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Effect of carbon nanotubes and fly ash on mechanical and microstructural properties of cement mortars

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Abstract: *This paper aims to evaluate the effect of various dosages of carbon nanotubes (CNTS) and fly ash (FA) on the mechanical and microstructural properties of mortar cubes. Cement was replaced with varying dosages of fly ash (5%, 10%, 15%, 20% and 25%) and CNTS (0.125%, 0.25%, 0.137% and 0.5%). In addition 10% fly ash was added independently with 0.125%, 0.25%, 0.137% and 0.5% carbon nanotubes. The addition of 10% fly ash in cement as an optimum dosage increased the compressive strength by 21.9%, 17.4%, and 80.2%, however, increase in fly ash dosage (25%) led to a decrease in mortar strength by 50.8%, 56.9% and 55.1% when specimens were subjected to compressive strength test at 7,28 and 90 days respectively. The study shows that the addition of 0.125% CNTS as an optimum dosage increased mortar strength up to 12.7%, 62.6%, and 48.7% at 7, 28, and 90 days respectively due to the bridging effect of CNTS. Similarly, the introduction of 10% fly ash with 0.25% CNTS as an optimum dosage led to an increase in compressive strength by 8.2%,20%, and 21.4% at 7,24, and 90 days respectively, however higher dosages of CNTS decreased mortar strength. Microstructural analysis shows improvement in bonding between matrix and aggregates due to the filling and bridging effect of fly ash and carbon nanotubes.*

Keywords: Carbon Nanotubes, Fly ash, Mortar, Mechanical properties, Compressive strength, Microstructural properties

1. Introduction

The use of nanomaterials in the construction industry has got prime importance due to their peculiarity in physical and chemical properties. Materials having a size equal to or less than 100 nanometers are usually associated with nanomaterials. Apart from being sustainable, these materials show resilience against fire, cracking, corrosion, and water penetration [1]. Eloquent research carried out in past shows the potential use of carbon nanotubes in enhancing various properties of cementitious materials [2], [3]. Due to the high aspect ratio, high young modulus, and availability of nanoparticles like nano-Fe_2O_3 and nano-SiO_2 in CNTS increase both compressive and tensile strength of cement mortars [4],[5]. Results of various researchers show that the use of carbon nanotubes acts as a filling agent which consequently leads to an increase in the density of microstructure and its strength by reducing permeability [6],[7].[8]. The study carried out by A. Chaipanich et al. [4] indicates that the use of 0.5% CNTS and 1% fly ash significantly increased the density of mortar at 28 days (2.29g/cm^3) as compared to mix without CNTS (2.19g/cm^3). Optimum dosage (0.01%) of carbon nanotubes increased led to an increase in compressive strength and stiffness of cement mortars [9].

The introduction of by-products as cementitious material such as fly ash produced by industrial expansion has also got warm attention. Early research carried out by (Haque, 1984) lead the way to introduce high volume fly ash in concrete. He found that 50% replacement of cement with fly ash could result in better performance without affecting its initial and final setting time. It is reported that the addition of 70% fly ash with 5% nano-silica substantially increased compressive strength up to 90% when used in cement mortars [10]. On contrary, the research carried by [11] shows a decrease in compressive strength by 76.98% when cement was replaced by 70% with fly ash. Furthermore, the study of [12] reflects that introduction of a high amount of fly ash in cement mortars (50,60, and 70%) decreases 28 days compressive strength by 40%, 46.57%, and 74.29% respectively.

When a building is subjected to high temperature or environmental changes, the building materials deteriorate and its mechanical properties become more dynamic. The unprotected concrete may lead to severe damage. Literature shows that extensive research has been carried out to analyze the behavior of fly ash in concrete but the use of fly ash and carbon nanotubes as an emerging material is still needed to be explored through various perspectives that could help to reinforce mortar to protect buildings and finished surfaces. In this study, different dosages of carbon nanotubes and fly ash were added to the cement. Mechanical properties such as compressive strength and microstructural properties of mortar are evaluated that would help to design optimum mix ratio to reinforce mortars which would provide an economical and sustainable solution.

