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Hybrid effects of nano-silica and graphene oxide on mechanical properties and hydration products of oil well cement

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HIGHLIGHTS

- The mechanical properties of oil well cement were improved by the hybrid NS/GO.
- The effect of hybrid NS/GO on hydration and pozzolanic reaction degree was discussed.
- The hybrid NS/GO could refine the pores of the matrix.
- The hybrid structure was beneficial for nano-materials' dispersity in alkaline cement.

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ABSTRACT

Hybrid effects of nano-silica and graphene oxide on mechanical properties and hydration products of oil well cement have been investigated by means of TEM, TGA, XRD, SEM, MIP and mechanical testing. The results showed the designed hybrid structure was beneficial for SiO_2 particles and GO nanosheets to disperse well in alkaline cement. The compressive and flexural strength of cement with hybrid nanomaterials of 1.5% NS and 0.03% GO was increased by 43.2% and 42% with 28 days of curing respectively, which was far better than cement with single NS or GO. Graphene oxide and nano-silica have a hybrid effect including better dispersion of nano-materials, higher degree of hydration and pozzolanic reaction, and network structure formation of hydration products, all of which were beneficial to reinforcing the mechanical properties of cement.

1. Introduction

Cement-based material is an intrinsically brittle matrix, which has low tensile strength and poor fracture toughness. In petroleum industry, the oil well cement must withstand high pressures and corrosive fluid attacks occurred in downhole environment [1–4]. The improvement of strength and ductility is a challenging task for application of oil well cement. Usually, blending with various reinforcing additives can be considered as economical and effective methods [4–10]. Therefore, it is necessary to explore excellent reinforcing additives to fabricate oil well cement with enough toughness and strength. The formation of cracks in cement based material originates from nano-cracks, which then combine to form micro cracks and eventually macro cracks [11,12]. In tradition, fibers and whiskers are used to restrain crack initiation and crack propagation in the macro and micro level [4–7]. Recently, nanotechnology has played an important role in improving properties of cement paste, mortar or concrete, which transfer the reinforcing behavior from the macro and micro to nano-scopic scale [8–12].

In recent years, many studies have found that nano-silica (NS) is a promising candidate to improve properties in cement based materials [2,13–17]. The research showed that the utilization of nano-silica in cement lead to higher compressive strength and increased the durability of the material by adding proper amount of nano-silica, usually 0–6% by weight of cement [2,13]. The hydration process would be accelerated due to the nucleation effect of nano-silica when NS act as a nucleation site for C—S—H seeds [14]. Also, its pozzolanic reaction with $Ca(OH)_2$ could produce more quantities of C—S—H so as to enhancing the mechanical properties [15,16]. Cements incorporated with nano-silica resulted in more compact microstructure with lesser amount of calcium hydroxide crystals [17].

As a novel class of two-dimensional nanoscale material, graphene oxide (GO) has attracted attention due to its high specific

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surface area and excellent mechanical properties [18,19]. There are a large number of hydrophilic groups on the surface of GO nanosheets, which make it easy to disperse in water [18]. With its unique structure and excellent property, GO can be beneficial for improving the properties of cement based materials [19]. The research of Zhu et al. [20] showed that the incorporation of 0.05 wt% GO in cement could increase the compressive and flexural strength by 33% and 41%, respectively. It was reported that the addition of GO can accelerate cement hydration and modify the microstructure of hydration crystals and the cement showed remarkable increase in tensile strength, flexural strength and compressive strength when the dosage of GO was 0.03 wt% [21]. Mokhtar et al. [22] found that the addition of GO could significantly reduce the pore size of the GO-modified cement pastes and lead to a consequent improvement in the mechanical properties of these composites.

Although a lot of studies have been conducted concerning the reinforcing effects of various nano-materials on cement, very few researches have been carried out on the hybrid effects of SiO_2 nano-particles and GO nanosheets on the performance of cement. In fact, the application of hybrid $nSiO_2$/GO in other fields was reported. Bakhsheshi et al. [23] found that NS/GO coating had more effective antibacterial activity and higher corrosion resistance in vitro, compared to the nano-SiO_2 coated and uncoated samples. The hybrid NS/GO composites with a critical concentration decreased the coefficient of friction by 20% while increasing the wear resistance 5.5 times [24].

In this study, a hybrid nano-dispersion was prepared by using nano-silica and graphene oxide, and the effect of the hybrid structure on mechanical properties of cement was studied. To further investigate the enhancing mechanism, thermal gravimetric analyser (TGA), scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP) and X-ray diffraction (XRD) were used to test the hydration process and microstructure of cement incorporating with hybrid nano-materials.

2. Experiment

2.1. Materials

Cementitious materials used ordinary class G oil well cement, of which the compositions are presented in Table 1. Graphene oxide and nano-silica were commercially available powder materials from DK nano Co. Ltd., Beijing, China, and the physical properties are shown in Table 2. The thickness of graphene oxide nanosheet was 0.6–1.2 nm and the length was 0.8–2 μm. The average particle size of nanosilica was 15 nm. A poly-carboxylate superplasticizer with solid content of 40% was used to disperse nano-materials in cement slurry paste. The poly-carboxylate superplasticizer was composed of comb-like copolymers with grafted chains of polyoxyalkylene groups and carboxyl groups.

