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Reinforcing graphene oxide/cement composite with NH_2 functionalizing group

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Abstract. In this study, pure and NH_2-functionalized graphene oxide (GO) nanosheets have been added to the cement mortar with different weight percents (0.05, 0.10, 0.15, 0.20 and 0.25 wt%). In addition, the effects of functionalizing GO on the microstructure and mechanical properties (flexural/compressive strengths) of cement composite have been investigated for the first time. Scanning electron microscopy (SEM) images showed that GO filled the pores and well dispersed in concrete matrix, whereas exceeding GO additive from 0.10 wt% caused the formation of agglomerates and microcracks. In addition, mercury intrusion porosimetry confirmed the significant effects of GO and functionalizing groups on filling the pores. NH_2-functionalizing helped to improve the cohesion between GO nanosheets and cement composite. Compressive strengths increased from 39 MPa for the sample without GO to 54.23 MPa for the cement composites containing 0.10 wt% of NH_2-functionalized GO. Moreover, the flexural strength increased to 23.4 and 38.4% by compositing the cement paste with 0.10 wt% of pure and NH_2-functionalized GO, compared to the sample without GO, respectively. It was shown that functionalizing considerably enhanced the mechanical properties of GO/cement composite due to the interfacial strength between calcium silicate hydrates (C-S-H) gel and functionalized GO nanosheets as observed in SEM images. The morphological results were in good agreement with the trend obtained in mechanical properties of GO/cement composites.

Keywords. Cement; mechanical properties; graphene oxide; microstructure.

1. Introduction

Concrete as the most widely manufactured construction material is a multiphase composite composed of an amorphous phase, nanometre- to micrometre-size crystals and bound water. Although various high-performance concrete composites have already been produced, crack formation due to brittleness and dimensional instability from thermal and moisture fluctuations are considered as the main problems [1,2]. As cement and concrete composites have relatively high compressive strength and low tensile and flexural strength, these composites are brittle materials. Therefore, many attempts have been directed at improving toughness and strength of cement and concrete composites by enhancing their properties with admixtures, supplementary cementitious materials and fibres [3–5]. Previous techniques recommend using reinforcing materials and neglect the influences of the microstructure, such as the shape of hydration and nanometre- to micrometre-size crystals of the cement paste. It is expected that the strengths and durability of concrete would be enhanced if the overall porosity and pore sizes in the cement paste decrease. In this case, incorporation of nano-materials into the composite matrix is a notable approach to improve mechanical properties of concrete and considered as a promising research field of nanocomposites. Nano-engineering of concrete can take place in three phases, including (a) in the solid phase, (b) in the liquid phases and (c) at the interfaces between liquid–solid and solid–solid [6]. More researches have been directed towards investigating the effects of using silica (SiO_2) [7–9] and titanium oxide (TiO_2) [10] nanoparticles on improving the mechanical properties of concrete composites; while other compounds such as nano-$CaCO_3$ [11], nanoalumina (Al_2O_3) [12] and nanoclay particles [13] have been less attractive.

In recent years, some carbon-based nanostructures such as graphite nanoplatelets [14], carbon nanotubes [15] and graphene oxide (GO) nanosheets [16] have been suggested as promising materials for reinforcing the concrete and cement composites. The important advantages of the two-dimensional GO, such as high specific surface area, ultrahigh strength and flexibility; rough surface and easily forming composites, have a favourable influence on the mechanical behaviour of concrete and cement composites. By compositing a small amount of GO as little as 0.05 wt%, the compressive and flexural strengths increased by 15–33 and 41–59%, respectively [17]. In addition, the elastic modulus calculated from the stress–strain curve showed an increase from 3.48 to 3.7 MPa. The increased strain capacity can be attributed to the delayed microcracks initiation. As reported by Gong *et al* [18], the compressive strength would be improved by

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46.2% besides increasing failure stress and strain in the composite with 0.03 wt% of GO. However, since the first reports on the carbon/materials composites, fewer attempts have been made to reinforce the materials with functionalized carbon-based nanostructures, GO in particular. For instance, it was found that PVA-functionalized carbon nanotubes showed much better mechanical properties comparing to the neat polymer film [19]. Li *et al* [20] showed that the flexural and compressive strengths had been improved by functionalizing carbon nanotube with H_2SO_4 and HNO_3 mixture. As a graphene derivative, GO is built up from a hexagon-structure carbons network bearing several functional groups such as hydroxyl, carboxyl and carbonyl. Since all of these functional groups contain oxygen, GO nanosheets are hydrophilic and highly dispersed in water. Consequently, GO nanosheets can provide a larger surface area for calcium silicate hydrates (C-H-S) nucleation than that of previously reported for CNTs [21]. Among the different functionalizing groups, NH_2 has been successfully examined to reinforce the GO/polymer nanocomposite [22]. Therefore, it is expected that the mechanical properties of GO/cement composite can be improved by functionalizing GO.