2. Experimental Program

2.1 Materials & Mix Proportions

Locally available *Fauji* Cement originated at (Fauji Cement Company Limited, n.d.) was used in this research. The cement (ASTM Type I) follows the requirements of (ASTM C150) [13]. Black-colored multi-walled carbon nanotubes having an outer diameter of 20-40nm and length of 5-15nm were used in this study as shown in Fig.1 (b). The CNTS were mixed with 0.1% plasticizer (poly-carboxylate) by using sonicator as shown in Fig.1 (c). The specific surface area of CNTS is 90-120 m^2g^{-1} having 97% purity. Locally processed class F fly ash meeting the standard of ASTM C 618 manufactured at 'Port Qasim Power Plant Karachi Pakistan' was used in research as shown in Fig.1. (a). The maximum nominal size of fine aggregates is 4.75mm which follows the specifications of ASTM C778 [14]. The amount of fly ash and CNTS is calculated by weight (Kg/m^3) and volume (%) of the total mix. The casting, drying, and testing of mortar cubes having the size of (70×70×70 mm^3) was done carefully.

Table.1 Mix proportion of mortar mixtures.

Batch No.	Mixture	w/c	Water Kg/m^3	Cement Kg/m^3	Sand Kg/m^3	Fly Ash		CNTS	
						Kg/m^3	%	Kg/m^3	%
1	Control	0.5	234	468	1414	0	0	0	0
	F1	0.5	234	445	1414	23	5	0	0
	F2	0.5	234	421	1414	47	10	0	0
	F3	0.5	234	398	1414	70	15	0	0
	F4	0.5	234	374	1414	94	20	0	0
	F5	0.5	234	351	1414	117	25	0	0
2	C1	0.5	234	467.4	1414	0	0	0.6	0.125
	C2	0.5	234	466.8	1414	0	0	1.2	0.25
	C3	0.5	234	466.2	1414	0	0	1.8	0.375
	C4	0.5	234	465.6	1414	0	0	2.3	1
3	CF1	0.5	234	419	1414	47	10	2	0.125
	CF2	0.5	234	418	1414	47	10	3	0.25
	CF3	0.5	234	416	1414	47	10	5	0.375
	CF4	0.5	234	414	1414	47	10	7	1

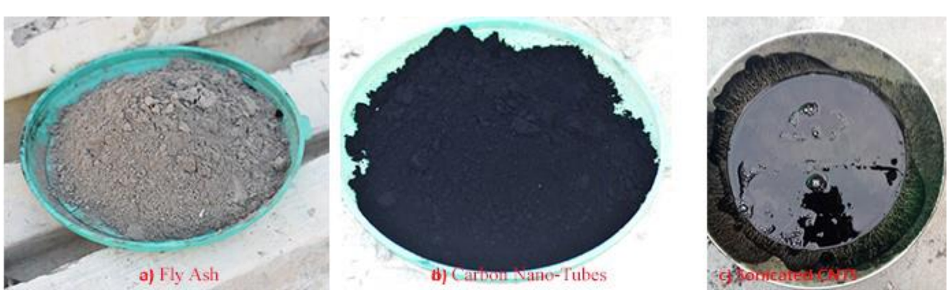

Fig 1. (a). Fly Ash (b). Dry CNTS (c). Sonicated CNTS.

3. Testing Program

3.1. Compressive strength test

The compressive strength of cubes was found according to the guidelines of ASTM C109. Cubes were subjected to the compressive testing machine having a loading capacity of 3000KN to determine the compressive strength of cubes. Tests at 7,28 and 90 days were performed to evaluate mortar strength. The loading rate and reference load was fixed as 1.8KN/sec and 1000KN respectively.

3.2. Microstructural analysis

The microstructural analysis was performed by spectral electron microscopy (SEM) to determine the structure of hydration products. SEM images were taken at different resolutions ranging between 5-50 µm.