2.2. Preparation and characterization of hybrid nano-dispersion

First, graphene oxide (GO), nano-silica (NS) and poly-carboxylate superplasticizer (PC) were dissolved in water respectively. Secondly, the PC solution was poured into graphene oxide solution, and the mixed solution was stirred for 15 min in a magnetic stirring apparatus at 60 °C to obtain graphene oxide dispersion. Thirdly, the nano-silica aqueous solution was mixed with the graphene oxide dispersion. Then, an ultrasound device (KQ-700VDV) from Ultrasonic Instruments Co. Ltd., Kunshan, China, was used to facilitate the dispersion of nano-silica particles on GO nanosheets. Finally, the hybrid nano-dispersion of graphene oxide and nano-silica was obtained after sonicating (100 W) for 30 min. And the ultrasonic was operated at a lower energy and circulating water condition in order to prevent over-heating of the hybrid suspensions, which might damage the hybrid structure [25]. After comparing dispersion effect after different ultrasonic treatment time, 30 min was chosen because the better dispersion effect could be achieved under this condition.

The morphology and dispersity of nano-materials were observed by digital camera and transmission electron microscope (TEM, JEOL JEM 1200EX, Japan). To characterize the interaction between GO and SiO_2 in hybrid nano-material, a Fourier-transform infrared spectroscope (FTIR) spectrometer iS50 (Thermo Nicolet, USA) was used to detect absorption band of neat nano-silica, neat graphene oxide and hybrid nano-material. Allowing for absorption coefficient differences with respect to various FTIR bands, a transmission mode with a resolution of 4 cm^{-1} was used. Hybrid nano-material powder was got after centrifugation and vacuum drying at room temperature for 30 min. Before FTIR measurement, the nanofiller powders were pressed to obtain a slice.

2.3. Mixing design and procedure of cement pastes

In order to investigate the effect of hybrid nano-materials on the performance of cement slurry, four kinds of cement samples were prepared: cement without any nano-materials (the reference sample), cement with graphene oxide, cement with nano-silica, and cement with hybrid nano-materials of GO and nano-silica. These four samples were labeled as blank cement, GO cement, NS cement and hybrid cement, respectively. The specific dosages of nano-materials depended on different tests of cement.

The graphene dispersion, nano-silica dispersion and hybrid dispersion were used to prepare GO cement, NS cement and hybrid cement, respectively. Based on the water to cement ratio (w/c) of 0.44, extra water and nano-addition dispersion was added to a shear mixer. The oil well cement was added to mixer at low speed (4000 r/min) for 15 s and continuously mixed at high speed (12,000 r/min) for an additional 45 s. All the cement pastes were prepared similarly as the above method according to the Chinese standard GB/T 19139-2012. After mixing, the fresh cement paste was poured into rectangle molds and cured at 30 °C with 100% relative humidity for 3, 7 and 28 days.

2.4. Testing and characterization procedures of hardened cement pastes

The cured rectangular specimens ($50.8 \times 50.8 \times 50.8$ mm^3) were used to measure compressive properties at a crosshead speed of 400 N/s using electronic hydraulic testing machines (Haizhi Technology Co. Ltd, Beijing, China). The cured rectangular specimens ($40.0 \times 40.0 \times 160.0$ mm^3) were used to measure flexural properties with 3-point-bending using a motorized bending tester (Jianyi Instrument & Machinery Co. Ltd, Wuxi, China) with span and crosshead speed of 100 mm and 0.02 mm/min. Five specimen were tested for each datum and the final results were the average of the five. The optimal dosages of nano-materials for four kinds of cement samples were investigated by testing compressive properties of cement with different dosage nano-materials and the mix design was shown in Table 3. Compressive and flexural properties of four kinds of cement samples with optimal dosage of nano-materials were compared and the mix design for mechanical tests was shown in Table 4.

Scanning electron microscopy (SEM, HITACHI SU8010, Japan) was used to test microstructure of the hydration products of cement. The SEM samples about 5 mm × 5 mm × 2 mm size were prepared from fragments after the compressive strength test. They were fixed on a copper mesh and coated with a thin layer of Au before test.

Table 1
Chemical compositions of class G oil well cement.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	MnO_2	Loss on ignition
22.62	3.4	4.8	65.6	0.9	0.36	1.20	0.1	0.26

Table 2
Physical properties of nanosilica and graphene oxide.

Species	Average size	Thickness	Length	Purity	pH	Specific surface face
Nano-silica	15 nm	–	–	≥99.9%	8–9	600–800 m^2/g
GO	–	0.6–1.2 nm	0.8–2 μm	≥99%	8–9	450–550 m^2/g