Effect of Hybrid Carbon Nanotubes/Graphite Nano Platelets on Mechanical Properties of Cementitious Composite

Furqan Farooq*[1], Arslan Akbar[2] , Rao Arsalan Khushnood[3]

1*. Furqan Farooq. Lecturer, COMSATS University Islamabad, Abbottabad Campus
Email: furqan@cuiatd.edu.pk

2. Arslan Akbar. Ph.D. Scholar, City University of Hong Kong
Email: aakbar4-c@my.cityu.edu.hk

3. Rao Arsalan Khushnood. Assistant Professor, National University of Sciences and Technology
Email: arsalan.khushnood@nice.nust.edu.pk

Abstract

Nanomaterials and its application in construction industry attracted researchers to explore their effect due to exceptional properties in term of mechanical and have the potential of reinforcing within cementious matrix. Among them carbon based nanomaterial exhibit tremendous advantages in the construction industry. In this study hybrid intrusion of carbon nanotubes with graphite nanomaterials were added with small dosage/concentration ranging from 0-0.08% to surfactant ratio of 1:1 in the cement matrix, to explore mechanical properties in term of flexural and compressive strength is explored. The result reveals that using a small percentage of nanomaterials enhances the flexural strength and compressive strength up to 185% and 70% respectively.

Keywords: carbon nanotubes, graphite nanoplatelets, flexural strength, compressive strength

1. INTRODUCTION:

Cementitious materials are widely used construction materials, due to having high exceptional compressive strength. However these conventional cementitious material offer good compressive values, but still limits the tensile capacity, which makes them vulnerable to cracking. These cracks propagate form micro level, which then conjoin to microcrack leading to failure of cementitious material. To tackle the mentioned issues various materials and techniques have been explored by several researchers which include the incorporation of SRMs, well-engineered steel fibres, Carbon nanofibers, Carbon nanotubes, Graphene oxide and carbonaceous nano/micro inert, to alter the traditional properties of composites and achieve the required milestones. These nanoscale fibers arrest the propagation of crack at the nanoscale, causing enhancement in mechanical properties. These nanomaterials have distant and fruitful properties when used in cementious material. Among various nanomaterials, carbon-based nanomaterials have the most enlightened properties. Small concentration increases the mechanical response of cementitious composite. Konsta-Gdoutous et al. used carbon nanotubes with small concentration of 0.08% in cement paste and reported 35% increase in flexural properties (Konsta-Gdoutos et al. n.d.). Wang et. al. used MWCNTs in cement paste and reported increase flexural and compressive strength up to 10% and 50% respectively (Wang et al. n.d.). Gong et.al incorporated GO sheets with small dosage of 0.03% in cementitious composite and reported 46% and 25% enhancement in compressive and flexural response. This is due to the refinement of pore size (Gong et al. 2015).

The properties of Carbon nanotubes can be influenced by its aspect ratio, diameter as well as from its chirality. Historically Carbon nanotubes were discovered in 1991 by sumio Lijima (Japanese Researcher) while investigating the surface of graphite electrodes as sown in Figure 1 (nature and 1991 n.d.) . This discovery of CNTs leads to a new dimension which opened a path towards utilization of CNTs in numerous fields of engineering. Based on its characteristics, properties and its production CNTs is used in numerous viable applications like rechargeable batteries, sporting goods and automotive parts (Volder et al. n.d.).

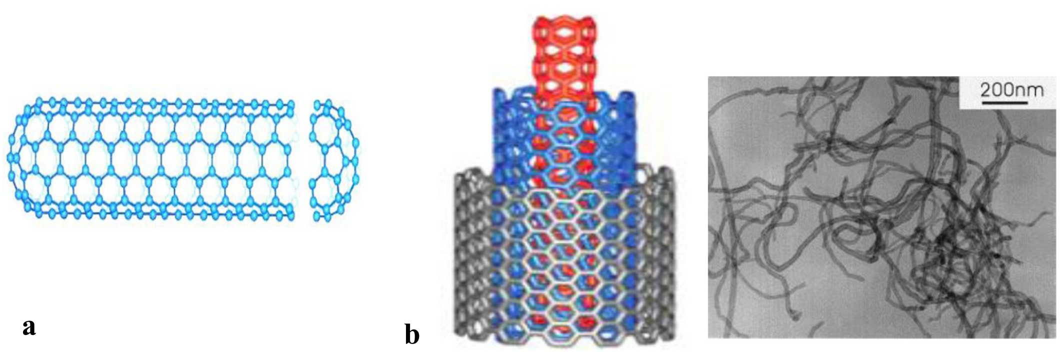

Figure 1: (a) Carbon nanotube (Breuer and Sundararaj 2004) (b) Schematics image and TEM image of MWCNTs (Breuer and Sundararaj 2004)
(Li et al. n.d.)