4. Results and discussions

4.1. Compressive strength

The results of 7, 28 and, 90 days compressive strength of mortars having fly ash are shown in Fig.2. Compressive strength was determined by replacing cement with 5%,10%,15%,20% and 25% fly ash. Results showed slight variation in compressive strength at 7 days but become more evident at 28 and 90 days. The gradual increase in compressive strength was noticed when cement was replaced by 10% FA which was followed by the reduction in strength at higher dosages of fly ash. At 10% replacement of fly ash, an increase of 5.2, 17.4, and 80.2% increase in compressive strength was noticed when specimens were tested at 7, 28, and 90 days respectively. The findings of Nasser et al. [15] show that 10% replacement of fly ash leads to higher compressive strength at 7 and 28 days. A higher dosage of fly ash leads to a decrease in compressive strength both at an early and late age. The addition of 25% fly ash brought to 55.% and 56.1% decrease in strength when mortars were tested at 28 and 90 days respectively. A similar trend of results was reported by S.W.M Supit [16] showing that reduction in 28 days compressive strength of mortar was 40%,54.29%, and 74.29% when cement was replaced with 50%, 60%, and 70% of fly ash respectively. Mortar cubes containing different proportions of carbon nanotubes were also tested for compressive strength at 7, 28, and 90 days as graphed in Fig.3. In general addition of CNTS by 0.125%, 0.25%, 0.375% and 0.5% showed marked difference in strength when tested at 7, 28 and 90 days. At an optimum dosage of CNTS an increase of 39.5, 62.6, and 48.7% compressive strength was recorded at 7, 28, and 90 days respectively. The addition of CNTS more than 0.125% of cement lead to a decrease in compressive strength. The strength exhibited by mortar specimens containing 0.25%, 0.375% and 0.5% CNTS was 62.6%, 30.1%, and 21.9% with respect to control sample which shows a considerable decrease in strength as compared to optimum mix. Similarly the tests performed at 90 days on specimens containing 0.5% CNTS shows that compressive strength of mortar became equivalent to control sample which reflects that higher dosage of CNTS leads to decrease in compressive strength. The research carried out by Amin et al. [17] shows that replacement of composite cement with 0.1% CNTS gives higher compressive strength and 0.2% CNTS leads to a decrease in strength. Another study shows that the introduction of 0.5% multi-walled CNTS in cement paste significantly lead to a decrease in compressive strength [18].

The combined behavior of carbon nanotubes and fly ash on compressive strength was also determined in this study as presented in Fig.4. In each mix of the third batch 10% fly ash was added with varying dosages of CNTS like 0.125, 0.25, 0.137, and 0.5%. In general addition of fly ash improved late strength but increasing concentration of CNTS led to a decrease in strength. The optimum dosage of CNTS (0.25%) with 10% FA increased mortar compressive strength by 8.2%, 20%, and 21.4% when subjected to loading at 7, 28, and 90 days. On the contrary increase in CNTS dosage by 0.5% showed only 5.7% and, 4.8% increase in strength at 28 and 90 days which reflects that the overall compressive strength of mortar has reduced as compared to the optimum mix named CF1 due to agglomeration of CNTS and incomplete hydration reaction. The addition of 0.5% CNTS with 10% FA reduced 7 days compressive strength by 20.2% which shows that the high dosage of CNTS with fly ash retard hydration reaction and increases the setting time of the mortar. The average compressive strength of all mixes having different dosages of CNTS with 10% fly ash was greater than the controlled mix. Similar results reported by R. Siddique [19] indicate that the addition of 1% multi-walled CNTS with 20% fly ash gives higher strength and the same trend is found for other mixes having CNTS and FA when tested at 60 days. This is also confirmed by [4] that the use of fly ash with CNTS leads to an increase in the compressive strength of mortars. The comparison of compressive strength between mixes of batch 2 containing CNTS and batch 3 having CNTS with fly ash is performed in Fig 5, Fig 6, and Fig 7 which reflects that mortar mixes containing CNTS showed greater strength as compared to mixes having CNTS and FA at both 7 and 28 days. Results show that optimum dosage of CNTS in mix C1 lead to an increase in 7, 28, and 90 days compressive strength by 36%, 42%, and 38% respectively as compared to optimum mix CF1 having CNTS and FA which indicates that use of fly ash with CNTS gives lower strength which is also uneconomical as compared to mixes only having CNTS. The mixing of CNTS with FA drives to decrease in mortar compressive strength but overall strength remains greater than control sample.

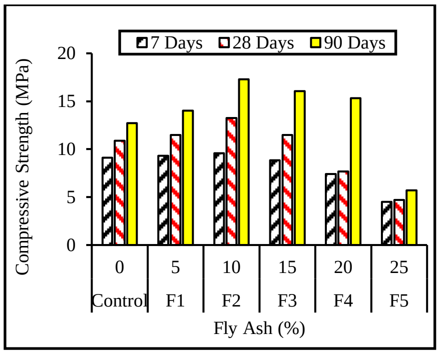

Fig.2. Compressive strength of specimens containing fly ash at 7, 2,8 and 90 days.

