

Synthesis and properties of a silane and copolymer-modified graphene oxide for use as a water-reducing agent in cement pastes

Qin Wang*, Shi-yu Li, Shuo Pan, Zi-wei Guo

Beijing Key Laboratory of Functional Materials for Building Structure and Environment Remediation, University of Civil Engineering and Architecture, Beijing 100044, China

Abstract: The addition of graphene oxide (GO) to cement paste significantly increases its toughness, however its fluidity is adversely affected. GO was first reacted with vinyltrimethoxysilane to produce a silane-modified graphene oxide (S-GO), which was then copolymerized with acrylic acid and a water reducing agent, isobutanol polyoxyethylene ether (molecular mass 2400), to obtain a silane and copolymer-modified GO (P-S-GO) which acted as a water-reducing agent of the cement paste. A copolymer without GO was prepared under the same conditions for comparison. The structure, elemental composition and dispersibility of GO, S-GO and P-S-GO in a simulated cement environment (saturated lime water) were investigated by FTIR, XRD and a sedimentation test. The fluidity and rheology of the cement pastes with added GO, copolymer or P-S-GO were investigated. Results showed that vinyltrimethoxysilane reacted with the -OH group on the GO sheets to form an ether bond and the copolymer was grafted onto a vinyl group of S-GO by an addition reaction to produce the P-S-GO. The P-S-GO has a better dispersibility in saturated lime water with a negligible amount of aggregation compared to GO and a significant agglomeration occurs for GO. The addition of the P-S-GO to the cement pastes improves the fluidity and rheological properties compared with GO, offsetting the negative impact of GO and increasing the toughness of the resulting cements.

Key Words: Graphene oxide; Silane coupling agent modified; Fluidity; Rheological property

1 Introduction

Concrete is a kind of cement-based composite materials, which is composed of cement, sand, stone and some mineral admixtures. Due to its low price, convenient construction and other characteristics, concrete is the most widely used building materials around the world. Nevertheless, with the development of the society, many problems also appear in the applications of concrete in practical engineering. Because of the brittleness and low toughness of the concrete itself, the concrete is prone to produce microcracks under the structure stress, so that the infiltration of the external erosion medium may lead to concrete damage, even results in a serious steel corrosion, further reduces the strength and durability of the structure, reduces the life of the concrete structure and eventually bring about security risks in the course of service^[1].

Cement, as the main clinker materials of concrete, will undergo a series of complex chemical reactions as soon as its touch with water, leading to the formation of a series of hydrated products such as calcium silicate gel (CSH), ettringite (AFt), calcium hydroxide crystals (CH) and

monosulfur calcium sulphoaluminate crystals (AFm). The main forms of hydration products are lamellar, needle-like and gel-type, which are the fundamental source of concrete strength. However, due to the complex hydration process of cement, the morphology and structure of hydration products will change in varying degrees, resulting in a large number of microscopic defects in the internal microstructure of cement stone, which are both a source of concrete brittleness and low toughness and the reason for poor resistance to environmental erosion. Therefore, the improvement of the microstructure of cement stone is the fundamental solutions of solving the problems of concrete brittleness and low toughness.

Since the middle of the last century, mineral admixtures and organic fibers such as polypropylene fiber and other blends began to be extensively used in the concrete, which formed a more reasonable multi-gel system rather than a single cement gel system, leading to the improvement of the toughness of concrete and other properties at a certain extent. And the use of mineral admixtures has also played a positive role in the durability of concrete^[2,3]. However, adding mineral admixtures and fibers into concrete does not change the nature of the microstructure of the cementitious material. After the

study of mineral admixtures and organic fibers, the researchers began to notice the application of nanomaterials in concrete. It was found that the strength and toughness of concrete filled with nanoparticles were significantly improved, and nanomaterial particles could more effectively counteract the microscopic defects, promote the formation of hydration products with more regular crystal and affect the proportion of hydration products through the secondary hydration, so as to effectively improve the microstructure of cement stone. Now the nano-materials which have been applied in the practical engineering are mainly nano-silica, nano-calcium carbonate, rice husk ash and so on. In recent years, some studies have found that the addition of graphene oxide (GO) and other new nano-carbon materials into the cement paste will also have a significant increase in cement toughness^[4-6]. The GO has a regulation effect on the hydration of cement, which improve the crystal arrangement of hydration products and the microstructure of cement stone, and enhances the strength and toughness of cement material.

