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Chemically functionalized graphene oxide as the additive for cement–matrix composite with enhanced fluidity and toughness

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HIGHLIGHTS

- The first way to use chemically functionalized graphene oxide solve negative influence of GO on the cement fluidity.
- First demonstration on the relationship of branched chain (polyether amine) molecular weight and cement properties.
- Provide a new direction of GO nanosheets were used for improving cement properties.

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ABSTRACT

Chemically functionalized graphene oxide (GOM) was synthesized by the chemical reaction of polyether amine with graphene oxide (GO). The mechanical properties, rheological properties, dispersion effectiveness, slump retention behavior and the mechanism of GOM modified cement were also researched. The results show that GOM have more effective toughing function than cement with GO. And GOM can increase the slump flow of cement. The slump flow, the dispersion effectiveness and slump retention of GOM modified cement increased with the increasing molecular weight of polyether amine. The main chain (sheets structure) of GOM adsorbed on the cement surface, and the branched chains (polyether amine) stretched into the water. The electrostatic repulsive forces of adsorption layers and steric hindrance of branched chains endowed the good fluidity of cement.

1. Introduction

As a kind of structural materials, cement is widely used in construction, road and bridge field, owing to its low price, high compressive strength and durability as well as its stability [1–5]. However, the defect of cement is poor flexural strength and low strain capacity in the application process. So the most important modified research for cement is the development of the tensile properties [6–9]. In recent years, so many kinds of nanocarbon materials, such as graphene oxide (GO), carbon nanotube and carbon fiber, have been reported have the effectively improve function on the properties of cement [10–15].

In our previous work, GO as an additive of could improve the mechanical properties and pore structure of cement paste [16]. According to the research by Pan et al. [17,18], introduction of 0.05 wt.% GO in cement increased the compressive and flexural strengths by 15–33 and 42–59% respectively. Horszczaruk [19] reported an increase in Young's modulus by using 3 wt.% GO in cement. Whereas, the defect of this modified method is that GO has the negative influence on the fluidity of cement. Yu et al. [20] discovered that he mini-slump diameter of cement decreased by 36.2% when GO content is 0.08%. Lv et al. [21] reported that nano-graphene oxide could make decrease of fluidity and setting time, they used superplasticizer to supply the fluidity lose. It is well known that the good fluidity is the guarantee of workability and pump ability, and essential for cement engineering applications. Also, low fluidity would lead the decrease of durability; in the cement application process, we have paid attention to the sustainability in recent years, it has a great significance in energy conservation and environmental protection [17–21]. Although the addition of GO can increase the properties of cement, but the fatal drawback of GO modified cement is the low fluidity. Hence, the most important problem of GO as cement admixture is to solve the negative influence on fluidity.

The presence of chemical groups is the starting point for binding the different chemical molecules polymer on the GO nanosheets, such as epoxy group () and carboxyl group

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(—COOH) [22,23]. In addition, the main chains of polyether amine contains ether bond (C—O—C), and the end group is amino (—NH_2). This chemical structure lead the strong hydrophilic of polyether amine, and —NH_2 in polyether amine can react with —COOH and  in GO nanosheets [24,25]. Based on our previous work, the hydrophobic GO nanosheets can adsorb on the surface of cement in the hydration process [26]. The interaction force between the GO layers leaded the cement particles near to each other. So the fluidity of cement decreased due to the addition of GO. As the water-reducing mechanism of polycarboxylate superplasticizer, the increase of fluidity is the result of co-action of electrostatic repulsion and steric hindrance, which the main carbon chain adsorbs onto the cement and the branched hydrophilic chain stretches in the water [27–29]. So we can utilize the strong adsorption ability of GO and the hydrophilic of polyether amine to improve the fluidity of cement.

Herein, we synthesized the chemical functional GO (GOM) by grafting polyether amine onto GO to modified cement. The polyether amine differs in its molecular weight, which are M1000 (M_n = 1000) and M2070 (M_n = 2000). Also, the modified mechanism in the GOM in cement hydration system was studied.

