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Research Article

Influence of graphene oxide on mechanical and microstructural properties of cement composites

Ramamohana Reddy Bellum[1,a], Yaswanth K K[*,1,b], Chereddy Sonali Sri Durga[2,c], Chava Venkatesh[2,d], Sridevi G[3,e]

[1]*Dept. of Civil Engineering, Aditya University, Surampalem, Kakinada, India*
[2]*Dept. of Civil Engineering, CVR College of Engineering, Managalpalli, India*
[3]*Dept. of Electronics and Communication Engineering, Aditya University, Surampalem, Kakinada, India*

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Abstract

A new nanomaterial known as graphene oxide (GO) has been discovered, and it has the potential to improve the tensile and elongation properties of cement-based composites. In this study, the influence of the content of GO, say 0.01% increment upto 0.05% on fluidity of cement composites was estimated. In addition, the mechanical properties of GO-based cement composites, such as compressive, split tensile, and flexural strengths, are presented with respect to the content of GO to figure out its effect and to identify the right proportion. In this paper, the deformability studies of GO-based cement composites, such as the elastic modulus (E), are also presented. To further investigate the formation of a denser matrix, microstructural studies are also carried out in GO-based cement composites. New avenues for high performance cement composites are opened up by this important and extensive study. The results are revealed that the inclusion GO has shown reduced fluidity values as compared to control mix in all stages of hydration process. Results revealed that the optimum content of 0.04% of GO enhanced the flexural strength by 67.52% which is quite phenomenal. GO with 31.24% of oxygen helps improving the microstructure by enhancing the modulus of elasticity and toughness of the composite.

1. Introduction

Special structures like high rise buildings, marine structures, hydraulic structures, cross sea bridges and under water tunnels desperately require the need of high-performance concrete because of its frequent exposure to the attacks of salts and alkali and would become deteriorated [1]. "Constructing a high-performance structure with high-performance concrete necessitates the use of materials that have several advantages over conventional concrete, such as increased strength and durability as well as improved chloride-ion migration resistance as well as freeze and sulphate resistance" [2]. The excellent compressive and poor tensile or flexural strengths clearly reveals the fractured nature of the concrete. Cement and carbon-based materials are highly improvised by cutting edge technologies like carbon nanotubes, carbon black etc. [3]. Because of the peculiar advantage of smaller size and high specific surface area [4].

Graphene oxide (GO) belongs to the graphite family that has undergone a chemical oxidation process [5,6]. A more compacted core and an increased rate of hydration

*Corresponding author: yaswanthk@adityauniversity.in
[a]orcid.org/0000-0002-0040-5812; [b]orcid.org/0000-0001-5587-6024; [c]orcid.org/0000-0003-0942-9252; [d]orcid.org/0000-0003-0028-7702; [e]orcid.org/0000-0002-7884-3409
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response are the end results of the high concentration of O_2 functional groups in GO and the high specific surface area it provides. Because of the presence of oxygen groups, the GO can be dispersed in water, but this is not enough to scatter carbon nanoparticles in cement mortar. More importantly, GO's high aspect ratio makes it an excellent light absorber. A large volume of water, preventing the cement paste from hydration [7]. Generally, graphene materials show excellent mechanical properties and good matrix adhesion, because of which it is emerged as a promising nano material in concrete-based composites. Graphene was initially isolated from graphite intercalation compounds in 2004 [8], when it was described as a single, planar, 2D honey comb shaped carbon layer.

Some research claim that graphene oxide has no influence on the hydration of cement in any way shape or form and it implies that adding GO does not affect the hydration of the cement process in its composites as demonstrated by Horszczaruk et al [9]. A study using X Ray Diffraction (XRD) demonstrated that the crystal phases of the cement hydration process remained unchanged after the addition of GO. If claims are to be believed, GO's primary function may be to stimulate or compel the twisting and deflection of paste-related fissures. According to certain researchers, GO also inhibited the spread of microcracks in cement-based products. There appears to be a lack of research in this area, hence it is uncertain how graphene oxide strengthens cement-based composites [10,11]. Research has shown that GO can help cement composites increase their strength and ductility, setting the stage for further development of cement composites to make it long-lasting and high-performance. Research into the properties of GO incorporated cement composites is still in its early phases, limited in scope and focused on specifics Few research has examined the impact of key factors. When it comes to concrete Composites of GO and cement, for example, water to cement ratio (w/c) influences the concrete's properties. [12] The high surface area, surface functionalisation and significant dispersibility of graphene oxide (GO) in aqueous media make it a possible solution. This study examines the influence of GO w.r.t workability, consistency, microstructural properties (surface morphology) and mechanical properties (compression and flexural tests) of cement pastes. Additionally, the mechanism of the reinforcing and toughening effect is explained [13].

From the literatures it was revealed that, researchers tend to study the content of water in GO based cement mortars upon the fluidity test and also the effect of different particle sizes upon the mechanical properties [12]. Similarly, the hydration of the cement incorporated with GO was studied with the pore structure testing and thermogravimetric analysis. The fracture properties of cement pastes, both with low and high w/c ratios, were evaluated utilizing SEM observation of the GO-cement system's cement hydration products in various spatial situations. GO on cement-based materials was studied for its strengthening mechanism by comparing results from earlier investigations particularly with respect to the influence of its GO content upon the strength characteristics. The impact of polycarboxylate ether superplasticizer use and GO flakes dispersion on material strength are also investigated. Examining the microscopic structures of the cement mortar with and without GO, allows us to detect the graphene dispersion into the cement matrix [14,15].

GO has shown improvement in the strength and hardness of cement concrete, but its penetration into cement paste and concrete can have an adverse effect on their fluidity. The objective of this paper is to experiment the addition of graphene oxide w.r.t various properties of cement composites such as fluidity, mechanical, modulus of elasticity and durability properties. GO dispersion morphology and bonding into cement composites was also studied by conducting microstructural tests. This study is significant as graphene oxide can be incorporated into cement composites to improve toughness and reduce brittleness, which has a wide range of applications in water tight structures, impact resistant buildings, and structural components where ductility is required. GO dispersion in cement pore solution and the strength of GO incorporated cement mortar could be improved using this study's one-pot method, which has many potential practical applications.

2. Properties of Common Cement Composite and Concrete Nanofillers

Reinforcement materials for fibre reinforced concrete (FRC) have been systematically investigated [30]. Table 1 shows the parameters of different fillers used in cement composites/concrete. When referred to Ordinary Portland Cement (OPC), they have a higher tensile performances. Cement composites' tensile and flexure properties will be enhanced by adding the reinforcing material.

Table 1. Various properties of concrete nanofillers and cement composite

Ref	Material	Thickness/ Diameter (mm)	Density (kg/m^3)	Aspect ratio	Surface area (m^2/g)	Modulus of elasticity (GPa)	Tensile strength (GPa)	Elongati @ break (%)
[16, 17]	Graphene	~0.08	2200	6000–600000	2600	1000	~130	0.8
[18, 19]	GO	~0.67	1800	1500–45000	700–1500	23–42	~0.13	0.6
[20, 21]	CNTs	15–40	1330	1000–10000	70–400	950	11–63	12
[22, 23]	Carbon fiber	6000–20,000	1770	100–1000	0.134	7–400	0.4–5	1.7
[24, 25]	Polymeric fiber (Polypropylene and Nylon)	18,000–30,000	900	160–1000	0.225	3–5	0.3–0.9	18
[26, 27]	Glass fiber	5000–10,000	2540	600–1500	0.3	72	3.45	4.8
[28, 29]	Steel fiber	50,000–900,000	7800	45–80	0.02	200	1.5	3.2

Steel, glass, polymeric, or carbon microfibers have been employed widely in the previous decades to reinforce cement composite/concrete. Table 1 shows the material parameters of these objects, which range from 10 to 1000 aspect ratios, based on existing literature. Steel and concrete structures are routinely retrofitted with carbon fibre [23] due to the material's high modulus of elasticity (above 200 MPa) and tensile strength (3.5 GPa). With the added benefit of limiting the expansion fractures generated by alkali silicate reaction and steel bar corrosion, steel fibres exhibit comparable mechanical properties [28].

