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Effect of fly ash on rheological properties of graphene oxide cement paste

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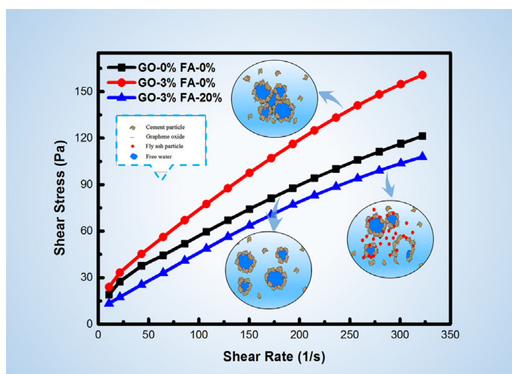
HIGHLIGHTS

- Fly ash (FA) increases fluidity and workability of graphene oxide (GO) cement paste.
- Fly ash improves the rheological properties of cement paste with graphene oxide.
- Shear rates, shear stress, yield stress and plastic viscosity of FA-GO-cement are delineated.
- A mechanism that can lessen viscosity in FA-GO cement paste was developed.

GRAPHICAL ABSTRACT



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ABSTRACT

While graphene oxide (GO) is found to have a potential to enhance the strength and toughness of cement based composites, it may reduce the cement paste fluidity and thus the workability of concrete. In this paper, a simple and economical additive, fly ash, is investigated to improve the rheological properties of cement paste when GO is present. Based on the quantitative analysis of the rheological parameters, it's shown that fly ash can offset the reduction of fluidity by GO. The effect of fly ash was studied with two dosages of GO, 0.01 wt% and 0.03 wt%. The yield stress and plastic viscosity of cement paste decreased with the increase of fly ash. At 0.01 wt% of GO and 20 wt% of fly ash, the yield stress of the paste decreased 85.81% and the plastic viscosity decreased 29.53% in comparison to the control sample (no fly ash or GO). At 0.03 wt% of GO and 20 wt% of fly ash, the yield stress of the paste is 50.33% lower and the plastic viscosity decreased slightly by 5.58%.The hysteresis area of the composite paste also decreased with the increase of fly ash. Meanwhile, the results indicated a good correlation between the fluidity and the plastic viscosity. The "ball" effect, grain size gradation and less water demand of fly ash can play an important role in improving the fluidity of the GO-cement systems. Moreover, GO can offset the delay in early-stage strength gain of fly ash-cement systems. When the dosage of fly ash is less than 15 wt%, the compressive and flexural strength of fly ash-GO-cement composites are all higher than the control sample at 3, 7, and 28 d. This indicates that the addition of fly ash is an economical and effective method to obtain desirable properties of GO-cement paste. The benefits of mixing fly ash and GO can help counteract the fluidity problems of the GO-cement paste on the workability of concrete.

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1. Introduction

At present, cement based materials such as cement and concrete are the most widely used structural engineering materials [1]. With the increase in volume and complexity of concrete construction, the need for a higher working performance during the mixing and pouring stages can be clearly seen. The main characteristic of modern concrete is its high fluidity and good homogeneity. To achieve homogeneity, we need to assure that the cement paste has sufficient viscosity to avoid segregation of the aggregate and maintain the stability of cement paste until hardened. The rheological properties of the new cement slurry have attracted much attention because of its significant influence on the homogeneity and workability of the fresh concrete [2,3]. The study of the rheological properties of cement paste is of great significance to the optimization of concrete mix proportion design [4].

Due to the shortcomings of concrete viscosity, which has to do with correct proportioning of the concrete during the mixing stage and homogeneous consistency during placing, problems can arise such as bleeding, early cracking, segregation (different size particle separation which affects consistency), and laitance (particles accumulating on the surface of fresh concrete) [5]. Recently, with the emergence of nanomaterials in building materials, the focus has shifted to the effect of nanomaterials on the strength and rheological properties of cement paste, such as graphene oxide (GO), nano-SiO_2, nano-TiO_2, nano-ZnO and carbon nanotubes [6–17].

Researchers [7–10] found that GO with high strength, surface area and oxygen-containing functional groups can significantly strengthen and toughen cement based composite materials. Nevertheless, due to the large specific surface area of GO [11], the addition of GO may dramatically increase the viscosity of cement paste and concrete and greatly reduce the workability performance [12,13], limiting its application. It is a bottleneck to improving the fluidity and workability of GO-cement slurry. Yu et al. [1] demonstrated that GO encapsulated silica fume better improves the rheological properties of cement paste than single-doped GO due to the synergetic effect of the surface activity of GO and the shape effect of silica fume. However, controlling the rheological properties of GO-cement paste by a simple and flexible method to reliably achieve the desired material properties remains a challenge [14,15].

