Significance of GOs, GNPs and CNTs' Nanomaterials on the Mechanical Properties of Cement

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Abstract

This study reports the statistical significance of using Graphene Oxides (GOs), Graphene Nanoplatelets (GNPs) and Carbon Nanotubes (CNTs) on the mechanical properties of cement paste. Samples containing several nanoparticles' weight fractions were prepared and tested for flexure and compression. The testing results were then statistically analysed using the t-statistical method to investigate the significance of using Nanomaterials on the properties of cement paste. The results highlighted the significance of using GOs and CNTs on the flexural strength of cement paste. Mixes containing 0.04% GOs, 0.08% GOs and 0.12% CNTs could enhance the flexural strength by at least 45% compared to the plain control mix. On the other hand, test results showed the significance of using 0.04% GNPs, 0.08% CNTs and 0.12 % GOs in increasing the compressive strength of cement paste by at least 10% compared to the plain control mix. Microstructural analysis using Scanning Electron Microscope (SEM) showed that proper Nanofilaments dispersion in most batches. Furthermore, the analysis highlighted the nanoparticles' impediment within the cement hydration products.

Keywords: Graphene Oxides; Cementitious Nanoparticles; Nano concrete; t-statistical analysis

1 Introduction

In recent years, Nano-inclusions have been given great interest for their use in building materials due to their exceptional thermo-physical, electrical, chemical, and mechanical properties at the Nanoscale (Balaguru & Chong, 2006). In the construction field, Carbon Nanotubes (CNTs), Graphene

Nanoplatelets (GNPs), and Graphene Oxide (GO) are the most promising Nanofillers used to develop concrete, cement mortar, and cement paste with high mechanical performance and smart characteristics. This is due to their unique properties, as each of CNTs, GNPs, and GO possess excellent mechanical properties, high tensile strength, and Young's modulus (Liu et al., 2012; Salvetat et al., 1999; Shen et al., 2013), as well as thermal and electrical conductivity. However, they all differ in structure. CNTs are 1D tubes of carbon with nanoscale diameters and a large aspect ratio (length-to-diameter ratio) (Iijima, 1991). While GNPs are made from a series of parallel 2D graphene sheets of approximately 0.7-100 Nano-meters variation in thickness (Suárez & Prolongo, 2020). On the other hand, GOs is a 2D Nanosheet of highly oxidized carbon atoms decorated with oxygen-containing functional groups on its edges and basal plane (Wang et al., 2010). A literature survey has indicated that incorporating a small dosage of CNTs, GNPs, or GO effectively improves the cement matrix's mechanical properties (Baomin & Shuang, 2019; Mohsen et al., 2017; Yang et al., 2017). No study has reported the best Nanomaterial to achieve the highest cement paste's mechanical properties. This study investigates the significance of using CNTs, GNPs and GOs on the flexural and compressive strength of cement paste.

2 Research Methodology

In this study, three types of Nanoparticles, CNTs, GNPs, and GOs, were added to the cement paste using three weight fractions of 0.04%, 0.08%, and 0.12% Nanofiller-to-cement weight. Table 1 provides a summary of the experimental design including the test groups, prepared batches, types of Nano-inclusions and weight fractions. The testing methodology consisted of preparing and testing hardened samples for flexure and compression after 90 days of curing. Then analysing the results statistically using the t-test method to report the significance of every group combination. Finally, the microstructure of the fractured samples was inspected using a scanning electron microscope (SEM).