Graphite nanoplatelet (GNP) is another form of graphite nanomaterials (GNMs) mainly carbon-based conductive nano-particles which is produced from graphite. Normal graphite consists of stratified layers including series of two dimensional (2D) graphene layers stacked together in the parallel form (Pierson 1993) as shown in Figure 2. However, graphite nanoplatelets can be obtained via exfoliation and intercalation of graphene layers.

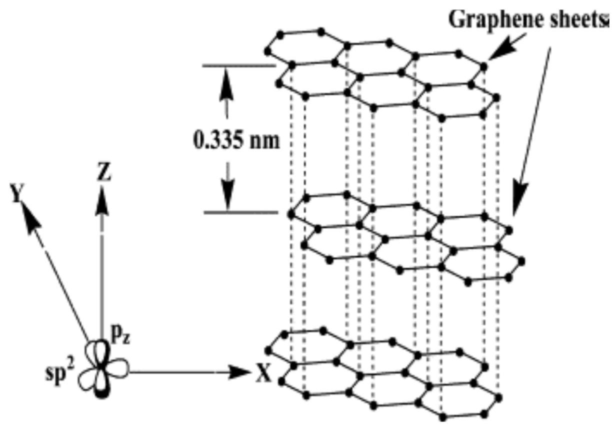

Figure 2: Structure of Graphite showing the sp2 carbon atoms bounded in hexagonal rings (Sengupta et al. n.d.)

Graphite nanoplatelets (GNPs) consist of many graphene layers bonded together with a Van Der Vaal forces, having a thickness in nano-meter and diameter ranges in microns. There nanoscale size, when used in cementitious composite, enhances the mechanical properties.

In order to improve the mechanical properties of composites with nanomaterial addition, it is mandatory to properly disperse it inside the matrix. The problem normally faced with improper dispersion of nanomaterial is the agglomeration and bundling of tubes inside the matrix for which different surfactants need to employ to make the nanomaterial homogenously disperse through cement matrix. In the continuation of mentioned topic an investigation on the dispersion of nanomaterial and its effects on the mechanical response of cementitious matrices (Sobolkina et al. n.d.), concludes that proper dispersion leads to 40% enhancement in compressive resistance. In most of the research investigations, it has been emphasized those nanomaterials agglomerates within the cement matrix without giving proper attention to dispersion (Luo, Duan, and Li 2009; Konsta-Gdoutos et al. n.d.). In this research dispersion of nanomaterials was done using acacia gum as surfactant with nanomaterial to surfactant ratio of (1:1), as it yields maximum dispersion.

In this paper, hybrid intrusion carbon nanotubes with graphite nanoplatelets in cement mortar, with dispersion and exploration of mechanical properties in term of flexural and compression has been reported.

2. Materials and Experiments

Type 1, Grade 53 Cement in line with ASTM C150 was used as binding material. The features properties of cement/binder can be seen in Table 1. Sand was obtained from lawrenecpur, with fineness modulus of 2.4 and superplasticizer obtained from BASF chemical for making cementitious mortar. The Multi-wall carbon nanotubes and graphite nanoplateletes used in this research were purchased from US Research

Nanomaterials and Deijung Company and their properties are listed in Table 2. Acacia gum used as surfactant for proper dispersal of nanomaterials in water. The features properties of superplasticizer are listed in Table 3.

Table 1: Properties of OPC

Elemental Composition	Content (%)
CaO	65.11
SiO_2	19.17
Al2O_3	4.96
Fe_3O_4	3.21
MgO	2.23
MnO + K_2O	0.55
TiO2	0.28
P_2O_5 + Na_2O	0.64

Table 2: Properties of MWCNTs and GNPs

MWCNTs Properties	External diameter (nm)	Internal diameter (nm)	Length (µm)	Purity (%)	Specific surface area (m^2/g)	Ash content (wt.%)	Density (g/cm^3)
	20-30	5-10	10-30	>97	110	<1.5	2.1
GNPs Properties	**Specific surface area (cm^2/g)**	**Particle size analysis (µm)**	**Specific gravity**				
	154	6.78	1.62				