Because fly ash (FA) is common mineral admixture and often used to improve the fluidity of slurry [16,17], and is known to increase cement strength and enhance durability in conventional cementitious system, we mixed fly ash into the GO-cement systems as a simple and economical method to improve the workability of the slurry in this research. The rheological parameters, such as the shear rate, shear stress, yield stress and plastic viscosity of FA-GO-cement systems were studied quantitatively, and a mechanism that can lessen viscosity was developed. The correlation between each parameter was also analyzed and discussed by mathematical fitting. To better elucidate the effect of FA on the fresh GO-cement systems, the strength of hardened cement paste was also determined. The methodology and results of this research follow.

2. Experimental

2.1. Raw materials

Pure grade Portland cement type (PI 42.5) was used to eliminate the effect of mineral mixtures on the tests. First grade fly ash (FAI) was provided by the Qingnian Road Concrete Company, the water requirement ratio was 96%. GO in water dispersion with a solid content of 2 g/L was provided by the Institute of Coal Chemistry, Chinese Academy of Sciences. Polycarboxylate superplasticizer (PCE) with a solid content of 20 wt% was purchased from Sika Corp. (Lyndhurst, NJ, USA).The GO sample was characterized by AFM, TEM and elemental analysis. The results are illustrated in Fig. 1. TEM image (Fig. 1a) demonstrates that GO is almost transparent nanosheet with many wrinkled and folded feature. AFM images (Fig. 1b and c) illustrate that GO sheets exhibit irregular shapes with a dimension of about 1 μm and a thickness of about 1 nm. Elemental analysis reveals that GO is consisted of 49.8 wt% C, 2.3 wt% H and 47.9 wt% O (by difference). Mixing water was ordinary tap water. The chemical composition of cement and fly ash is shown in Table 1, and the particle size distribution is shown in Fig. 2.

2.2. Preparation of cement paste

To investigate the influence of FA on the GO-cement systems, cement pastes with different replacement ratios of FA (0 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt%) were investigated when the dosage of GO was 0.01 wt% and 0.03 wt% by weight of cementitious material, respectively. In addition, there was a plain cement sample without fly ash and GO that serves as the control sample. The W/C (water to cement ratio) of rheological testing cement paste in this paper was kept at 0.3. The mix proportion is shown in Table 2.

2.3. Texting methods

2.3.1. Fluidity measurements

The effect of fly ash on the fluidity of GO-cement paste was characterized by a mini-slump test. After preparation of cement paste, it was poured into a mini-cone(top inside diameter: 36 mm, bottom inside diameter: 60 mm, height: 60 mm). The testing method is according to GB/T8077-2000 (National Standard of China). The fluidity of cement paste at5 min, 30 min, 60 min, 90 min and 120 min were recorded.

2.3.2. Rheological measurements

The rheological parameters of cement paste were characterized by BROOKFIELD RST-CC rheometer. The sample cup FTK-RST and spindle CC3-40 were used. Before testing, the cement paste was prepared according to Chinese standard GB/T8077-2000. The mixing procedure is described as follows: GO is first added to the water. The PCE is then added and mixed with a glass rod for 30 s, after which, the GO-PCE mixture is added to the FA-cement systems in a container for agitation. The FA-GO-cement mixture is then stirred at 62 rpm for 2 min. After a 10 s interval, the mixture is then stirred at 125 rpm for an additional 2 min to assure the homogeneity of cement paste. As soon as the mixing stops, the sample is then poured into the sample cup to carry out the rheological measurement. During the rheological test, the shear rate was increased from 5 to 150 s^{-1} and then back to 5 s^{-1} with 16 speed intervals. The rheological parameters, apparent viscosity and shear stress of cement paste with different mixture proportions were measured. The data were analyzed using the software RHE3000.Two rheological parameters of yield stress and plastic viscosity were widely used to characterize the rheological properties of cement paste [1–4,18–20]. The plastic viscosity (η_p) and shear stress (τ_0) can be obtained from the slope and intercept of the linear relationship between shear stress and rate, which can be calculated as:

$$\tau = \tau_0 + \eta_p \cdot \gamma \quad (1)$$

where τ is the shear stress (Pa), η_p is the plastic viscosity (Pa·s), γ is the shear rate (s^{-1}), and τ_0 is the yield stress (Pa).