It is possible for glass fibres to improve cement's tensile and flexural strength because of their 72.4 GPa elastic modulus [26] and 3.45 MPa tensile strength. strong alkaline medium of OPC can be resisted by the surface treatments and the usage of high zirconia glass and achieve the aforementioned degree of improvement [26]. Mechanical properties can strengthen the fragile cementitious matrix even with polypropylene fibres with weak mechanical characteristics [27]. Cement matrix is strengthened by fibres, which carry a portion of the applied load and are also capable of crack and pore-bridging. Fibers must have a high aspect ratio and high inherent strength in order to provide reinforcement. Using microfibers as a bridging mechanism has increased the tensile strength and toughness. Microfibers have been shown to form a dense network of microcracks instead of large cracks, but they do not stop the initiation of cracks. Compressive strength is not influenced by the incorporation of microfibers into those material [39]. Furthermore, microfibers in the reinforced cement are a problem because they trap air voids and reduce the workability of the material. Carbon and polymer fibres can be functionalized to form bonds with the cement matrix, but their smaller surface area limits the strength [40]. Compared to traditional fibres, nanomaterials offer a better solution because they can be reinforced or modified at the nanoscale.

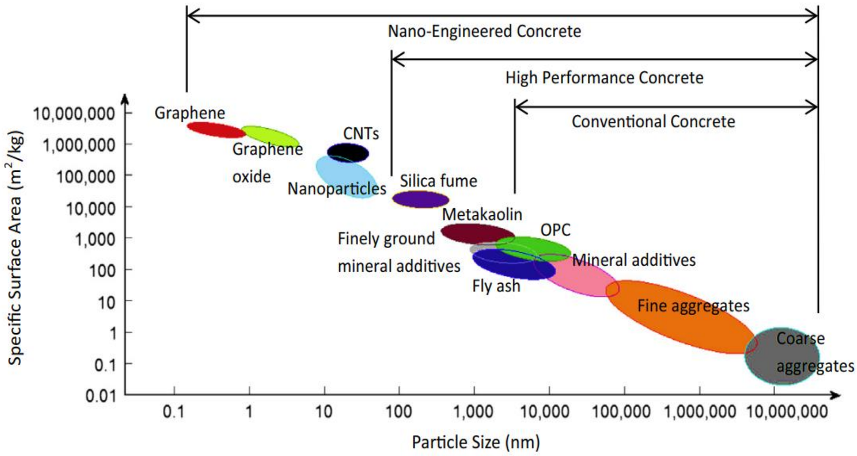

Fig. 1. Nanofillers versus additional cementitious materials in concrete [15]

Nanofillers can enhance the strength and durability of cement composites by using CNTs and GO as well as other nanoparticles. As illustrated in Fig. 1, their dimensions are comparable to the typical components of cement and concrete. Traditional concrete was traditionally held together by cement, which was considered the best ingredient for a strong bond between the aggregates. Supplementary cementitious ingredients like fly ash, slag and metakaolin were introduced after the demand for high performance concrete. Nanomaterials have been incorporated into cement based concrete composites due to advancements in nanotechnology [28,29]. Reinforcing the cement matrix at the nanoscale is expected to improve performance, due to the fact that the size of those particles is similar to the range to that of calcium silicate hydrate (C-S-H) gel.

When it comes to C–S–H nucleation, 2D GO has a higher surface area than even CNTs, which have been extensively studied [22-27]. As a result, GO nanomaterials are extremely reactive because of their vast surface area and numerous functional groups. The functionalization process would affect the mechanical characteristics of graphene as presented in [30]. To put it another way, graphene sheets have much higher mechanical strengths, such as tensile strength and modulus of elasticity, than those made of GO, in spite of the fact that cement has low tensile strength and elastic-modulus compared to GO-based cement composites. While nanoparticles have been shown to enhance hydration rates, nanofibers and 2D nanosheets have also been shown to strengthen the cement matrix due to their huge aspect ratios. As a result, even at extremely low concentrations of nanomaterial, the properties of nanocomposite can be developed. Nanocomposites' improved performance and unique functionality can be attributed to their surface effects rather than their bulk features. Nanomaterials' reactivity is boosted by their larger surface areas. Using these nanomaterials, the average diameter of C-S-H has been determined to be 5 nm [30]. The strength of cement is derived from its high specific surface area and, as a result, its ability to adhere to surfaces.

3. Experimental Programme

3.1 Materials

OPC 43 cement was used in the study according to ASTM C 150-19a [31] and is obtained from UltraTech Cements Limited, India. The specific gravity and blaine's surface area are 3.13 and 370m^2/ kg respectively. The specific surface area of GO is tested to be 0.122×10^7 m^2/kg. Locally available river sand is used as fine aggregate. Table 2 and 3 represents the chemical analysis test results of cement and GO respectively.

Table 2: Cement- chemical composition

Composition	SiO_2	CaO	Al_2O_3	Na_2O	Fe_2O_3	SO_3	K_2O	MgO	LOI	TiO_2
Cement	21.4	65.1	4.18	0.63	3.10	1.96	1.01	1.97	0.37	-

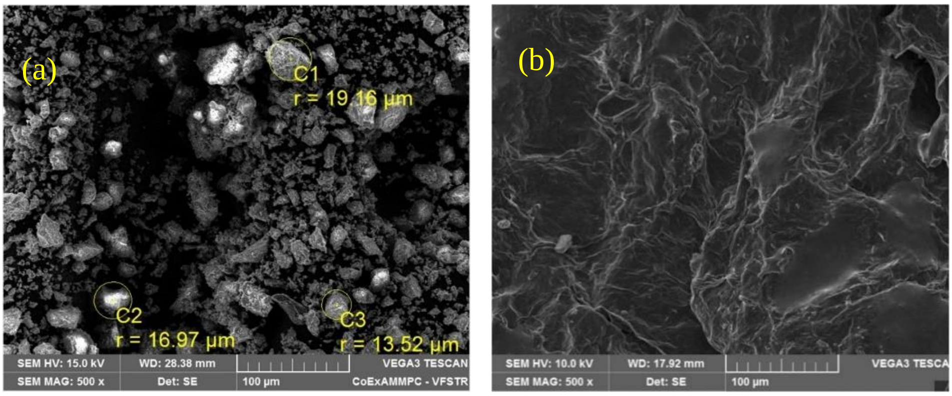

Fig. 2. SEM image, a) cement, b) graphene oxide

Table 3. Composition of GO

Material	C	O	SI	AI	S	MG
GO	66.41	28.95	1.78	0.68	1.67	0.51

Fig. 2 illustrates the SEM images of raw cement and GO where the spherical and irregular shape of particles can be observed (Fig. 2(a)). While the SEM image of GO represents that the particles are closely packed and a denser image was noticed from Fig. 2(b). The closely packed particles can have high specific surface area, that what the GO is called as nanofiller materials to pack the pores present in cement composites.