In this paper, the effects of NH_2-functionalized GO on the microstructure, density and flexural and compressive strengths of the GO/cement composites have been investigated.

2. Experimental

2.1 *Preparation of NH_2-functionalized GO*

In order to prepare NH_2-functionalized GO, 0.5 g of GO powder (XFNANO Materials Tech, China) with the layer thickness of 0.8–1.2 nm was dispersed for 20 min in 150 ml of ammonia in a glass flask placed in an ultrasonic bath. The mixture was stirred and refluxed for 24 h in the preheated oil bath. Next, it was extracted and poured into deionized water to quench the reaction. The graphene–water suspension was sonicated for 5 min, filtered, and washed to neutral pH for six times. The final product was obtained after drying at 120°C for 12 h. Formation of NH_2 groups on the surface of GO nanosheets was checked by FTIR spectroscopy.

2.2 *Preparation of cement composites*

Standard sand and ordinary Portland cement type 2 were the main materials used in this research. The chemical composition of the cement is given in table 1. Portland cement type 2 was used as a binder with a specific area of 0.32 $m^2\ g^{-1}$ (blaine fineness) and the average particle size of the sand was 0.3 mm. Pure and NH_2-functionalized GO nanosheets were used as the reinforcing materials of the cement. Cement composites were prepared with binder/sand weight ratio (B/S) of 0.36 and water/binder (W/B) of 0.48 according to ASTM-C109, i.e., 83.3 g cement, 229.1 g standard sand, 40.33 g mixture of water and certain amounts of pure and functionalized GO (0.05, 0.10, 0.15, 0.20, 0.25 wt%).

The samples were moulded into a cubic form with a size of $5 \times 5 \times 5$ mm to test the flexural and compressive strengths. A vibrator was used to facilitate compaction and decrease the amount of air bubbles. Then the moulds were removed after 24 h and the samples were continued to be cured in a standard curing box at $23 \pm 2°$ for 14 days before testing.

2.3 *Structural, microstructural and mechanical testing*

FTIR spectroscopy was used to check the formation of NH_2 groups on the surface of GO nanosheets. The fracture surfaces of the composites were monitored by scanning electron microscopy (SEM). The density of the samples cured in water for 14 days was measured by Archimedes technique according to B 328-96.

To investigate the effect of functionalization on the porosity behaviour of GO/cement paste, the porosity measurements of the samples have been performed by mercury intrusion porosimetry (MIP) with a maximum pressure of 600 MPa. To prepare the samples for testing, they were cured in water for 14 days followed by soaking in acetone for 24 h to stop the hydration reaction, and then dried in an oven at 60°C.

In order to determine the compressive strength of the samples, compressive test was applied at the speed of 0.9 MP s^{-1}. A three-point flexure-testing machine determined the flexural strength. The ratio of pressure change was adjusted at 0.25 MPa s^{-1}.

3. Results and discussions

3.1 *Structural properties*

The FTIR spectrum of the NH_2-functionalized GO is shown in figure 1. The characteristic absorption peaks at 1098 and 1393 cm^{-1} corresponding to C–O and at 1621 cm^{-1} relating to C=C double bonds located near the functionalized sites are clearly observed. The bands at 3159 and 3409 cm^{-1} are assigned to N–H and O–H bond stretching vibrations, respectively. From the FTIR results obtained for NH_2-functionalized GO, it can be concluded that the amine groups have been incorporated into the sheets of GO.

Table 1. Chemical compositions of cement.