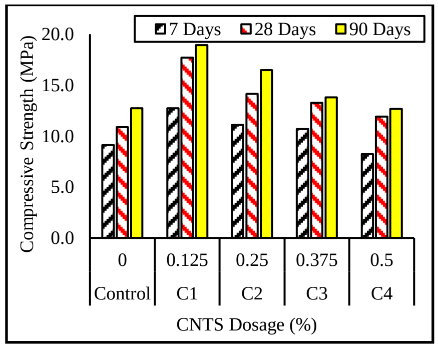

Fig.3. Compressive strength of specimens containing CNT's at 7, 28, and 90 days.

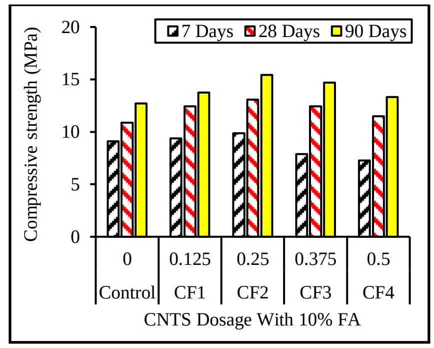

Fig.4. Compressive strength of specimens containing CNT's with 10% FA at 7, 28, and 90 days.

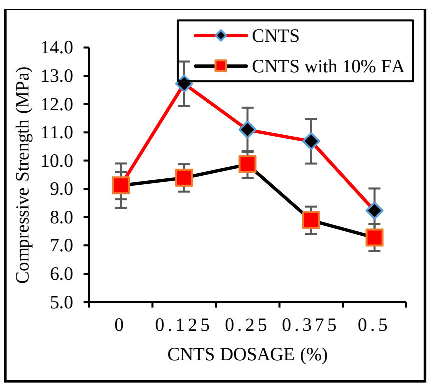

Fig.5. Strength comparison of specimens containing CNT's and CNT's+ 10% FA at 7 days.

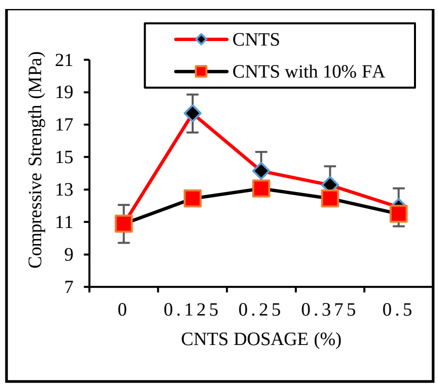

Fig.6. Strength comparison of specimens containing CNT's and CNT's+ 10% FA at 28 days.

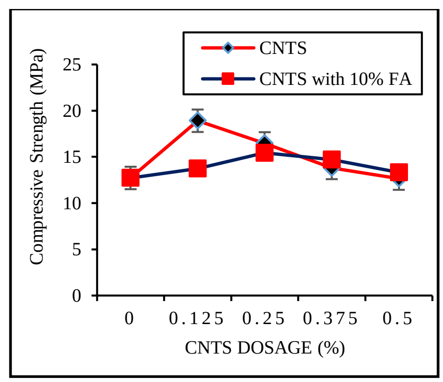

Fig.7. Strength comparison of specimens containing CNT's and CNT's+ 10% FA at 90 days.

4.2. Microstructural Analysis

The analysis of the control sample of mortar shows needle-shaped crystals of ettringite and prismatic crystals of calcium hydroxide, however, there has been the formation of micro-cracks and voids as shown in Fig.8. The addition of 10% fly ash accelerated ettringite formation and C-S-H gel which reinforced the matrix in some ways by binding the hydration products as shown in Fig.9. Similarly, the addition of CNT's enhanced the interfacial interaction between hydration products and carbon nano-tubes which lead to the formation of stable and denser microstructure. The nano-sized reinforcements of CNT's interacted intimately with C-S-H gel creating bridges between matrix and fine aggregates which provided sufficient resistance to cracks and enhanced the load-carrying capacity of mortar specimens. The bridging of CNTS is evident from Fig.10.