3.2 Mix calculations

In this work, samples were prepared using GO with the contents of 0%, 0.01%, 0.02%, 0.03%, 0.04% and 0.05%, w.r.t cement's weight. Table 4 presents the mix proportioning of

GO-based cement composites. The parameters of GO-based cement samples are compared using a single control mix (C). A control mix is used to compare samples of GO-based cement composites with those of the cement composite sample.

Table 4. Mix calculations (kg/m^3)

Mix id	Cement	GO (%)	Fine aggregate	Water
C	410	-	820	164
CG1	410	0.01	820	168
CG2	410	0.02	820	171
CG3	410	0.03	820	173
CG4	410	0.04	820	176
CG5	410	0.05	820	177

3.3 Dispersion of GO in Cement Samples

Cement composites can benefit greatly from the incorporation of GO into their formulation, but the process of dispersing graphene into water, which is particularly difficult due to the van der Waals force and the hydrophobic nature of GO, is also a challenge [32]. In case of improper dispersion of GO in cement matrix, it results in defects and the reinforcement terminology is affected [17]. Graphene dispersion in cement matrix has previously been accomplished using three different dispersion techniques viz., dry dispersion (with an electric concrete mixer for mixing), wet dispersion (using a surfactant with mechanical stirs); and another wet dispersion method which uses ultrasonic treatment along with surfactant and mechanical stirrer. Wet dispersion (without ultrasonic treatment) was used in this study due to the fact that this method produces more stronger reinforced composite as per the study [33]. With Graphene oxide to Dispersant ratio of 1:1.25 and ultrasonication time of 40 minutes and ultrasonic power and frequency of 200 W/30 kHz with polycarboxylic ether was used in the dispersion process of GO in cement composites.

3.4 Methods

3.4.1 Fluidity test

According to Indian National Standard IS 1199-1991 [34], the slump-flow of GO-reinforced cement was estimated. First step was to combine 300 g of cement, 100 g of H_2O, and 2 g of GO in a 2-minute mixing period. Then the combination was placed in the cone, which has the dimensions of 60mm, 36mm and 60mm as base diameter, top diameter and height respectively. This newly formed GO-based cement composite will crumble and spread as it is lifted 150 mm above its surface. The horizontal and vertical diameters of the spread were d_1 and d_2. The $(d_1 + d_2)/2$ value is the fluidity of the composite [35].

3.4.2 Water absorption

The cubes of size 70.6mm x 70.6mm were cast using cement composite and utilized to conduct the test in accordance with ASTM C1585-13 [36]. After that, specimens were allowed to cure in water for 28 days. Moisture content, if any, is eliminated by keeping the samples in hot air oven at 90°C for 24 hours. The samples were then weighed to determine their dry weight (W_1). Specimens were immediately preserved in water for 3-4 hours. The specimens were then weighed again, and the wet weight was taken into account (W_2). Average of three specimens were cast and tested for each mix for each curing day. Water absorption is calculated using the Eq (1);

$$Water\ absorption\ (\%) = \left[\frac{(W_2 - W_1)}{W_1}\right] X\ 100 \qquad (1)$$

3.4.3 Sorptivity

Sorptivity was measured by using the ASTM C1585-20 [37] standard test procedure. To produce GO-based cement composites for sorptivity test 70.6 mm samples were used, the average three samples sorptivity values were noted. When determining the sorptivity, Eq. 2 was utilised. Average of three specimens were cast and tested for each mix for each curing day.

$$\frac{i}{\sqrt{t}} = S \tag{2}$$

3.4.4 Mechanical Properties

GO-reinforced geopolymer composite compressive strength is measured using ASTM C109/C109M-20b [38] on 70.6 mm cube moulds. Conventional water saturation curing method was followed for all experimentations. Similarly, C1006M-20a [39] and ASTM C293M-16 [40] are used to determine flexural and split tensile strengths on the moulds 50 × 100 mm and 40 × 40 × 160 mm prism (third-point loading), respectively. Average of three specimens were cast and tested for each mix for each curing day.

3.4.5 Modulus of Elasticity

Disc specimens (size 50mmx100mm) made following ASTM C469/C469M -14 were used in this test [41]. Average of 3 specimens were cast and tested for each mix for each curing day. Fig. 3 shows the test setup of all experimentations in this research.

3.4.6 Microstructural Studies

Various microstructural studies including Scanning Electron Microscope (SEM), X-ray diffraction analysis (XRD) and Energy Dispersive X-ray analysis (EDAX) were considered. Broken samples were carefully prepared and subjected to SEM test and similarly the powdered matrix samples were adopted for the XRD analysis such that the influence of GO can be clearly subjected to the test. The chemical elements and the chemical compounds of the hardened matrix materials were analyzed using the EDAX.

(a) (b)

(c)

(d)

(e)

Fig. 3. Experimental setups (a) fluidity test, (b) sorptivity test, (c) compression test, (d) splitting tensile test, and (e) flexural test

4. Result and Discussions

4.1 Fluidity

Fig. 4 presents the fluidity of GO-based cement composite samples. Higher fluidity reduction was observed in the mix CG5 with the inclusion of 0.05 wt% of GO. It was clear that the addition of GO in cement samples has showed in improved hardness and toughness properties, this was one of the major reasons for decrease in the fluidity. Fluidity decreased by 11.16, 10.71, 9.04, 12.78, and 9.38 % for mix CG1 compared to control mixture over various hydration times of 5, 30, 60, 90, and 120 min, respectively. While in the mix CG2 it was decreased by 16.26, 19.39, 15.25, 16.86, and 18.75 % in different hydration periods such as 5, 30, 60, 90, and 120 min, respectively. A huge decrease in the fluidity was observed due to the increase in the GO from 0.01 to 0.05%. The decreased fluidity values were 38.60, 38.87, 39.55, 44.77 and 48.75% for the hydration times of 5, 30, 60, 90 and 120 min, respectively as compared to reference mix. These values are clear that involvement of GO has shown negativity in the improvement of workability of the cement composites. The reason behind the decrement in the fluidity of GO-based cement composites is that the GO is one of the nanomaterials which will help to fill the pore-spaces between the cement particles and enhances the hardening time, so the fluidity of the fresh composites was decreased with the increase in hydration time as well as increase in the GO content.

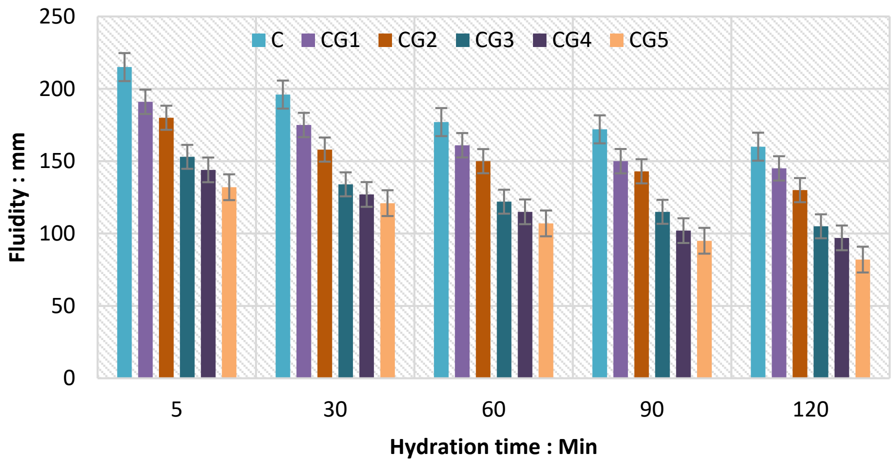

Fig. 4. Fluidity of GO-based cement composites

4.2 Water absorption

Fig. 5 depicts the influence of GO on the water absorption percentage of the composites. According to the findings, the inclusion of small amounts of GO had a vital impact on the water absorption of cement samples.