Component	SiO_2	CaO	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O
Content (%)	20.5	65.0	4.6	3.5	1.5	1.5	0.5	0.3

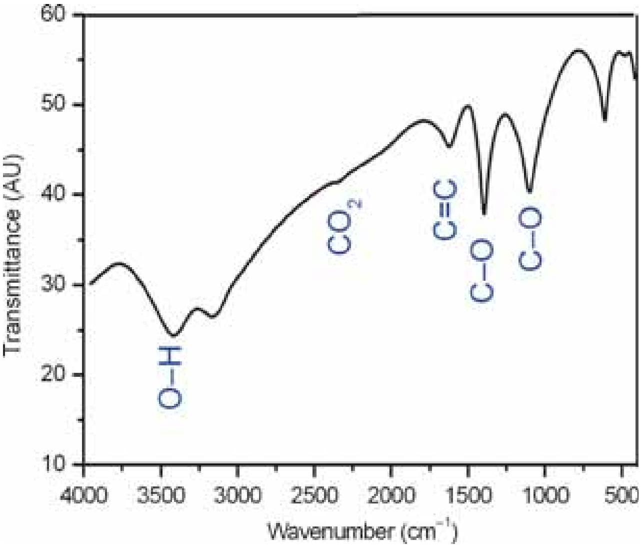

Figure 1. FTIR spectra of NH_2-functionalized GO.

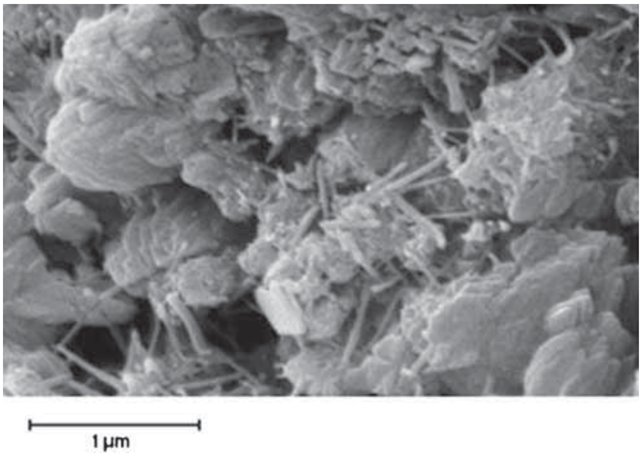

Figure 2. SEM images of the cement that was cured in water for 14 days. The cement hydration crystals were observed on the surfaces in the form of needle-like crystals disorderly stacked corresponding to the cement hydration crystals observed on fracture surfaces.

3.2 *Microstructural properties*

The physical and mechanical properties such as chemical, corrosion and wear resistance, strength, toughness, and hardness considerably depend on the microstructure of the material. Figure 2 shows the microstructure of the cement composite not containing GO. Many needle- and bar-like crystals disorderly stacked corresponding to the cement hydration crystals were observed on fracture surfaces. SEM images of cement composites mixed with different contents of pure and NH_2-functionalized GO are shown in figure 3a–c and d–f, respectively. The results showed that GO helped in further filling up the pores and perfectly dense structures.

Total porosity of all the composites obtained by MIP is given in table 2. The porosity of Portland cement was 26.3% and the value observed in the pure GO/cement composite slightly decreased, while functionalizing GO with NH_2 resulted in a considerable decrease in the porosity to ~21.5%. It has been shown that GO whether in the form of pure or functionalized with NH_2 could fill in the pores between the hydration products of Portland cement, decreased the porosity and consequently reduced the total pore volume. However, it was observed that the porosity has not been significantly changed due to the increase of the pure and functionalized GO. As can be seen in table 2, the NH_2-functionalization considerably enhances the pore refinement. It was concluded that there was a limit for pore refinement by compositing cement paste with GO so that the total porosity was found to steeply decrease with the increase of GO content up to 0.10 wt% and a slight downward trend was observed for the composites containing more GO. Therefore, GO nanosheets have not actively participated in filling the pores of the composites with higher concentrations of GO and might form agglomerations in the composite matrix.

The microstructure in figure 3a–c indicates that there is no good adhesion between the nanosheets and the concrete matrix, while functionalizing the surface of the GO nanosheets with NH_2 groups increases the cohesion and interfacial strength of the matrix and nanosheets. In the case of the sample containing 0.10 wt% GO, the nano-platelets were well dispersed in cement paste and almost no agglomerates were observed. However, increasing the weight percent of GO nanosheets resulted in forming agglomerates (as shown by arrows in figure 3f) and micro-cracks. It seems that at higher concentrations of GO, nanosheets slided on each other and subsequently caused the formation of micro-cracks and weak bonds in the microstructure. The main product of the hydration process is a rigid gel called calcium silicate hydrates (C-S-H) that are responsible for cohesion and strength of the concrete structures. When nanosheets of pure GO were used to prepare the cement composite, the interfacial strength between C-S-H gel and GO nanosheets was very low. As theoretically reported by Alkhateb *et al* [23], the functional groups on the surface of the graphene nanosheets would enhance the interfacial strength.