Table 1: Test Batches

Test Group	Batch #	Batch Name	Nano-cement Wt.%
Control	1	Plain	-
CNTs	2	0.04 CNT	0.04
	3	0.08 CNT	0.08
	4	0.12 CNT	0.12
GOs	5	0.04 GO	0.04
	6	0.08 GO	0.08
	7	0.12 GO	0.12
GNPs	8	0.04 GNP	0.04
	9	0.08 GNP	0.08
	10	0.12 GNP	0.12

2.1 Materials and Equipment

The cement used was Pozzolana Portland Cement (PPC), complying with EN 197-1:2011. The CNTs used were multi-walled carbon nanotubes of 10-20 nm diameter and 30 µm. The GOs used was a few-layer graphene oxide produced by a modified hummer's method with a layers' thickness of 1 nm. The GNPs used were COOH-functionalized Graphene Nanoplatelets consisting of several sheets of graphene that are chemically exfoliated from natural graphene. Finally, the surfactant used in the dispersion process was a polycarboxylic ether-based superplasticizer. The equipment used included a laboratory mixer, an ultrasonic wave mixer, a strength testing machine and a scanning electron microscope (SEM).

2.2 Mixing and Testing

The mixing process started by performing the Nanofilaments' dispersion in an aqueous solution using an ultrasonic wave mixer for 30 min at a power of 400 W. The cement was added to the solution, and samples were poured, demoulded after 1 day, and cured for 90 days. After curing, flexural and compressive strength tests were performed according to ASTM C348 and ASTM C109.

2.3 Microstructural Analysis

Microstructure analysis was done using SEM to understand the dispersion and compatibility of the added nanoparticles within the cement hydration products. The procedure was performed using fractured samples that were dried and coated with conductive palladium.

2.4 t-Statistical Analysis

t-statistical tests were used to evaluate the significance of using Nanoparticles compared with the plain cement paste batch. The test determines if a difference in the means of two groups happens due to a random possibility. The following conditions were taken into consideration:

- A two-tailed significance level of 0.05 was considered.
- The null hypothesis is correct when the average strength values of the Nanocomposite mix and the control are equal.
- The null hypothesis is rejected if the t-statistic (τ_{st}) is equal to or larger than the critical t-test value (τ_{cr}).
- When the null hypothesis is rejected, the strength value of the composite mix and the control are considered not equivalent, indicating that the incorporated Nanoparticles improve the strength significantly.
- The degree of freedom (D_f) was determined as:

$$D_f = [(S_1^2/ y_1) + (S_2^2/ y_2)]^2/ [[(S_1^2/ y_1)^2 / (y_1-1)] + [(S_2^2/y_2)^2/ (y_2-1)]] \quad (1)$$

  Where, S_1, S_2 are the standard deviations of samples; 1, 2 and y_1, y_2 are the size of samples 1, 2.

- The standard error (SE) could be computed by the following equation:

$$SD = \sqrt{\left(\left(\frac{S_1{}^2}{y_1} + \frac{S_2{}^2}{y2}\right)\right)} \quad (2)$$

- The T-statistics value (τ_{st}) is determined by:

$$\tau_{st} = |(\boldsymbol{\mu}_1-\boldsymbol{\mu}_2) / SE| \quad (3)$$

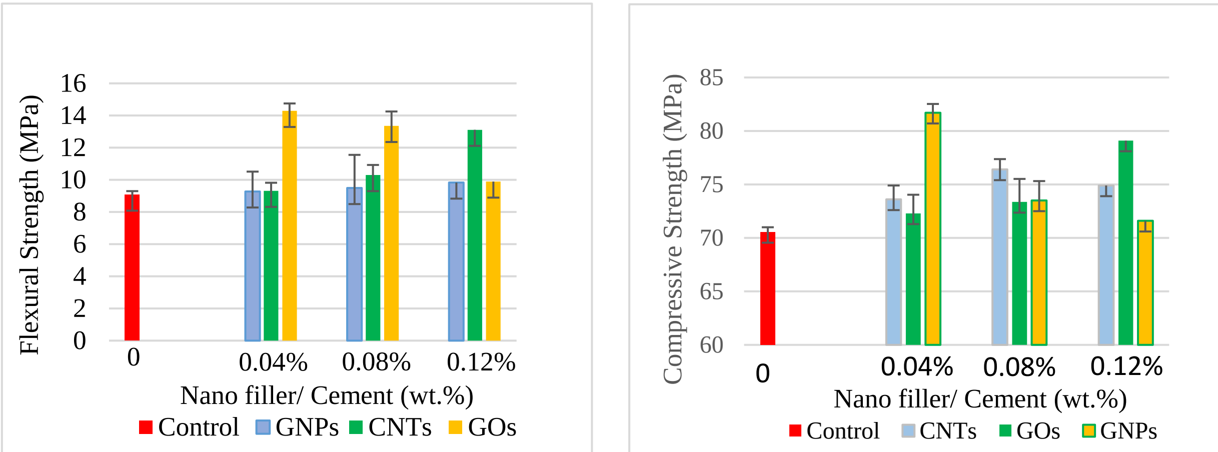
  where$\boldsymbol{\mu}_1$ = average value of sample 1, and $\boldsymbol{\mu}_2$ = average value of sample 2.