Table 3: Properties of third generation superplasticizer

Master Glenium ®51	Aspect	Relative Density	pH	Chloride ion content
	Light Brown Liquid	1.08 ± 0.01 at 25°C	≥6	<0.2%

2.1 Mixing regime of nanocomposite cement mortar

The homogenous solutions of graphite nanomaterials (GNM's) after dispersion were used to make nanocomposite cement mortar. The water to binder ratio of 0.38 was selected for all formulation and binder to sand ratio of 1:1.5 was used for casting of cement mortar. The mixing of all formulation was done by using Hobart mixer of 5 litre capacity. After mixing, and for the evaluation of mechanical properties, prisms mould having dimensions of 160x40x40mm^3 were casted. The details of formulation and the mixing time taken by each formulation has been listed in Table 4 and Table 5

Table 4: Formulation regime

S.No.	Formulation	CNT (%)	GNP (%)
1	CS	0	0
2	C	0.08	0
3	CG	0.04	0.04
4	G	0.	0.08

* CS control sample, C carbon nanotubes, CG hybrid carbon nanotubes/graphite nanoplatelets, G graphite nanoplatelets

Table 5: Mixing regime

Mixing regime	Time of mix
Dry mix	Half minute (gentle mix)
Dry mix + Dispersed GNM’s	1 minute (gentle mix)
Dry mix + Dispersed GNM’s	2 minutes (fast mix)

3. Result and Discussion

3.1 Dispersion

The dispersion of nanomaterials was checked by using Uv-spectroscopy. The dispersed solution of nanomaterials was diluted by using lambert beer law, before using spectroscopy. The wavelength was kept between 200-1100 nm and 500 nm wavelength was kept to check the dispersed solution of nanomaterials, as it is unaffected at ambient conditions (Baloch et al. n.d.). It can be seen that graphite nanomaterials (CG) having small concentration with GNMs to surfactant ratio of 1:1 yield maximum absorbance. This is due to the synergistic effect of nanomaterials as shown in Figure 3.

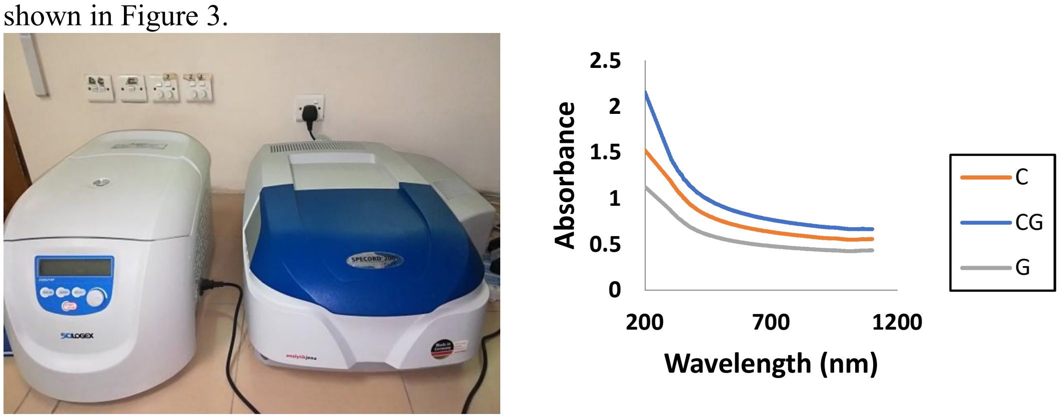

Figure 3: UV-Spectroscopy of nanocomposite

3.2 Flexural Strength

The flexural strength of all prisms was performed according to ASTM C348, under bending setup on load controlled machine as shown in Figure 4. The flexural test was performed after 28 days of curing. It can be seen in Figure 5 that the flexural strength of nanocomposite increases as compared to the control sample. Also, concentration (CG) increases the flexural strength up to 185% compared to control specimen. This is due to the synergistic effect, which enhances the microstructure causing an increase in load carrying capacity