3.3 *Mechanical properties*

The densities of the samples compositing with different concentrations of pure and NH_2-functionalized GO cured in water for 14 days are given in figure 4a. The density of pure GO/concrete decreased with the increase of GO content, while NH_2-functionalizing caused a slight increase up to 2.32 g cm^{-3} for the sample containing 0.10 wt% GO, followed by an expected decrease with the increase of GO content corresponding to the low density of graphene-based materials. For example, Yan *et al* [24] and Tao *et al* [25] prepared graphene nanosheets with the density of 1.03 and 1.58 g cm^{-3}, which are considerably lower than that of obtained for the cement composites. The agglomeration of nanosheets in the samples with higher concentrations of GO can be considered as the main effective factor in decreasing

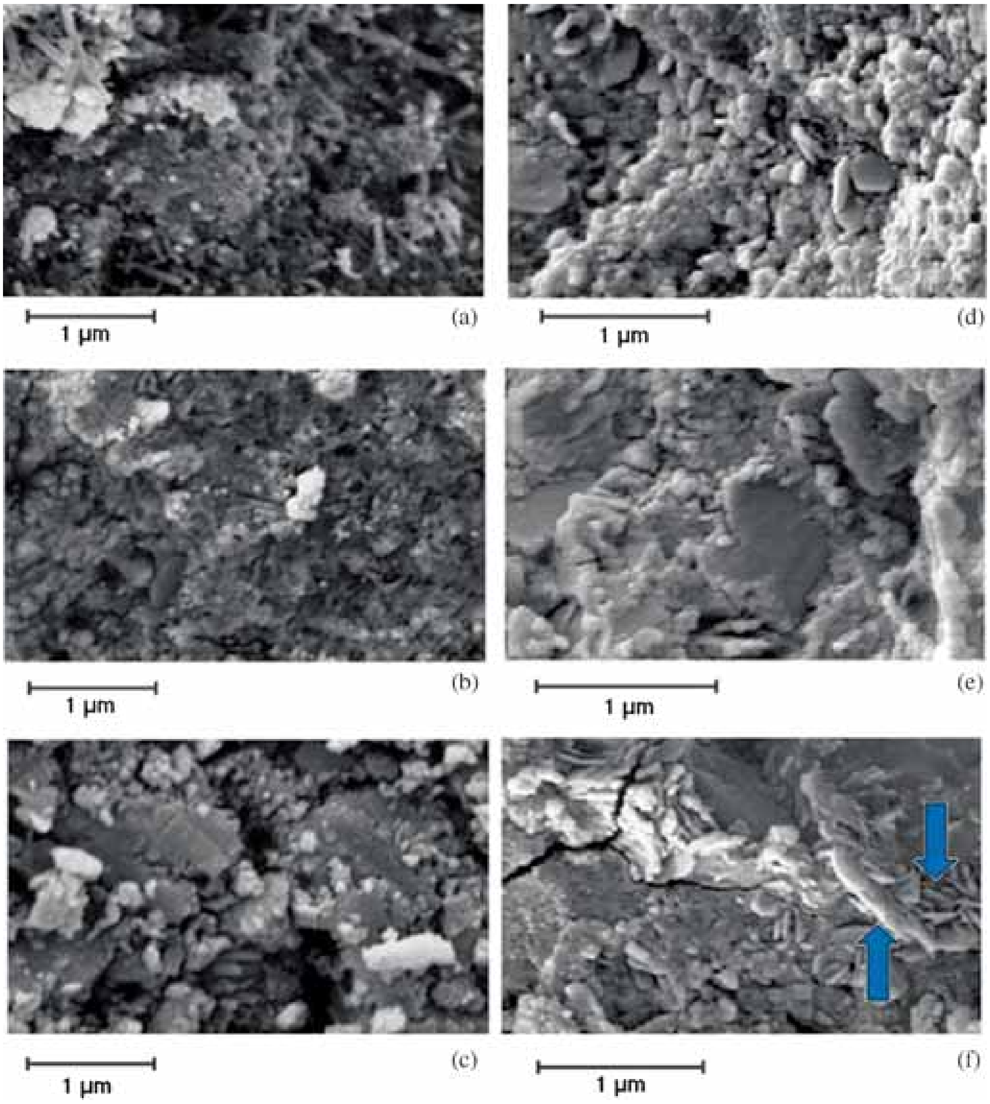

Figure 3. SEM images of the cement compositing with different amounts of GO (**a**) 0.10 wt%, (**b**) 0.15 wt% and (**c**) 0.25 wt% and NH_2-functionalized GO (**d**) 0.10 wt%, (**e**) 0.15 wt% and (**f**) 0.25 wt%.