3 Results and Discussion

3.1 Flexural and Compressive Strength

Figures 1a and 1b show the flexural and compressive strength results of all batches. Among all batches, the mix containing 0.04 wt.% GOs attained the maximum flexural strength of about 58% compared to the plain cement paste mix. In addition, the mix having 0.08 wt.% GOs had an enhancement of about 48%

compared to the control cement paste mix. For CNTs, the mix containing 0.12% CNTs could attain a flexural strength increase of about 45% compared to the control mix. Unlike GOs and CNTs, GNPs did not show outstanding flexural strength increments regardless of the weight fraction used. All GNPs cementitious composites improvements were in the range of 2-8%. Compressive strength results showed that composites with 0.04 wt.% GNPs attained the highest strength improvement of about 16% compared to the plain cement batch. For CNTs, the results showed that the maximum compressive strength improvement of about 10% could be obtained using a CNTs' weight fraction of 0.08wt.%. For GOs composites, compressive strength results showed that the batch containing 0.12% GOs achieved the greatest improvement of about 12% compared to the control mix.

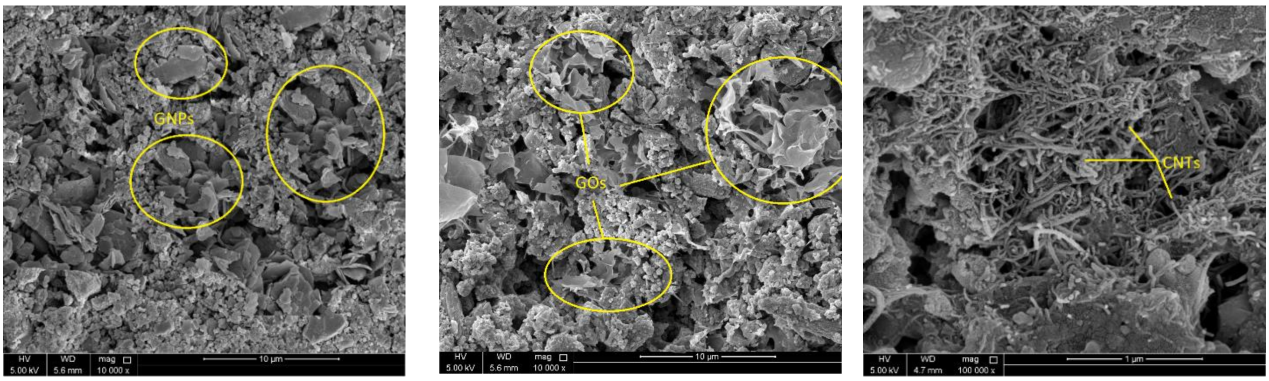


(a) (b)

Fig. 1: (a) Flexural Strength Test Results, and (b) Compressive Strength Test Results

3.2 Microstructural Analysis

SEM images showed that the Nanoparticles were impeded within the cement hydration products. Microstructural investigations of the fractured surfaces did not show clumps or agglomerations, indicating the success of the implemented dispersion procedures. GNPs (Figure 2a) appeared very similar in shape and size to the Calcium hydroxide (CH) hydration products. Similarly, GOs with larger surface areas and a more ductile appearance were impeded into the hydration products showing dense pore structure (Figure 2b). Unlike GNPs and GOs, CNTs were easily located due to their 1 D shape (Figure 2c). CNTs appeared to be dispersed well in all implemented weight fractions representing a proof sheet filing the Nanoscale voids.