2. Experimental section

2.1. Cement

Ordinary Portland cement type 52.5R was used in this study. The chemical composition of cement were listed in Table 1

2.2. Chemicals

Graphite (Layer thickness <15 nm), concentrated sulfuric acid (H_2SO_4, 98%), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2, 30%), N,N-Dimethylformamide (DMF), JEFFAMINE polyether amine (M2070 and M1000, 98%) was purchased from Suzhou Long Branch Industrial Co. Ltd., 4-dimethylaminopyridine (DMAP) and N,N′-Dicyclohexylcarbodiimide (DCC) were purchased from Aladdin Chemistry Co. Ltd., which were all analytically pure.

2.3. Synthetic procedures

2.3.1. Preparation of the chemically functionalized GO

A reaction scheme illustrating of the chemically functionalized GO (GOM) is displayed in Fig. 1. Firstly, the modified Hummer's method which contained oxidation, filtration and exfoliation was used to prepare GO [16,26]. Secondly, GO, M1000/M2070 and DMAP were dispersed in DMF for 5 min of ultrasonic. Subsequently, the mixture was cooled in the ice-bath; DCC was dissolved in DMF, and the solution was added to the mixture dropwise for 3 h. After the addition, dislodged the ice-bath and stirred the mixture at 35 °C for 12 h. Then, removed the DMF by rotary

Table 1
Chemical composition of cement (%).

Composition	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	LOI
Content	65.1	21.3	5.1	2.9	1.1	1.8	0.7	0.3	1.7

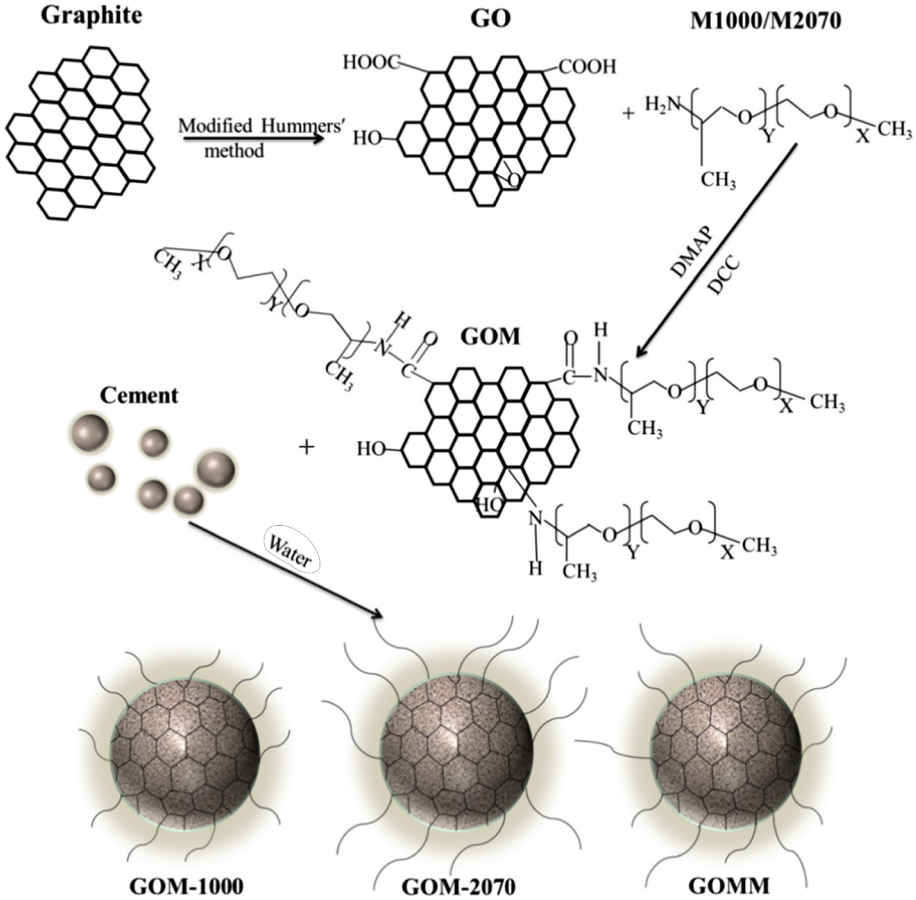

Fig. 1. Schematic illustration of GOM modified cement.