the density. As discussed above about pore refinement in the functionalized GO/cement composite, it was clarified that NH_2-functionalizing enhanced the process of pores filling and consequently the density of the composite up to 0.1 wt% GO. As the nanosheets have not filled more pores with increasing GO contents, the excessive amounts of GO nanosheets agglomerated in the composite matrix and the density decreased due to the low density of graphene-based materials. As can be compared between the porosity and the density obtained for the pure GO/cement composite, it seems that the nanosheets can fill the pores to some extent but not enough to enhance the density.

The compressive strength offers the ability of a material or structure to withstand loads. The ultimate compressive is defined as the value of uniaxial compressive stress when the material fails completely. Figure 4b shows the compressive strengths of cement composites cured in water for 14 days and containing different amounts of pure and NH_2-functionalized GO. Compressive strength of pure GO/cement composite increased with increasing GO content up to 0.10 wt%. The compressive strength of the sample with 0.10% pure GO increased by 8.5%, compared to that without GO that can be attributed to the pore refinement. However, further increases in GO concentration from 0.10 to 0.25 wt% resulted in the decrease of compressive strength from 42.3 to 40.10 MPa due to the agglomeration of the GO nanosheets and subsequently reduce their surface energies. In this case, the nanosheets were not well dispersed in the matrix. In addition, low interfacial strength between C-S-H gel and GO nanosheets can be considered as another reason for not expected increase in compressive strength of pure GO/cement. Reinforcing cement with GO compared to the conventional fibres originates in a large aspect ratio of nanosheets. GO acts as seeds for the growth of the hydration

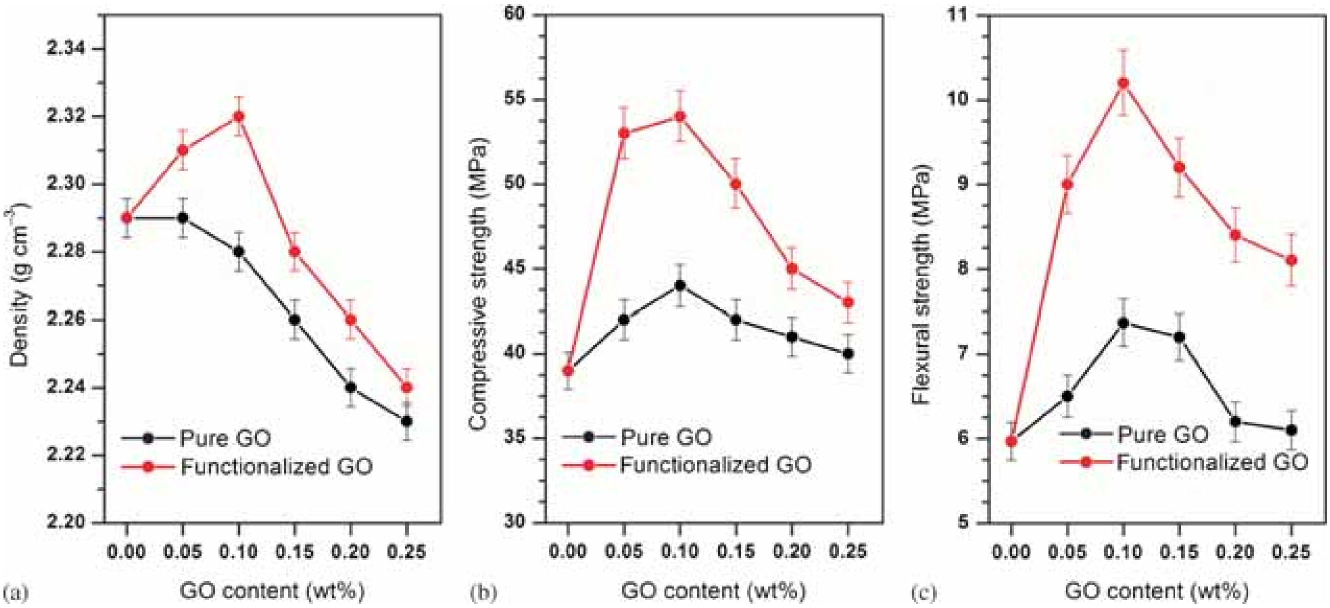

Figure 4. (**a**) Density, (**b**) compressive strength and (**c**) flexural strength of the cement composites with different amounts of GO and NH_2-functionalized GO after curing for 14 days.