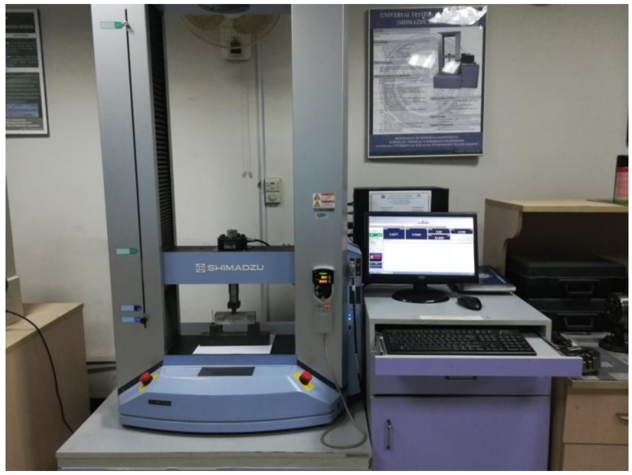

Figure 4: Bending test assembly

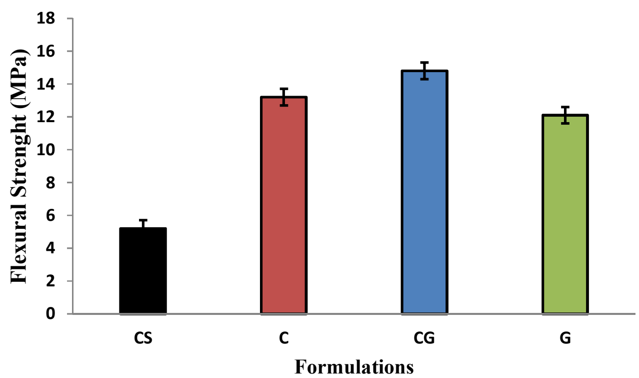

Figure 5: Flexural response of nanocomposite at 28days

3.3 Compression Strength

The compression test was performed according to ASTM C349-14 on two broken pieces of prism after the flexural test as shown in Figure 6. It can be seen in Figure 6 that the compressive strength of nanocomposite (CG) increases up to 70% as compared to control sample, as these fiber enhances the load carrying capacity between fiber to fiber and with the adjacent matrix.

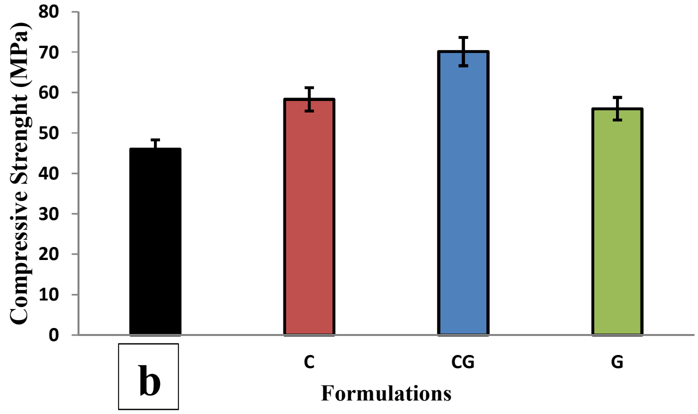

Figure 6 (a) Assembly of compression test, (b) Compressive strength of nanocomposite at 28days

4. Conclusions

From the study and research regarding nanomaterials, following conclusion has been drawn by using small concentration of nanomaterials in cementitious mortar.

1. Dispersion of Hybrid CNTs/GNPs (CG) nanomaterials with nanomaterials to surfactant ratio of (1:1) yield maximum dispersal. This is due to the synergistic effect, as these both fibers belong to the family of graphite nanomaterials
2. Intrusion of hybrid CNTs/GNPs (CG) by small dosage of 0.04/0.04% in cementitious mortar increases the compressive strength up to 70% compared to control specimen. This is due to enhancement in load carrying capacity

3. Intrusion of hybrid CNTs/GNPs (CG) with small dosage increases the flexural response of nanocomposite of hardened mortar sample. The bending test elucidated that using small concentration increases the flexural response up to 185% as compared to the control specimen.

Bibliography

Ahmad, S, RA Khushnood, P Jagdale, JM Tulliani - Materials & Design, and undefined 2015. n.d. "High Performance Self-Consolidating Cementitious Composites by Using Micro Carbonized Bamboo Particles." *Elsevier*. Accessed April 30, 2019. https://www.sciencedirect.com/science/article/pii/S0261306915001454.

Baloch, WL, RA Khushnood, W Khaliq - Construction and Building Materials, and undefined 2018. n.d. "Influence of Multi-Walled Carbon Nanotubes on the Residual Performance of Concrete Exposed to High Temperatures." *Elsevier*. Accessed May 2, 2019. https://www.sciencedirect.com/science/article/pii/S0950061818317240.

