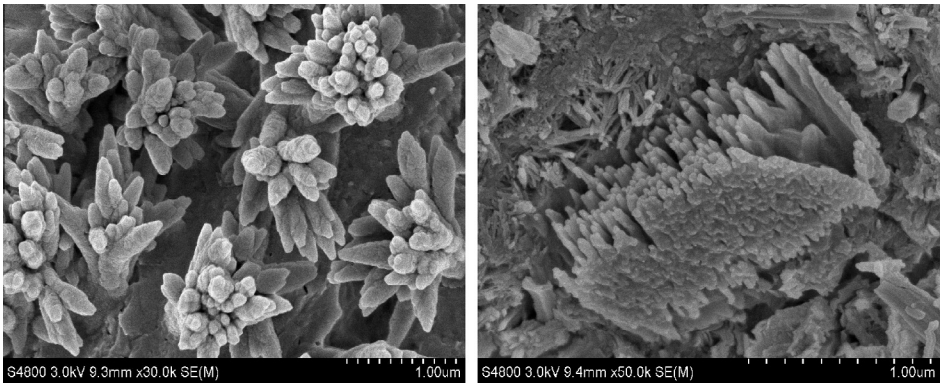
Shenghua Lv *, Jingjing Liu, Ting Sun, Yujuan Ma, Qingfang Zhou

College of Resource and Environment, Shaanxi University of Science and Technology, Xi'an, PR China

HIGHLIGHTS

- Different dispersive graphene oxide (GO) nanosheets were obtained by ultrasound technique.
- GO nanosheets can construct the bar-like crystals into flower-like and polyhedral crystals.
- Flower-like and polyhedral crystals can improve flexural strength and compressive strength.
- Formation process of cement hydration crystals are proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 January 2014
Received in revised form 18 March 2014
Accepted 4 April 2014
Available online 4 May 2014

Keywords:
Cement
Hydration reaction
Hydration crystals
Formation process

ABSTRACT

The effects of graphene oxide (GO) nanosheets with different sizes and dosages on cement hydration crystal shapes and the mechanical strength of cement paste are investigated. It is found that flower-like crystals are more prominent at low GO dosage (<0.03%) and polyhedral or lamellar crystals at high dosage (>0.03%). The flexural and compressive strengths of cement paste with smaller GO nanosheets are clearly improved. Formation processes for hydration crystals are proposed based on scanning electron microscopy images. GO nanosheets can promote assembly of flower-like and polyhedral structures from rod-like crystals, with the ultimate formation of a dense structure.

1. Introduction

Modern concrete is mainly composed of cement paste, sand, stones, steel bars and other reinforcing materials. Of these components, it is the cement paste whose properties and structure have the most important influence on those of the concrete. Essentially, cement paste is an aggregation of complex hydration products, and during hardening of the concrete, it undergoes a transition from soft paste to hard solid. Its role is to bind the sands, stones and steel bars together to produce concrete with good mechanical properties. Generally, concrete possesses high compressive but low flexural strength, a combination of properties that have significant effects on its durability. Therefore, improving the strength, particularly the flexural strength, of concrete has been a subject of much research in recent decades.

At present, there are two ways to improve the compressive and flexural strength of concrete: addition of reinforcing materials and reduction of the water-to-cement (w/c) ratio. The former remains the simplest and most convenient strengthening and toughening method. However, it leads to improvements only in the mechanical

* Corresponding author. Tel./fax: +86 2986168291.
E-mail address: lvsh@sust.edu.cn (S. Lv).

http://dx.doi.org/10.1016/j.conbuildmat.2014.04.061
0950-0618/

properties of the concrete as a whole, with those of the cement paste, especially the flexural strength, changing very little. Thus, the principal defects of hardened cement paste, namely cracking and permeation, remain and become the main factors affecting the durability of concrete. The reason for this is that the reinforcing materials, mainly steel fibers, inorganic fibers and polymer fibers, cannot change the microstructure of the cement paste [1–4].

Decreasing the w/c ratio by using superplasticizers such as polycarboxylates in the preparation of concrete is another appealing approach because it can change the microstructure of cement paste, leading to distinct improvements at low cost. Therefore, this method has been applied widely [5]. Superplasticizers can retard the hydration reaction that occurs in the initial stage of hardening, thus allowing more time for long-distance transport of fresh concrete. They can also promote the formation of larger and denser rod-like crystals during the later curing process [6], resulting in clear improvements in compressive strength, although the increase in flexural strength is negligible [7]. The w/c ratio has been used in evaluating the efficiency of superplasticizers, and it has an important impact on the microstructure of cement paste [8]. The use of superplasticizers has already allowed the w/c ratio to be reduced from its original value of 0.6 to the minimum possible value of 0.25 [9], so this method of increasing the mechanical strength has already reached its limit.

Generally, the crystals resulting from the hydration of cement are composed of ettringite (AFt), monosulfate (AFm), calcium hydroxide (CH) and calcium silicate hydrate gel (C—S—H), which are produced from hydration reactions of the cement's active ingredient such as 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 [10]. These cement hydration products can bind sand, stone and steel bars together to form concrete during the curing process. AFt, AFm, CH and C—S—H usually exhibit different crystal shapes, including rod-like, needle-like and lamellar crystals, as well as amorphous solids [11,12]. These shapes, as well as the numbers of such crystals in the cement paste, have an important impact on the mechanical strength of concrete. There is a considerable degree of random variation in both shape and number of the hydration crystals in cement paste, and experimental investigations have suggested that if these parameters, as well as the distribution of the hydration crystals, could be controlled, this could lead to great improvements in mechanical strength.