products and subsequently affects the cement hydration kinetics. The functional groups of GO play the main role in interfacial adhesion, as also reported by Li *et al* [20] for functionalized CNTs. The strong covalent bonds on the GO interfaces with hydration products on the nanosheets considerably enhance the mechanical properties of cement matrix. As shown in figure 4b, the compressive strength obtained for the cement compositing with NH_2-functionalized GO confirms the effect of enhancing the covalent bonds with hydration products on improving the mechanical properties. The compressive strength of the samples containing 0.05 and 0.10 wt% NH_2-functionalized GO nanosheets increased by 25.5 and 23.0%, compared to those compositing with the same amounts of pure GO, respectively. In addition, according to the results obtained from MIP, functionalizing group considerably enhanced the pore-filling process that could be considered as one of the significant factors in the improvement of mechanical properties [20].

Table 2. Porosity, density, flexural and compressive strengths of the cement compositing with different contents of pure and NH_2-functionalized GO after curing in water for 14 days.

GO content, wt%	Porosity (%)	Density (g cm^{-3})	Flexural strength (MPa)	Compressive strength (MPa)
0.00	26.3	2.29	5.97	39
Pure GO				
0.05	25.1	2.29	6.50	42.30
0.10	24.8	2.28	7.37	44.08
0.15	24.7	2.26	7.21	42.44
0.20	24.5	2.24	6.25	41.02
0.25	24.5	2.23	6.15	40.10
Functionalized GO				
0.05	23.7	2.31	10.01	53.10
0.10	22.0	2.32	10.20	54.23
0.15	21.8	2.28	9.20	50.36
0.20	21.6	2.26	8.40	45.09
0.25	21.4	2.24	8.10	43.12

Flexural strength is defined as a parameter to investigate the ability of brittle materials to resist deformation under loads such as tensile stress. Most materials fail under the tensile stress before the compressive stress. Therefore, the maximum tensile stress value that can be sustained by a beam or rod is the flexural strength. The flexural strength of the cement composites with different contents of pure and functionalized GO cured in water for 14 days is shown in figure 4c. The results showed that the increase observed in flexural strength were more than that of measured for the compressive strength, while the trend of changes were similar. Flexural strength of 0.10 wt% pure GO/cement composite increased by 23.4%, compared to that without GO. Moreover, the flexural strength of the samples containing 0.05 and 0.10 wt% NH_2-functionalized GO nanosheets increased by 54.0 and 38.4%, compared to those compositing with the same amounts of pure GO, respectively. The considerable increase observed in flexural strength of the composites containing functionalized-GO can be attributed to good adhesion between the nanosheets and the concrete matrix due to functionalization of GO surfaces with NH_2 groups. The flexural/compressive strengths obtained for the samples with different contents of pure and NH_2-functionalized GO after curing for 14 days are summarized in table 2. According to the SEM images and mechanical properties of GO/cement composites, GO-based materials can be promisingly suggested to improve the microstructure and mechanical properties of concrete.

4. Conclusions

In this work, the effects of NH_2-functionalized GO on reinforcing the cement composite have been investigated for the first time. The porosimetry test of the composites showed that the porosity decreased with pure GO addition, whereas the porosity exhibited much more decrease in NH2-functionalized GO/cement paste. However, with the increase of GO content, nanosheets could not fill the pores anymore and consequently agglomerated in the matrix and resulted in the decrease of density. It has been shown that the flexural strength considerably increased from 5.97 MPa for the sample without GO to 7.37 and 10.20 MPa for the cement composites containing 0.10 wt% of pure and functionalized GO, respectively. The mechanical results showed that the compressive and flexural strengths enhanced in the cement compositing with NH_2-functionalized GO, compared to pure GO due to the interfacial strength between calcium silicate hydrates (C-S-H) gel and functionalized GO nanosheets. However, further increase in GO concentration led to a strong decrease in mechanical properties that could be attributed to the formation of agglomerates, microcracks and weak bonds in the microstructure. In summary, GO can be a promising material to reinforce cement composites and concrete instead of the conditional fibres if the formation of agglomeration and microcracks in concrete is avoided and the cohesion between GO nanosheets and cement composite is improved by functionalizing as well.

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