(a) (b) (c)

Fig. 2: SEM image of mix containing (a) 0.12wt. % GNPs, (b) 0.12wt. % GOs, and (c) 0.12 wt. % CNTs

3.3 t-Statistical Analysis

t-statistical analysis of the flexural and compressive test results is presented in Tables 2 and 3, respectively. The results showed a significant enhancement in the batches containing 0.12 CNTs, 0.04 GOs and 0.08 GOs. When analyzed statistically, most remaining batches showed no significant enhancement in their flexural strength compared to the control mix. For compressive strength improvements, the statistical analysis showed that significant enhancements occurred in the batches containing 0.08 and 0.12 wt.% CNTs. Also, significant compressive strength enhancements were seen in the batches containing 0.12 GOs and 0.04 GNPs. These findings indicate the significance of adding Nanoparticles to increase both the flexural and compressive strength of cement paste.

Table 2: Flexural Strength Results t-Test

Mix	Degree of Freedom (DF)	Standard Error (SD)	T-Statistic Value (Tst)	Critical T-test Value	Remarks
0.04 CNTs	1	0.264	0.9	12.71	A
0.08 CNTs	2	0.305	3.99	4.303	A
0.12 CNTs	2	0.376	10.73	4.303	R
0.04 GOs	3	0.399	13.04	3.182	R
0.08 GOs	3	0.285	14.98	3.182	R
0.12 GOs	2	0.528	1.54	4.303	A
0.04 GNPs	2	0.684	0.29	4.303	A
0.08 GNPs	2	0.097	4.23	4.303	A
0.12 GNPs	1	0.097	7.69	12.71	A

* A: Accept Null Hypothesis, No Significant Enhancement
** R: Reject Null Hypothesis, Significant Enhancement

Table 3: Compressive Strength Results t-Test

Mix	Degree of Freedom (DF)	Standard Error (SD)	T-Statistic Value (Tst)	Critical T-test Value	Remarks
0.04 CNTs	2	1.213	2.52	2.571	A
0.08 CNTs	2	0.794	7.42	4.303	R
0.12 CNTs	3	0.615	7.12	3.182	R
0.04 GOs	3	0.502	3.47	3.182	A
0.08 GOs	2	1.04	2.7	2.571	A
0.12 GOs	2	1.269	6.72	4.303	R
0.04 GNPs	2	1.546	7.19	4.303	R
0.08 GNPs	2	1.083	2.7	4.303	A
0.12 GNPs	2	0.257	4.24	4.303	A

* A: Accept Null Hypothesis, No Significant Enhancement
** R: Reject Null Hypothesis, Significant Enhancement

4 Conclusions

This study investigates the significance of adding various concentrations of CNTs, GNPs, and GOs on the mechanical properties of cement paste. Mixes containing several Nanoparticles weight fractions were tested for flexure and compression and the results were statistically analysed. SEM images were also captured to visualize the reinforcing mechanism of the Nanoparticles. The following conclusions have been drawn:

i. CNTs, GNPs, and GO exhibited varying behaviors in terms of compressive and flexural strengths; however, all dosages demonstrated an improvement in mechanical properties over the control mix at 90 days.

ii. Among all mixes, the one prepared with 0.04% GNPs achieved the highest compressive strength, while the mix containing 0.04% GO achieved the highest flexural strength, with an increment of about 16% and 58%, respectively, compared to the plain cement paste mix.

iii. t-statistical analysis confirmed the significance of using 0.12 CNTs, 0.04 GOs and 0.08 GOs in increasing the flexural strength of cement paste.

iv. On the other hand, the statistical analysis showed the significance of using 0.12 GOs and 0.04 GNPs in increasing the compressive strength of cement paste.

v. Microstructural analysis using SEM highlighted the impediment of the Nanoparticles within the cement hydration products with proper dispersion all over the matrix.

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