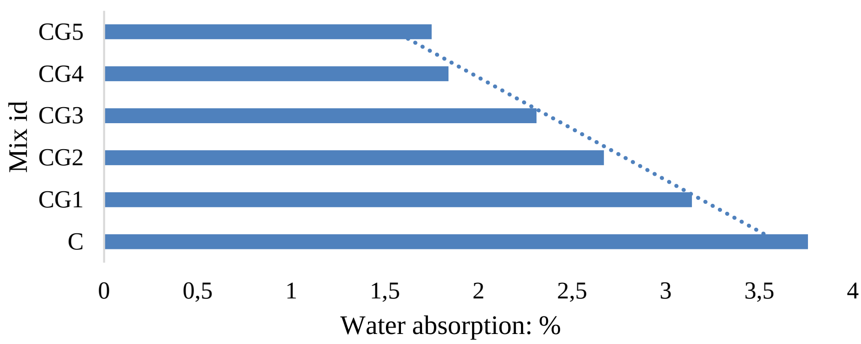

Fig. 5. Water absorption of GO-based cement composites

However, as the amount of GO in cement samples increased, water absorption decreased dramatically. This demonstrates that the inclusion of GO reduces the pore percentage in the composites. The water absorption percentage values for various levels of GO in cement composites mixes CG1, CG2, CG3, CG4 and CG5 are 3.14, 2.67, 2.31, 1.84 and 1.75%, respectively.

4.3 Sorptivity

It can be observed in Fig. 6 that the water sorptivity of GO-based samples is the lowest. Information of this sort indicated that capillary forces of 0.05 w/w % of GO samples shown lowest water permeability into cement samples. There is a reduction in the amount of water carried by samples of GO-based cement compared to other GO replacement samples. This empirical evidence demonstrates that cement samples fortified with GO have greater resistance to water penetration. The inclusion of GO to cement composites, however, has been shown to improve microstructure parameters in terms of porosity, water absorption, and sorptivity. All five GO-based cement composite mixes (CG1, CG2, CG3, CG4, and CG5) have different sorptivity values: 0.133, 0.097, 0.068, 0.045, and 0.038. These numbers are extremely low in comparison to the control mixture. This is quite similar to research carried by Devi et al [42], as they revealed 0.08% reduces the sorptivity by 46%.

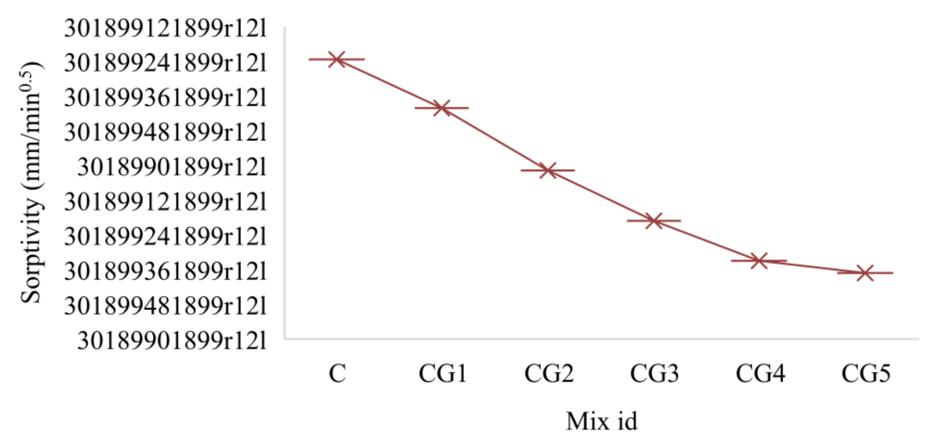

Fig. 6. Sorptivity values of GO-based cement composites

4.4 Compressive Strength

Nanomaterials, such as graphene, nanofibers, nano-silica, or nano-clay, have the potential to increase mechanical qualities because of their huge surface area. Higher efficiency during the early stages w.r.t the mechanical properties are evidence of the usefulness of nanoparticles in promoting the development of tensile and compressive strengths [43]. Cement composites benefit from the GO's particular properties, such as its surface roughness and functional group. As small as 0.05% w/w GO boosts the compressive strength to 51 % [44]. Fig. 7 depicts the test results of GO-based cement composites under different water curing. It was found that adding GO up to 0.04 wt.% increased compressive strength in the experiments. The strength of samples was reduced as the GO level was increased further. The samples with 0.04 w/w % GO doses at 28 days curing had a 27.26 % increment in compressive strength than the samples without GO. As demonstrated in Fig. 7, the compressive strength of cement composite with 0.05 w/w % of GO dose at 28 days of curing increased by 24.63 %. It was clear that the optimum inclusion of GO in the cement samples is limited to 0.04%. However, the microstructural studies are indicated that the inclusion of GO has shown greater impact in the formation of denser structure and leads to good compressive strength compared to reference mix.

GO blended cement samples had an impressive impact on strength properties, as the results of the experiments showed. On the other hand, GO inclusion showed altered microstructure, with the denser structure showing improved mechanical properties being achieved. Similar studies were made by Devi et al [42] and Reddy et al [45], where Devi et al have used the dosage of 0.02% increment upto 0.08% and Reddy et al have used 0.25% increment. In all these literatures, the experimental parameter was to identify the right content of GO oxide towards various properties of concrete. Reddy et al revealed that inclusion of 0.1% of GO was best and it has improved upto 38.46% towards compressive strength. similarly, Sharma et al [46] revealed 1% inclusion of GO improved upto 85% in compressive strength. this study showed up to 28% improvement when 0.05% GO is used which is highly economical and efficient.

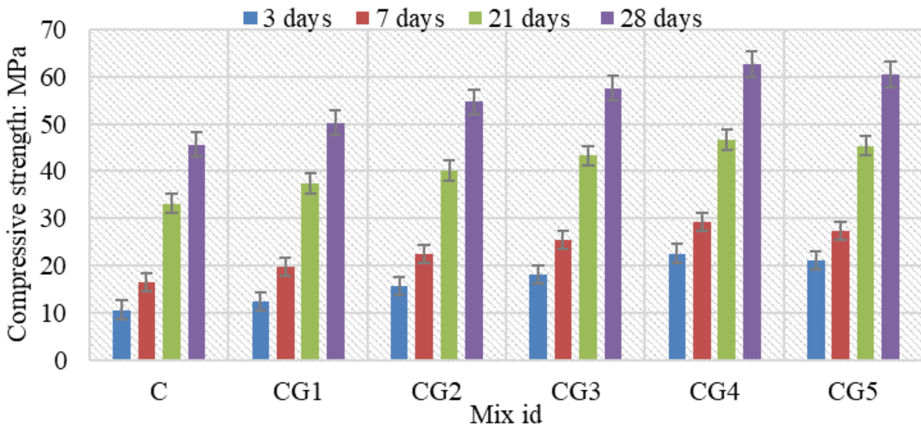

Fig. 7. Compressive strength of GO-based cement composites

4.5 Splitting Tensile Strength

Fig. 8 enumerates the splitting tensile results of GO-based composites. The presence of GO in samples has shown different morphology. However, it was clear that the inclusion GO up to 0.04 wt.% the tensile properties were enhanced gradually while further increase in the GO contents the tensile properties were reduced. The microstructural modifications were also observed in the GO-based cement samples such as identification of better C-S-H gel formation, wrinkle morphology, denser structure and interlocking of particles.

