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MECHANICAL PROPERTIES OF CEMENT MORTAR WITH GRAPHENE OXIDE

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Abstract
These days, nanotechnology has already influenced many fields of science and technology, including civil engineering. Cementitious composites incorporating various nanomaterials have emerged as novel materials with improved microstructure, mechanical properties and durability. Over the past decades, graphene oxide has appeared as one of the most promising nanomaterials for civil engineering applications. However, the effect of graphene oxide addition on the properties of cementitious composites has not yet been fully investigated. The paper presents the studies on the mechanical properties of cement mortar reinforced with the 0.03 wt.% of graphene oxide (dosage by weight of cement). Graphene oxide proved to accelerate the cement hydration, in particular at the early stages of mortar hardening, hence improving the mortar performance during mechanical tests. The significant enhancement of the flexural, cubic and cylindrical compressive strength has been reported, thus showing the great nanotechnology potential for concrete structures.

Keywords: **Cement mortar; Compressive strength; Concrete nanotechnology; Graphene oxide; Poisson's ratio; Young's modulus.**

1. INTRODUCTION

Over the past decade, nanotechnology has attracted considerable attention in many areas of science and technology, including civil engineering and concrete structures. Since 1974, when the term "nanotechnology" was first created by Norio Taniguchi, the definition of "nanotechnology" has evolved over the years [1]. Today, one can define it as understanding, modifying and controlling matter at the atomic and molecular level to obtain novel, high performance materials featured with enhanced properties and new capabilities [1, 2]. In this perspective, nanotechnology of concrete involves the two main research paths: nanoscience and nano-engineering. The former one is focused on the advanced characterization of cement paste hydrates using novel and sophisticated research techniques, including atomic force microscopy, nuclear magnetic resonance spectroscopy, X-ray or neutron scattering, to name a few, while the latter one covers the studies on nano-modification of the microstructure of cementitious composites aiming at the improvement of already existing properties or the development of completely new functionalities of these materials [2]. Basically, nano-engineering of cement composites involves the incorporation of nanomaterials into cement paste matrix. Due to the high surface area with the simultaneous nano-size of particles, nanomaterials possess a high chemical reactivity and therefore may promote the growth of cement hydrates. Moreover, nanoparticles can be also considered as nano-reinforcement with remarkable mechanical properties or fillers reducing the porosity of cement composites [2]. Numerous exciting nanomaterials were incorporated into cement matrix up to date, including nano-silica [3, 4], nano-alumina [5], nano-titania [6], nano-clay particles [7] or carbon nanotubes [8, 9]. Depending on the chosen material, the addition of nanoparticles may lead to the improvement of both composite strength [3, 5, 7–9] and corrosion resistance [3], the nucleation of cement hydration [4, 7], the reduction of porosity [3, 7–9] and the initiation of self-cleaning, air polluting and antimicrobial properties [6].

Due to the extraordinary mechanical properties of graphene and the high effectiveness of the graphene-matrix bonding, graphene has emerged as one of the most promising nanomaterials to be applied in concrete structures. Graphene, defined as a single, planar, 2-dimensional, honeycomb-shaped carbon layer, has been isolated from graphite intercalation compounds for the very first time in 2004 [10]. With the intrinsic tensile strength of a single, defect-free graphene layer of 130 GPa and corresponding strain up to 0.25, graphene has been introduced as "the strongest material ever measured" [11, 12].

Graphene oxide (GO) – the best-known graphene derivative – has one major advantage, if compared to graphene, i.e. GO exhibits high dispersibility in water due to the oxygen functional groups attached on its sheets [13]. Clearly, the oxidation leads to the deterioration of mechanical properties of graphene, however, GO still features with remarkable mechanical properties, such as Young's modulus of 32 GPa and tensile strength of 130 MPa [14]. The initial approach to manufacture cement-GO composites was simply ultrasonication of GO with water, prior to adding cement [15–16]. As revealed by previous studies, the addition of 0.01–0.05 wt.% of graphene oxide enhances the microstructure of hardened cement paste reducing its porosity [16–18], promotes the cement hydration, in particular the early-age hydration [16, 19 ,20] and increases the compressive and tensile strength of cementitious composites up to 48% and 79%, respectively [15, 17–21]. Authors [17, 22] attributed the strengthening mechanism of graphene oxide to the reaction between -OH, -COOH and -SO_3H functional groups attached to the GO nanosheets being the nucleation sites and C_3S, C_2S, C_3A compounds existing in cement, as a result of which the additional growth points for cement hydrates are created and micropores can be significantly filled. Additionally, according to Wang et al. [23] and Zhao et al. [24], the enhanced mechanical properties of cement composites modified with graphene oxide originate from the reaction between Ca^{2+} ions present in cement and -COOH groups from GO sheets. This reaction leads to more compact, denser, reinforced 3D structure composed of GO nanosheets and cement hydrates. Interestingly, Gholampour et al. [25] have investigated the effect of various levels of oxygen functional groups of graphene on the properties of cementitious nanocomposites. The results have revealed that the mechanical properties of hardened cement-GO composites are highly dependent on the oxygen groups level and the crystallinity of graphene.