The use of graphene oxide (GO) nanosheets offers a possible way to achieve such control. The results of our previous research have shown that GO nanosheets can regulate the cement hydration reaction to form regular hydration crystal shapes with a uniform distribution in the cement paste, resulting in a clear increase in mechanical strength, especially flexural strength [13]. In this paper, the effects on cement hydration crystal shapes of GO nanosheets with different degrees of dispersion and dosages are investigated, as is the correlation of hydration crystal shapes and the mechanical strength of the related hardened cement paste. In addition, the formation mechanism and growth process of the cement hydration crystals are investigated based on the micromorphology of hardened cement paste.

2. Experimental

2.1. Chemicals and materials

An aqueous dispersion of GO nanosheets was prepared according to our earlier work [13]. The functional groups and oxygen content were determined by Fourier transform infrared (FTIR) spectroscopy and energy-dispersive X-ray spectroscopy (EDS), respectively. The major functional groups were found to be —OH, —COOH and —SO_3H groups, and the oxygen content was 33.45%.

Polycarboxylate superplasticizer (PCs, 20%) was supplied by Xi'an Daliang Concrete Additive Co. Ltd. (Xi'an, China). Its water-reducing ratio was 32%, and its M_w and M_n were 126,382 and 98,736 Da, respectively.

Table 1
Chemical, mineral composition and fineness of the Portland cement.

Calcium oxide (CaO)	65.16%
Silicon dioxide (SiO_2)	21.25%
Aluminum oxide (Al_2O_3)	4.21%
Ferric oxide (Fe_2O_3)	3.35%
Alkalis (Na_2O equivalent)	0.50%
Magnesium oxide (MgO)	2.90%
Sulfur trioxide (SO_3)	0.72%
Loss on ignition (LOI)	0.85%
Tricalcium silicate (C_3S)	54.56%
Dicalcium aluminate (C_3A)	18.92%
Tetracalcium aluminoferrite (C_4AF)	6.91%
Blaine fineness	399.4 m^2/mg

The Portland cement (Shengwei 42.5R) used in the study was produced by Qinling Cement Co. Ltd. (Xi'an, China). The main chemical and physical parameters are shown in Table 1.

2.2. Preparation of cement paste

The cement paste was prepared by mixing cement, water, PCs and GO. The water/cement weight ratio remained 0.3. The PCs dosage was 0.2%. The dosage of GO nanosheets was varied according to the test scheme. The dosages of PCs and GO were solid dosage and calculated by weight of cement (bwoc).

The preparation procedure of cement paste followed GB/T 8077-2000 of the national standard of the People's Republic of China, which is about methods for testing the uniformity of a concrete admixture. Water, PCs and GO were added to a stainless steel container in turn and mixed well. The cement was then added and the mixture was stirred at low speed for 1 min and then at high speed for 1 min. The resulting cement paste was immediately poured into a 40 mm × 40 mm × 160 mm mold for the flexural strength/compressive strength tests. After 24 h, the specimens were removed from the mold and cured at 20 °C ± 1 °C and 90% relative humidity until test strength.

2.3. Test for mechanical strength of hardened cement paste

The flexural strength and compressive strength were tested according to GB/T 17671-1999 of the national standard of the People's Republic of China, which is about testing methods for flexural and compressive strength. The flexural strength was determined using a DKZ-500 concrete three-point flexural strength tester (Wuxi, China) at a loading increasing rate of 0.04–0.06 kN/s. The compressive strength was tested on a JES-300 concrete compressive strength tester (Wuxi, China) at a loading increase rate of 1 2.2–2.6 kN/s. For each recipe of cement paste, five samples were tested and the average was taken. The test results were evaluated according to the standard deviation.

2.4. Test for microstructure of GO nanosheets and hardened cement paste

The degree of dispersion of GO nanosheets was characterized according to the sheets' average size and thickness using an SPI3800N/SPA400 atomic force microscope (AFM) (Seiko, Japan). The test samples were prepared by putting a drop of very dilute GO suspension (a 0.2% GO suspension was diluted 800–1200 times) on a piece of monocrystalline silicon (5 mm × 5 mm × 0.45 mm) and dried naturally in an airtight dryer. The average thickness and size of the GO nanosheets were obtained from the AFM images by statistical analysis.

The microstructure of the fracture surface of hardened cement paste was observed by SEM using a Hitachi S-4800 field emission scanning electron microscope (Hitachi, Japan). The dried cement pastes were glued to an aluminum stub and coated with gold by a sputter process for good conductivity.

The pore structure of the hardened paste was tested using an Autopore® IV9500 automatic mercury porosimeter (Micromeritics Co., USA). The hardened cement paste was fragmented to about 1 cm size and dried in a vacuum dry box at 100 °C for 12 h. Then, the samples were weighed accurately, placed in an expansion joint and sealed, subjected to low pressure (0–30 MPa), reweighed, and then tested at high pressure (30–400 MPa). Each sample was tested three times and the results averaged.

3. Results and discussion

3.1. Characterization of degree of dispersion of GO

Previous results have shown that oxygen content and GO dosage have a significant impact on the shapes of cement hydration crystals and the mechanical strength of the resulting cement paste [13]. To further probe the effect of the degree of dispersion of GO