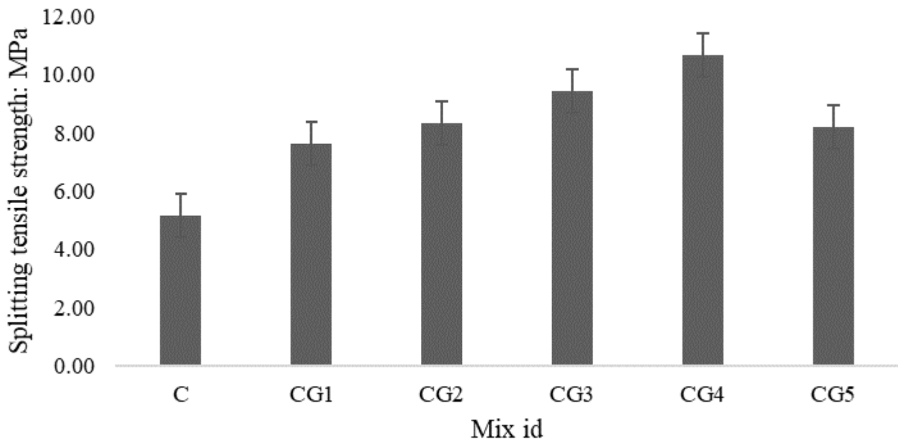

Fig. 8. Splitting tensile strength of GO-based cement composites

The samples with 0.04 w/w % GO doses at the age of 28 days had 51.59 % increase in splitting tensile strength than the reference mix. As demonstrated in Fig. 8, split tensile strength of samples with 0.05 w/w % of GO dose at 28 days of water curing increased by 36.95%. It was clear that the optimum inclusion of GO in cement samples is limited to 0.04 wt.% in order to improve the tensile properties. It was clear that the inclusion of GO has shown impact in the improvement of splitting tensile strength than the compressive strength. Graphene oxide (GO) of 0.04 wt. % with O_2 content of 28.95 % was found to give cement composites their toughness, according to the results. The micro-structural condition of hydration crystals in those proposed composites has a major impact on mechanical properties.

Similar studies like Devi et al [42] also insisted that higher content of GO does not adhere the tensile properties and they revealed that 0.03% improved the tensile strength by 45%. Similar results were observed in this study as 0.04% was identified to be the most optimum with 51.59% enhancement.

4.6 Flexural Strength

The flexural strength of GO-based cement samples was presented in Fig. 9. Better flexural strength has been achieved with the addition of GO to cement samples of varying microstructural morphology. However, it was evident that the bending properties were gradually improved by the inclusion of GO up to 0.04 wt.%, but were weakened by further increase in the GO content. Better C-S-H gel formation, wrinkle morphology, a denser structure, and particle interlocking were majority of the microstructural changes seen in the GO-based cement samples compared to control mix. This will create more CSH gel and enhances the absorption capacity, and nano-filler effect makes the cement matrix more compact and refined by filling. These are the major reasons for better enhancement in the flexural properties of GO-based composites.

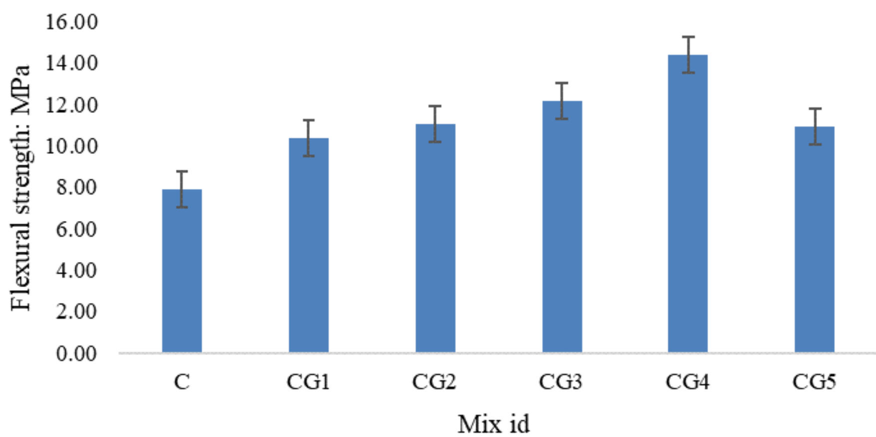

Fig. 9. Flexural strength of mixes

Whereas, increase in the GO content also increases the flexural strength. The inclusion of 0.01, 0.02, 0.03 and 0.04 wt.% of GO in cement composites enhances the strength percentage as 23.88, 28.57, 35.19 and 45.23%, respectively than the reference mix. However, further increment in the GO the reduces the strength. Fig. 9 shows that after 28 days of water curing, the splitting tensile strength of a cement composite with a 0.05 wt.% GO dose is 27.77% higher than it was with no GO addition. This value is lower than that seen with the inclusion of 0.04 w/w% of GO-based samples. This is similar to studies like

Reddy et al [45] where it revealed that 0.1% GO improve the flexural strength by 12.07%. It was observed that the GO nano particle fills the minute pores of the microstructure making it denser thereby showing improvement in tensile and flexural properties, however researchers suggest to figure the optimum content which may depend on other material properties.

4.7 Modulus of Elasticity

The modulus of elasticity results are depicted in Table 5. The addition of GO to cement composites improved the modulus of elasticity. After 28 days, the mixes CG1,CG2,CG3,CG4, and CG5 mixes showed 35.83, 36.57, 38.75, 40.12, and 37.48 GPa, respectively; the control mix was 34.41 GPa. Cement based samples containing 0.04 wt% GO had the highest elastic modulus, whereas samples containing 0.01 or 0.02% GO had the lowest elastic modulus values. As the GO content in the samples increases by 0.04 wt%, the modulus of elasticity decreased. When up to 0.04 wt% GO was added to cement composites under conventional water curing conditions, parameters are improved. The experiments revealed that the inclusion of GO improved the elastic modulus than the control mix. Certain codes and literatures recommended to predict the young's modulus which are as follows,

- As per ACI 318-14 [47], the young's modulus can be calculated using Eq. (3).

$$E_C = 0.043 \times \rho^{1.5} \times \sqrt{f'c} \quad (3)$$

Where, f'c = Characteristic compressive strength (MPa); E_c = Modulus of elasticity (MPa); f_c = Avg 28-day compressive strength in MPa, ρ = Density of concrete (kg/m³);

- Eq. (4) can be used to calculate the elasticity modulus in accordance with AS 3600 [48].