The present paper introduces the study on the mechanical properties of the cement mortar reinforced with graphene oxide. The water-to-cement ratio of mortar is 0.5 with the graphene oxide loading of 0.03 wt.% (dosage by weight of cement). The effect of GO on the flexural, cubic and cylindrical compressive strength as well as Young's modulus has been investigated and benchmarked with the performance of plain cement mortar. The preliminary results of this study have been presented in [26, 27].

2. MATERIALS AND METHODS

Cement, sand, distilled water and graphene oxide have been used to fabricate cement mortar. Portland cement CEM I 32.5R was employed in this study to manufacture both reference mortar (labelled as R) and mortar with the addition of 0.03 wt.% of GO (GO dosage by weight of cement, mortar labelled as GO0.03). The chemical and physical properties of cement are listed in Tab. 1, while the results of sand sieve analysis are shown in Fig. 1. Graphene oxide was purchased from Graphenea. The as-received GO was of high purity (> 95%) with the lateral size of particles not exceeding 10 µm. According to the elementary analysis, the oxygen content was of 41–50% [28]. The water-to-cement and sand-to-cement ratios were kept constant for both mixes at 0.5 and 3.0, respectively. The exact composition of fabricated cement mortars is presented in Tab. 2.

To provide the uniform dispersion of graphene oxide within cement matrix, graphene oxide was first ultrasonicated with a certain amount of water for ca. 15 min using a compact ultrasonic homogenizer (UP50H Hielsher, 30 kHz, 50 W). The dispersion with the concentration of 4.6 mg/ml was thus obtained. Cement mortars were then fabricated according to PN-EN 196-1 [29] procedure. In case of cement mortar containing GO, GO dispersion was added to cement simultaneously with the remaining

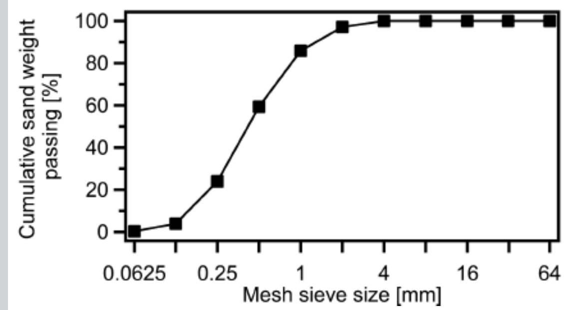

Figure 1.
Results of the sand sieve analysis

Table 1.
Chemical and physical properties of cement

	Average values
Loss on ignition [%]	2.99
Insoluble residue [%]	0.81
SO_3 content [%]	3.20
Cl^- content [%]	0.063
Na_2O content [%]	0.75
Start of setting time [min]	217
Compressive strength after 2 days [MPa]	26.5
Compressive strength after 28 days [MPa]	51.4
Stability of volume [mm]	0.80
Specific surface area [cm^2/g]	3416

Table 2.
Composition of fabricated cement mortars

Sample	Components				
	Cement [g]	Water for GO disper-sion [g]	Remaining water [g]	Sand [g]	Graphene oxide [g]
R	3400	0	1700	10200	0
GO0.03	3400	222	1478	10200	1.02

Table 3.
Results of the flexural and cubic compressive strength tests at the age of 28 days [26]

Sample	Parameters					
	Flexural strength			Compressive strength		
	Force [kN]	Strength [MPa]	Average strength [MPa] (increase)	Force [kN]	Strength [MPa]	Average strength [MPa] (increase)
R	1.78	4.17	**4.00 (0%)**	64.55	40.34	**39.90 (0%)**
				60.94	38.08	
	1.75	4.10		62.10	38.81	
				64.91	40.57	
	1.59	3.73		65.71	41.06	
				64.84	40.52	
GO 0.03	1.74	4.07	**4.52 (13%)**	80.81	50.50	**49.00 (23%)**
				79.94	49.96	
	2.23	5.22		69.80	43.65	
				79.92	49.94	
	1.82	4.26		80.21	50.13	
				79.69	49.80	

water. Both resulting cement mixes were placed into steel molds in a few layer and each layer was vibrated on the vibration table. Three rectangular samples with the dimensions of 40×40×160 mm, five cylindrical samples with the diameter of 60 mm and the height of 120 mm and fifteen cylindrical samples with the diameter of 60 mm and the height of 80 mm were manufactured for both types of mortars. All molds were immediately covered with polyethylene foil and after 24 h the specimens were demolded and conditioned in water. Samples were dried for 24 h in the air before mechanical tests.