However, it was found that the addition of GO in the cement paste could obviously increase the viscosity of the paste, and decrease the fluidity, resulting in the decrease of the working performance of the cement paste. In order to ensure the working performance of the paste, it is necessary to further mix polycarboxylate superplasticizer to improve the fluidity of the cement paste. Although GO can be easily dispersed in the aqueous phase, the dispersibility of GO in the cement paste with high alkaline is not easily determined and difficult to control. If the dispersibility is poor, the performance of the cement can also be adversely affected.

The purpose of this study is to use chemical methods to graft the molecules of polycarboxylate on the graphene oxide layer to modify the graphene oxide (S-GO) by polycarboxylate water reducing agent to prepare a polycarboxylate nanoparticle complex(P-S-GO). With the aim of solving the adverse effect of the graphene oxide on the working performance of the cement paste by a combination of the polycarboxylate water reducing agent and the graphene oxide.

2 Experimental

2.1 Materials

The chemicals used in the experiment are highly active graphene oxide powder (GO), and analytic pure vinyltrimethoxysilane (Silane coupling agent KH-171 or A-171, purity>98%), anhydrous ethanol, glacial acetic acid, acrylic acid (AA), HPEG macromonomer (relative molecular

mass of about 2400 g/mol), ammonium persulfate (APS), mercaptopropionic acid and ascorbic acid (Vc).

The cement used in the fluidity and rheological tests is the reference cement produced by Qufu Zhonglian Cement Co., Ltd., and its chemical composition, mineral composition and physical properties are shown in Tables 1, 2, and 3, respectively.

2.2 Silicane modification of graphene oxide (S-GO)

Distilled water and anhydrous ethanol were mixed in a mass ratio of 1:1 in a conical flask with a stopper, the pH value of the solution was adjusted to 4 to 5 with glacial acetic acid, and then the vinyltrimethoxysilane was added. The mass ratio of GO to vinyltrimethoxysilane was 1:2. The mixed solution was pre-hydrolyzed in a water bath at 30-40 °C for 30 min. After completion of the pre-hydrolysis, a certain amount of GO was then mixed with the pre-hydrolyzed solution. After ultrasonic dispersion for 30min, the dispersion was transferred into a three-necked flask in a 80 °C water bath under stirring for about 5 h for reaction. After completion of the reaction, the reaction solution was cooled to room temperature and then filtered, washed three times with a 1: 1 aqueous ethanol solution and dried at 60 °C for 8 h to obtain the products^[7-9]. The reaction scheme is shown in Fig. 1.

2.3 Synthesis of silane modified graphene oxide-polycarboxylate composites (P-S-GO)

A certain amount of the modified GO was placed in distilled water and pre-ultrasonically dispersed for 0.5-1 h^[10-12]. After dispersion, a mixture of the HPEG macromonomer and APS initiator was added to the pre-dispersed liquid in a four-necked flask, which was placed into a 80 °C water bath and stirred to fully dissolve the solid. The mass ratio of GO: HPEG: APS was 1:17.5:0.2. The A reaction solution was prepared according to the ratio of AA to mercaptopropionic acid of 4.5:0.2 with a certain amount of distilled water. The B reaction solution was an ascorbic acid aqueous solution (about 0.2%). The A and B reaction solutions were added dropwise to the flask through a peristaltic pump. The dropping times of the A and B solution were 1.5 and 2.0 h, respectively. After completion of dropping, it was maintained at this temperature for 0.5-1 h. After completion of the reaction, the reaction solution was cooled to room temperature. The product was washed with distilled water several times to ensure that the free polycarboxylate superplasticizer was completely washed to avoid affecting the subsequent tests. The products were dried at about 60 °C for 8-10 h, and milled to get the final products^[13-15]. The synthesis mechanism is shown in Fig. 2.

Table 1 Chemical composition of the reference cement.

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O(eq)	f-CaO
Percentage (wt%)	22.10	4.53	3.43	64.90	3.35	0.40	0.51	0.92

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