$$E_C = \rho^{1.5}(0.02430\sqrt{f'c} + 0.12) \quad (4)$$

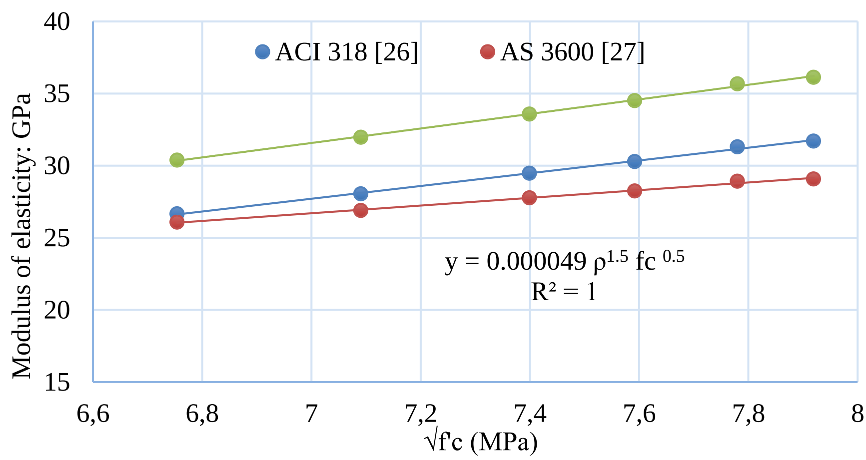

Fig. 10. Predicted modulus of elasticity of GO-based cement composites

Eq. (5) shows the calculation methodology of GO based composites with respect to experimental value of compressive strength. Fig: 10 shows the model of predicting the young's modulus of GO added cement mortar samples which can be anticipated after 28 days of water curing.

$$E_C = 0.000049 \times \rho^{1.5} \times \sqrt{fc} \tag{5}$$

Table 5 shows the elastic modulus of the cement samples as per the codal provisions and this paper. At 0.04 weight percent, the GO-based cement composite samples had a higher modulus of elasticity than the control mix.

Table 5. Experimental and predicted modulus of elasticity values

Mix id	Compressive Strength (MPa)	Density (Kg/m^3)	Modulus of Elasticity (E_c) GPa			
			Experimental (28 days), GPa	ACI 318 [26]	AS 3600 [27]	Present paper
C	45.62	2035	34.41	26.66	26.08	30.38
CG1	50.28	2038	35.83	28.05	26.89	31.97
CG2	54.75	2047	36.57	29.47	27.77	33.58
CG3	57.64	2049	38.75	30.28	28.24	34.50
CG4	62.72	2054	40.12	31.70	29.08	36.12
CG5	60.53	2061	37.48	31.30	28.92	35.67

4.8 X-Ray Diffraction

The XRD peaks indicate that the hydration crystals contained hydration products like AFt, AFm, C-H and C-S--H, and that count on those could be enhanced by increasing the hydration duration, as per Fig. 11. The peaks of CH in each sample were nearly identical; this could be because GO mostly promoted hydration in the early stages. The development of hydration crystals with respect to GO doses revealed that GO may affect the hydration process, marked impact on the mechanical parameters of the cement mortar was framed by the acquired data. The addition of 0.04 wt% of GO has shown better formation of C-S-H gel. This proves that the inclusion of GO in cement composites produces enriched hydration products and steady matrix. These are the additional characters in the improvement of mechanical properties for GO-based cement samples.

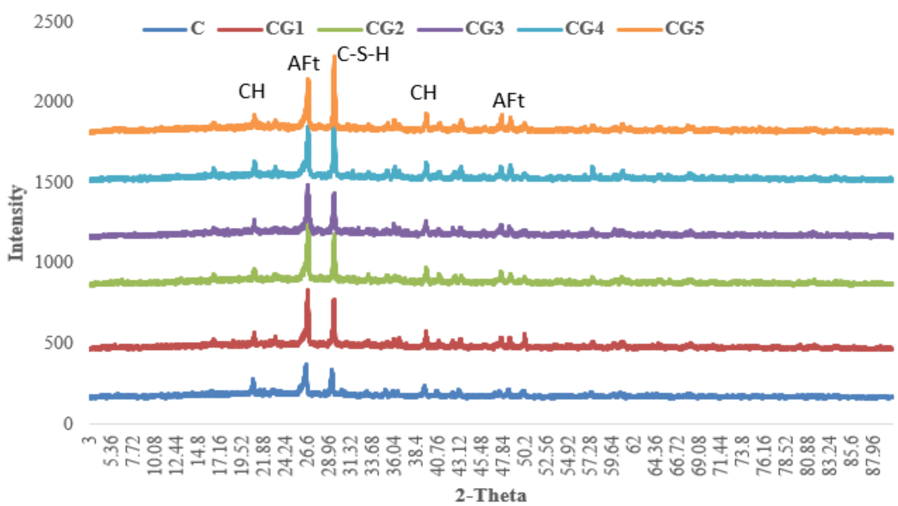

Fig. 11. XRD analysis of GO reinforced cement mixtures

4.9 Scanning Electron Microscope

When it comes to cement composites, the microstructural condition of the hydration crystals is most important for improving mechanical and durability properties [49,50]. It was found through the SEM images that the oxygen functional groups on GO's nanoparticle surfaces react with one another to form C-S-H and CH nano-hydration crystals as well as AFt and AFm hydration crystals. To make dense compacted structures, the hydration crystals can eventually grow and fill in the gaps, which enhances the toughness of cement composites magnificently in the presence of GO. A GO-based cement composite is likely to have better mechanical and durability properties as a result of its incorporation [51].

When GO is incorporated into cement composites, interlinked dense structure is appeared as hydration crystals, as shown in Fig. 12. As a result, at a GO content of 0.01 %, only a weaker C-S-H gel is formed. However, at 0.02 % and 0.03 % of GO content, a medium range of hydration crystal formations were observed, and at 0.04 %, increased gel forms and good dispersion were achieved, allowing the GO to be distributed in a similar pattern in the voids of cement composites.

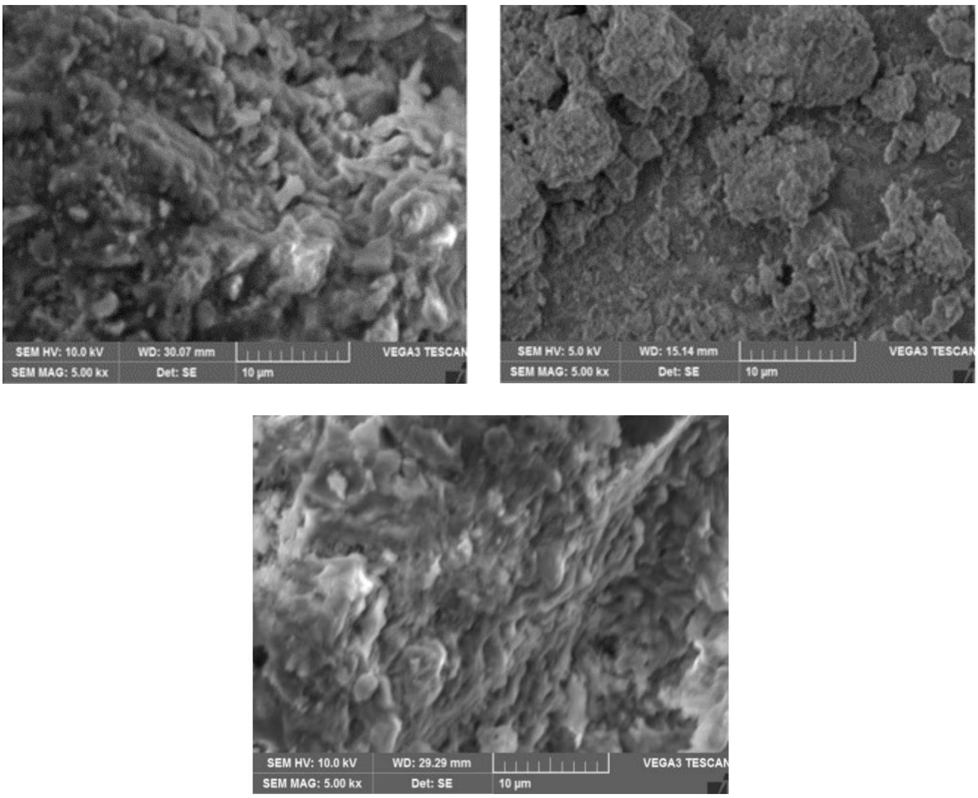

Fig. 12. SEM images of GO-based cement composites, (a) mix-C, (b) mix-CG1 and (c) mix-CG5

With an increase in the GO content, SEM pictures show that the cumulative volume of pores reduced. The cement mortar's pore volume has reduced significantly since the GO was added. furthermore, GO plays an important role in the increasing of hardening time.