At the age of 28 days rectangular samples 40×40×160 mm were subjected to bending to obtain the flexural strength of tested hardened mortars and then the remaining halves were compressed to obtain the cubic compressive strength. The loading rates for bending and compression were 0.05 kN/s and 2.4 kN/s, respectively. The compressive strength of cylindrical samples with the height of 80 mm was measured at the age of 7, 14 and 28 days to investigate the variability of the compressive strength in time. Five specimens were tested at each hardening age with a loading rate of 0.5 kN/s. In addition, the compressive strength tests were also performed on the cylindrical specimens with the height of 120 mm at the age of 28 days. To obtain the compression stress-strain curves and to calculate the values of Young's modulus and Poisson's ratio, two pairs of linear strain gauges were used for each sample to measure axial and transverse strain. The gauge factor of strain gauges was of 2.13.

3. RESULTS AND DISCUSSION

The results of the flexural and cubic compressive strength tests conducted on rectangular samples are shown in Tab. 3. The addition of 0.03 wt.% of GO increased the flexural strength of cement mortar up to 13%. Simultaneously, the cubic compressive strength is enhanced by 23%.

The variability of the cylindrical compressive strength of plain cement mortar and mortar reinforced with GO are presented in Fig. 2a. Noteworthy, compression tests performed on the cylindrical samples have revealed higher improvement of nanocomposite strength than in the case of cubical samples. The results indicate that the strength of nanocomposite is considerably enhanced during the entire process of cement hydration. The increase of the strength is equal to 29% and 31% for specimens evaluated at the age of 14 and 28 days, respectively. Significantly, on the basis of mechanical properties tests as well as the previous studies [16, 19, 30], one may suppose that the addition of GO proved to accelerate cement hydration, in particular at the early stages of mortar hardening, since the cylindrical compressive strength measured after 7 days of samples curing is remarkably increased by 40%.

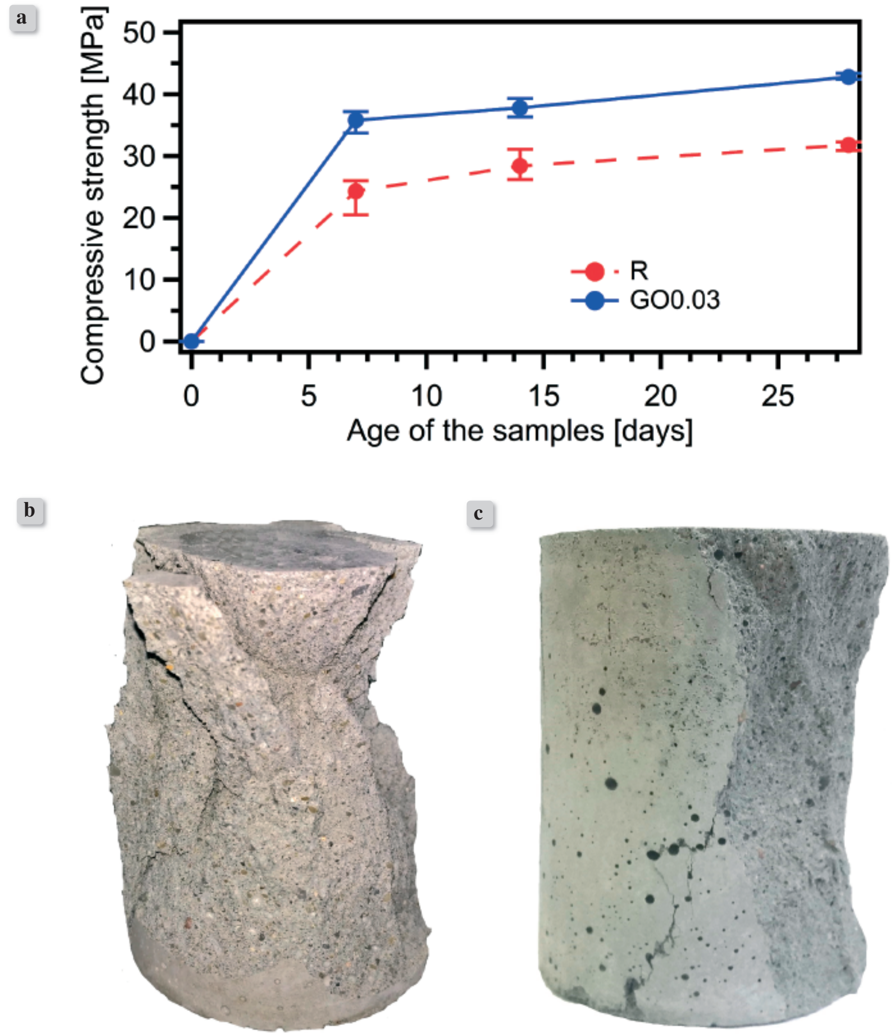

Figure 2.
Results of compression tests conducted on 60×80 mm cylindrical specimens. a) The variability of compressive strength in time [26, 27] b) Plain mortar sample and c) cement-GO sample after compression test at the age of 14 days [26]