Breuer, O., and Uttandaraman Sundararaj. 2004. "Big Returns from Small Fibers: A Review of Polymer/Carbon Nanotube Composites." *Polymer Composites* 25 (6): 630–45. https://doi.org/10.1002/pc.20058.

Gong, Kai, Zhu Pan, Asghar H. Korayem, Ling Qiu, Dan Li, Frank Collins, Chien Ming Wang, and Wen Hui Duan. 2015. "Reinforcing Effects of Graphene Oxide on Portland Cement Paste." *Journal of Materials in Civil Engineering* 27 (2):

A4014010. https://doi.org/10.1061/(ASCE)MT.1943-5533.0001125.

Khushnood, RA, S Ahmad, L Restuccia, … C Spoto - Frontiers of Structural, and undefined 2016. n.d. "Carbonized Nano/Microparticles for Enhanced Mechanical Properties and Electromagnetic Interference Shielding of Cementitious Materials." *Springer*. Accessed April 30, 2019. https://link.springer.com/article/10.1007/s11709-016-0330-5.

Khushnood, RA, S Ahmad, P Savi, JM Tulliani - … and building materials, and undefined 2015. n.d. "Improvement in Electromagnetic Interference Shielding Effectiveness of Cement Composites Using Carbonaceous Nano/Micro Inerts." *Elsevier*. Accessed April 30, 2019. https://www.sciencedirect.com/science/article/pii/S0950061815003244.

Konsta-Gdoutos, MS, ZS Metaxa, SP Shah - Cement and Concrete, and undefined 2010. n.d. "Highly Dispersed Carbon Nanotube Reinforced Cement Based Materials." *Elsevier*. Accessed May 2, 2019a. https://www.sciencedirect.com/science/article/pii/S0008884610000542.

———. n.d. "Multi-Scale Mechanical and Fracture Characteristics and Early-Age Strain Capacity of High Performance Carbon Nanotube/Cement Nanocomposites." *Elsevier*. Accessed May 5, 2019b. https://www.sciencedirect.com/science/article/pii/S0958946509001632.

Li, GY, PM Wang, X Zhao - Carbon, and undefined 2005. n.d. "Mechanical Behavior and Microstructure of Cement Composites Incorporating Surface-Treated Multi-Walled Carbon Nanotubes." *Elsevier*. Accessed May 2, 2019. https://www.sciencedirect.com/science/article/pii/S0008622305000199.

Luo, Jianlin, Zhongdong Duan, and Hui Li. 2009. "The Influence of Surfactants on the Processing of Multi-Walled Carbon Nanotubes in Reinforced Cement Matrix Composites." *Physica Status Solidi (A)*, July, NA-NA. https://doi.org/10.1002/pssa.200824310.

nature, S Iijima -, and undefined 1991. n.d. "Helical Microtubules of Graphitic Carbon." *Nature.Com*. Accessed May 1, 2019. https://www.nature.com/articles/354056a0.

Pierson, HO. 1993. "Chapter 15,'The Fullerene Molecules' in Handbook of Carbon, Graphite, Diamond and Fullerenes."

Sengupta, R, M Bhattacharya, … S Bandyopadhyay - Progress in polymer, and undefined 2011. n.d. "A Review on the Mechanical and Electrical Properties of Graphite and Modified Graphite Reinforced Polymer Composites." *Elsevier*. Accessed May 2, 2019. https://www.sciencedirect.com/science/article/pii/S0079670010001231.

Sobolkina, A, V Mechtcherine, … V Khavrus - Cement and Concrete, and undefined 2012. n.d. "Dispersion of Carbon Nanotubes and Its Influence on the Mechanical Properties of the Cement Matrix." *Elsevier*. Accessed May 2, 2019. https://www.sciencedirect.com/science/article/pii/S095894651200162X.

Volder, MFL De, SH Tawfick, … RH Baughman -, and undefined 2013. n.d. "Carbon Nanotubes: Present and Future Commercial Applications." *Science.Sciencemag.Org*. Accessed May 1, 2019. https://science.sciencemag.org/content/339/6119/535.short.

Wang, B, Y Han, S Liu - Construction and Building Materials, and undefined 2013. n.d. "Effect of Highly Dispersed Carbon Nanotubes on the Flexural Toughness of Cement-Based Composites." *Elsevier*. Accessed May 5, 2019. https://www.sciencedirect.com/science/article/pii/S0950061813003310.