4.10 Cost analysis

The cost analysis of the graphene oxide has been compared with other nano materials to check the efficiency and the benefit of the utilization of GO in cementitious materials and presented in Fig. 13. It was observed from the figure that, compared to popular nano materials like nano silica, nano iron oxide etc., GO is considered to be very much cost efficient. The cost of GO is almost similar to Nano alumina and it is 50% less than that of Nano iron oxide. Further, GO is 5 times cost effective than nano silica. Apart from other nano materials, the most expensive one is the carbon nano tubes which is about 200 times to that of other common nano materials. However, it is also to be analyzed that the quantity of GO required for effective utilization is very small compared to other nano materials.

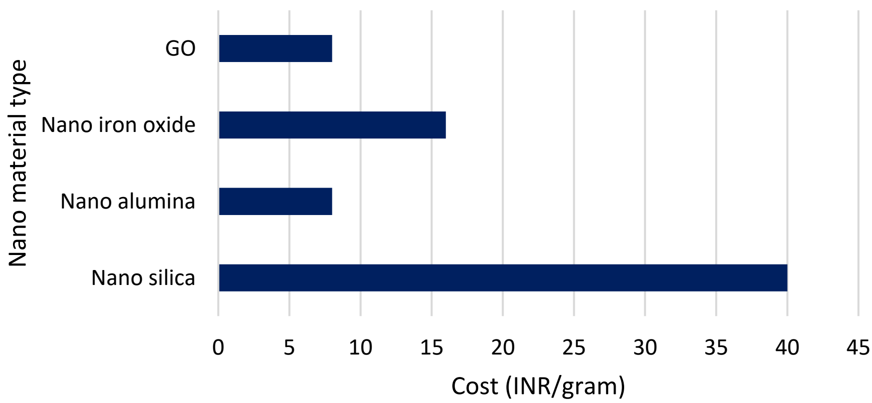

Fig. 13. Cost comparison of different nano materials in concrete

Conclusions

This paper attempted to use GO in cement-based composites with respect to mechanical and microstructural properties. Based on the several experimentations, the following conclusions are made.

- By separating calcium ions adhering to graphene oxide nanosheets, 0.04 wt % of GO was found to improve dispersion of GO, which prevented graphene oxide nanosheet aggregation in cement paste.
- Increase in GO reduces the fluidity of the samples. This clearly indicates the GO helps in improving the hydration process.
- The GO densifies the internal microstructure thereby water absorption and sorptivity is reduced. This relies the addition of GO minimizes the pore structure which also increases the durability.
- At a graphene oxide concentration of 0.04%, flexural strength increased by 67.52%, while at a concentration of 0.05%, cement composites improved by 50.21% after 28 days when compared to the control mix.
- The microstructure of hydration crystals in cement composite was modified by adding GO with a content of 31.24% oxygen, increasing the cement composite's modulus of elasticity and toughness.

- When graphene oxide was added, the hydration crystals were altered and the toughness of the composites increased, resulting in an overall improvement in their toughness.

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References

[1] Tang J H, Cai J W, Zhou M K. The status of researching and developing in high performance concrete. Science and Technology of Overseas Building Materials, 2006,27 (3): 11-15.
[2] Sun M, Liu Q, Li Z, et al. A study of piezoelectric properties of carbon fiber reinforced concrete and plain cement paste during dynamic loading. Cement and Concrete Research, 2000, 30(10):1593-1595. https://doi.org/10.1016/S0008-8846(00)00338-0
[3] Rawat, G., Gandhi, S. & Murthy, Y.I. Strength and rheological aspects of concrete containing nano-titanium dioxide. Asian J Civ Eng. 2022; 23: 1197-1208 . https://doi.org/10.1007/s42107-022-00476-2
[4] Pathak, S.S., Vesmawala, G.R. Influence of Nano-TiO2 and water to cement ratio on fracture parameters of concrete. Asian J Civ Eng. 2023; 24: 1969-1979. https://doi.org/10.1007/s42107-023-00616-2
[5] Hou Y G, Lv S H, Liu L P, Liu X. High-quality preparation of graphene oxide via the Hummers' method: Understanding the roles of the intercalator, oxidant, and graphite particle size. Ceramics International, 2020, 46(2): 2392-2402. https://doi.org/10.1016/j.ceramint.2019.09.231
[6] Liu, J., Zhao, L., Chang, F. et al. Mechanical properties and microstructure of multilayer graphene oxide cement mortar. Front. Struct. Civ. Eng. 2021; 15: 1058-1070. https://doi.org/10.1007/s11709-021-0747-3
[7] Babak, F, Abolfazl, H, Alimorad, R, et al. Preparation and mechanical properties of graphene oxide: cement nanocomposites. The Scientific World Journal 2014; 276323. https://doi.org/10.1155/2014/276323
[8] Singh, V., Joung, D., Zhai, L., Das, S., Khondaker, S. I. & Seal, S. Graphene based materials: Past, present and future. Progress in Materials Science. 20211; 56: 1178-1271. https://doi.org/10.1016/j.pmatsci.2011.03.003
[9] Horszczaruk, E.; Mijowska, E.; Kalenczuk, R.J.; Aleksandrzak, M.; Mijowska, S. Nanocomposite of cement/graphene oxide-Impact on hydration kinetics and Young's modulus. Constr. Build. Mater. 2015, 78, 234-242. https://doi.org/10.1016/j.conbuildmat.2014.12.009
[10] B. Wang, D. Shuang, Effect of graphene nanoplatelets on the properties, pore structure and microstructure of cement composites, Mater. Exp. 2018; 8(5): 407-416. https://doi.org/10.1166/mex.2018.1447
[11] W.J.Long J.J wei.H. Ma. F. Xing, Dynamic mechanical properties and microstructure of grapheme oxide nanosheets reinforced cement composites, Nano materials. 2017; 7(12): 407. https://doi.org/10.3390/nano7120407
[12] Alla, S., Asadi, S. Investigation on fluidity, microstructure, mechanical and durability properties of snail shell-based graphene oxide cement composite material. Asian J Civ Eng. 2023; 24: 189-204. https://doi.org/10.1007/s42107-022-00497-x
[13] Yang Y G, Chen Ch M, Wen Y F, et al. Oxidized graphene and graphene based polymer composites. New Carbon Materials, 2008, 23(3): 193-200.