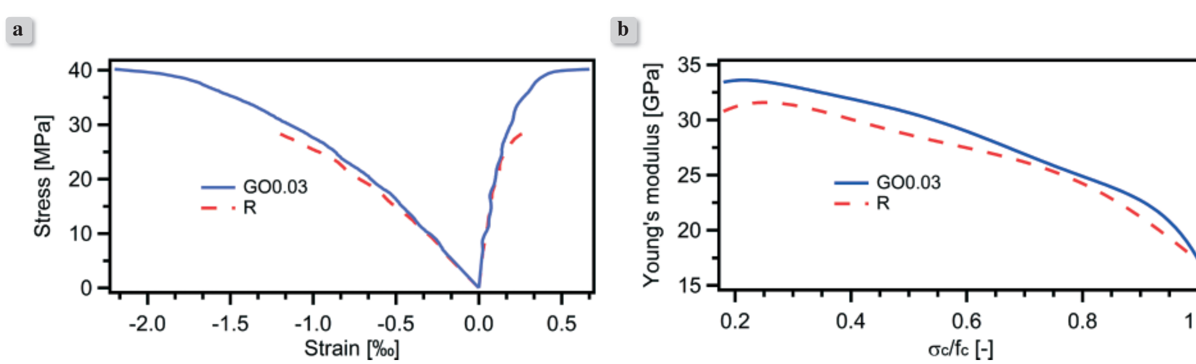

Figure 3.
Results of compression tests conducted on 60 x 120 mm cylindrical specimens.
a) Stress-strain curves and b) variability of Young's modulus values under increasing load [27]

Interestingly, further comparison of reference mortar and mortar with GO has revealed that these two types of mortar differ also visibly in the forms of damage of compressed cylindrical samples. In particular, the unique influence of GO addition was highly visible in samples cured for 7 days. The complete damage of reference mortar occurred rapidly in these specimens, while cracking and loosing of cement-GO mortar occurred only on sides of the samples showing the typical cone shape of damage. After 14 and 28 days of mortar hardening, the cone shape of damage is clearly noticeable in both cement mortar samples (Fig. 2b and c), yet the incorporation of GO has resulted in less rapid damage of the specimens.

The studies on the variability of cylindrical compressive strength in time were followed by tests in the uniaxial stress state using cylindrical samples with the height twice their width, that was 60×120 mm. In this case, the average compressive strength at the age of 28 days is improved by 28% (Tab. 4). Moreover, on the basis of strain gauges' measurements (Fig. 3a), the Young's modulus was determined for both types of cement mortar. The same trend in Young's modulus variability under increasing load can be observed for both mortars (Fig. 3b). However, the values for cement-GO mortar are slightly higher than those for reference mortar achieving the increase of 6% for the Young's modulus calculated according to PN-EN 1992-1-1:2008 as a secant value between zero stress and stress equal to 40% of the average compressive strength (see Tab. 4).

Table 4.
Results of the uniaxial cylindrical compressive strength and Young's modulus tests at the age of 28 days [27]

Sample	Parameters				
	Force [kN]	Strength [MPa]	Average strength [MPa] (increase)	Young's modulus [GPa]	Average Young's modulus value [GPa] (increase)
R	88.65	31.25	**32.12 (0%)**	30.61	**30.10 (0%)**
	95.69	33.84		28.74	
	87.20	30.74		27.16	
	101.12	35.76		32.75	
	81.74	28.91		31.24	
GO0.03	118.08	41.78	**41.18 (28%)**	31.52	**31.90 (6%)**
	113.10	40.02		30.63	
	115.02	40.70		30.43	
	120.45	42.62		33.23	
	115.30	40.78		33.69	

4. CONCLUSION

Cement mortar with the incorporation of 0.03 wt.% of graphene oxide has been fabricated to investigate the mechanical properties of produced nanocomposite. The addition of GO proved to enhance both the flexural and compressive strength of cement mortar. The increase up to 13%, 23% and 28% has been reported for the flexural, cubic compressive and uniaxial cylindrical compressive strength, respectively. The investigation of the variability of compressive strength in time has revealed that GO accelerates the cement hydration, in particular the early age hydration. Noteworthy, the significant improvement of mechanical properties has been achieved with simultaneous low material consumption. Such findings indicate the great potential of reinforcing cementitious composites with GO and represent a step forward towards practical applications of nanomaterials in civil engineering.

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