[14] Wang, B.; Jiang, R.; Wu, Z. Investigation of the mechanical properties and microstructure of graphene nanoplatelet-cement composite. Nanomaterials 2016; 6: 200. https://doi.org/10.3390/nano6110200
[15] Sobolev K, Gutierrez MF. How nanotechnology can change the concrete world. Am Ceram Soc Bull 2005;84(11):16-9.
[16] Lee C et al. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science 2008;321(5887):385-8. https://doi.org/10.1126/science.1157996
[17] Stankovich S et al. Graphene-based composite materials. Nature 2006;442(7100):282-286. https://doi.org/10.1038/nature04969
[18] Zhu Y et al. Graphene and graphene oxide: synthesis, properties, and applications. Adv Mater 2010;22(35):3906-24. https://doi.org/10.1002/adma.201001068
[19] Dikin DA et al. Preparation and characterization of graphene oxide paper. Nature 2007; 448:457-60. https://doi.org/10.1038/nature06016
[20] Yu M-F et al. Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. Science 2000;287(5453):637-40. https://doi.org/10.1126/science.287.5453.637
[21] Peigney A et al. Specific surface area of carbon nanotubes and bundles of carbon nanotubes. Carbon 2001;39(4):507-14. https://doi.org/10.1016/S0008-6223(00)00155-X
[22] Li VC, Obla KH. Effect of fiber length variation on tensile properties of carbonfiber cement composites. Compos Eng 1994;4(9):947-64. https://doi.org/10.1016/0961-9526(94)90037-X
[23] Banthia N, Djeridane S, Pigeon M. Electrical resistivity of carbon and steel micro-fiber reinforced cements. Cem Concr Res 1992;22(5):804-14. https://doi.org/10.1016/0008-8846(92)90104-4
[24] Wang Y, Li VC, Backer S. Tensile properties of synthetic fiber reinforced mortar. Cem Concr Compos 1990;12(1):29-40. https://doi.org/10.1016/0958-9465(90)90033-T
[25] Pelisser F et al. Effect of the addition of synthetic fibers to concrete thin slabs on plastic shrinkage cracking. Constr Build Mater 2010;24(11):2171-6. https://doi.org/10.1016/j.conbuildmat.2010.04.041
[26] Benmokrane B, Chaallal O, Masmoudi R. Glass fibre reinforced plastic (GFRP) rebars for concrete structures. Constr Build Mater 1995;9(6):353-64. https://doi.org/10.1016/0950-0618(95)00048-8
[27] Trens P, Denoyel R, Guilloteau E. Evolution of surface composition, porosity, and surface area of glass fibers in a moist atmosphere. Langmuir 1996;12(5):1245-50. https://doi.org/10.1021/la950531e
[28] Yao W, Li J, Wu K. Mechanical properties of hybrid fiber-reinforced concrete at low fiber volume fraction. Cem Concr Res 2003;33(1):27-30. https://doi.org/10.1016/S0008-8846(02)00913-4
[29] Yazici S, Inan G, Tabak V. Effect of aspect ratio and volume fraction of steel fiber on the mechanical properties of SFRC. Constr Build Mater 2007;21(6):1250-3. https://doi.org/10.1016/j.conbuildmat.2006.05.025
[30] Samuel Chuah, Zhu Pan, Jay G. Sanjayan, Chien Ming Wang, Wen Hui Duan. Nano reinforced cement and concrete composites and new perspective from graphene oxide. Construction and Building Materials. 2014: 73; 113-124. https://doi.org/10.1016/j.conbuildmat.2014.09.040
[31] ASTM C150/C150M-19a, Standard Specification for Portland Cement, www.astm.org.
[32] H. Du, S. Dai Pang, Dispersion and stability of graphene nanoplatelet in water and its influence on cement composites, Constr. Build. Mater. 2018; 167: 403- 413. https://doi.org/10.1016/j.conbuildmat.2018.02.046
[33] H. Sixuan, Multifunctional graphite nanoplatelets (GNP) reinforced cementitious composites, National University of Singapore, Singapore, 2012. Master's Theses.

[34] IS 1199- 1991: Methods of sampling and analysis of concrete, Bureau of Indian Standards manak bhavan, 9 bahadur shah zafar maro, new delhi-110002.
[35] M. Ilg, J. Plank, A novel kind of concrete superplasticizer based on lignite graft copolymers, Cem. Concr. Res. 2016; 79: 123-130. https://doi.org/10.1016/j.cemconres.2015.09.004
[36] ASTM C1585-13, Standard Test Method for Measurement of Rate of Absorption of Water by HydraulicCement Concretes, www.astm.org.
[37] ASTM C1585-20, Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes.
[38] ASTM C109/C109M-20b Standard Test Method for Compressive Strength of Hydraulic Cement Mortars, 2020, www.astm.org.
[39] ASTM C1006 / C1006M-20a, Standard Test Method for Splitting Tensile Strength of Masonry Units, ASTM International, West Conshohocken, PA, 2020, www.astm.org.
[40] ASTM C293 / C293M-16, Standard Test Method for Flexural Strength of Concrete (Using Simple Beam With Center-Point Loading), ASTM International, West Conshohocken, PA, 2016, www.astm.org.
[41] ASTM C469 / C469M-14, Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression, ASTM International, West Conshohocken, PA, 2014.
[42] Devi, S.C., Khan, R.A. Effect of graphene oxide on mechanical and durability performance of concrete. Journal of Building Engineering. 2020; 27: 101007. https://doi.org/10.1016/j.jobe.2019.101007
[43] Vera-Agullo J et al., Mortar and concrete reinforced with nanomaterials, in nanotechnology in construction, vol. 3. Springer; 2009. p. 383-388. https://doi.org/10.1007/978-3-642-00980-8_52
[44] Makar J. The effect of SWCNT and other nanomaterials on cement hydration and reinforcement in nanotechnology in civil infrastructure. Springer; 2011. p. 103-130. https://doi.org/10.1007/978-3-642-16657-0_4
[45] Reddy, P. V. R. K., & Ravi Prasad, D. Graphene oxide reinforced cement concrete-a study on mechanical, durability and microstructure characteristics. Fullerenes, Nanotubes and Carbon Nanostructures. 2023; 31(3): 255-265. https://doi.org/10.1080/1536383X.2022.2141231
[46] Sharma, S., & Kothiyal, N. C. Influence of graphene oxide as dispersed phase in cement mortar matrix in defining the crystal patterns of cement hydrates and its effect on mechanical, microstructural and crystallization properties. Rsc Advances. 2015; 5(65): 52642-52657. https://doi.org/10.1039/C5RA08078A
[47] ACI 318-14, Building Code Requirements for Structural Concrete and Commentary, American Concrete Institute, Farmington Hills, MI 48331, U.S. A., 2014.
[48] AS 3600-2009, Reinforced Concrete Design, Cement Concrete and Aggregates Australia, Australian Standards, GPO Box 476 Sydney NSW 2001.
[49] Yaswanth, K. K., Reddy, K. H. K., Anusha, N., Praveen, B., Chippymol, J., Revathy, J., & Isleem, H. F. Engineered geopolymer composites: a comprehensive state-of-the-art review on materials' perspective. Archives of Civil and Mechanical Engineering. 2024; 24(3): 193. https://doi.org/10.1007/s43452-024-01007-3
[50] Kuppusamy, Y., Jayaseelan, R., Pandulu, G., Sathish Kumar, V., Murali, G., Dixit, S., & Vatin, N. I. Artificial neural network with a cross-validation technique to predict the material design of eco-friendly engineered geopolymer composites. Materials. 2022 15(10); 3443. https://doi.org/10.3390/ma15103443
[51] H. Du, H.J. Gao, S. Dai Pang, Improvement in concrete resistance against water and chloride ingress by adding graphene nanoplatelet, Cem. Concr. Res. 83 (2016) 114-123. https://doi.org/10.1016/j.cemconres.2016.02.005