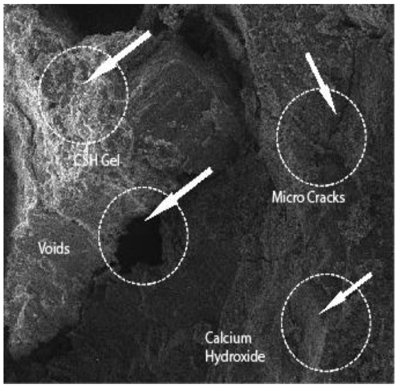

Fig.8. SEM image of control specimen at 50µm.

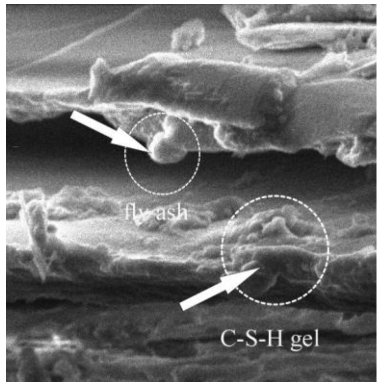

Fig.9. SEM image of specimen containing fly ash at 10µm.

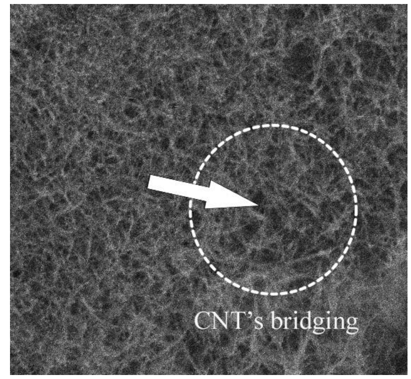

Fig.10. SEM image of specimen containing CNT's at 5µm.

5. Conclusion

In this study the cement was replaced with varying dosages of fly ash (5%, 10%, 15%, 20% and 25%) and CNTS (0.125%, 0.25%, 0.137% and 0.25%). Similarly, 10% fly ash was mixed with different dosages of CNTS (0.125%, 0.25%, 0.137%, and 0.25%). Following conclusions are made from this study.

- The use of 10% fly ash as an optimum dosage has increased 7, 28, and 90 days compressive strength by 9.7%, 21.9%, and 35.7% respectively. On contrary, an increase in fly ash dosage by 25% led to a decrease in strength by 50.8%, 56.9%, and 55.1% on the same days due to incomplete hydration reaction.
- The addition of CNTS showed improvement of compressive strength in general but higher dosage reduced strength slowly. The addition of 0.125% CNTS significantly increased in strength by 21.6%,27.6%, and 29.4% due to bridging action when the mix was tested and compared at 7,28, and 90 days separately.
- The early strength of mortar both at 7 and 28 days considerably increased due to the incorporation of fly ash as compared to fly ash which contributed to late strength (at 90 days) due to the formation of ettringite and hydration products.
- The study showed that the addition of 10% fly ash with 0.25% CNTS in mortars raised its strength to 8.2%, 32.4%, and 21.4% due to the bridging and filling effect of CNTS and fly ash at 7,28 and 90 days respectively.
- The development signifies that even small replacements with CNTS and fly ash significantly improves mortar compressive strength which suggests their use to reinforce mortar to protect structures in extreme loadings and environmental conditions.

6. Further Work

The addition of carbon nanotubes and fly ash imparted a positive effect on strength but other parameters such as workability and the impact resistance of various mixes are still needed to be studied further.

References

[1] D. Vollath and D. V. Szabó, "Synthesis and Properties of Nanocomposites," *Advanced Engineering Materials*. 2004, doi: 10.1002/adem.200300568.

[2] G. Y. Li, P. M. Wang, and X. Zhao, "Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes," *Carbon N. Y.*, 2005, doi: 10.1016/j.carbon.2004.12.017.

[3] S. Parveen, S. Rana, and R. Fangueiro, "A review on nanomaterial dispersion, microstructure, and mechanical properties of carbon nanotube and nanofiber reinforced cementitious composites," *Journal of Nanomaterials*. 2013, doi: 10.1155/2013/710175.

[4] A. Chaipanich, T. Nochaiya, W. Wongkeo, and P. Torkittikul, "Compressive strength and microstructure of carbon nanotubes-fly ash cement composites," *Mater. Sci. Eng. A*, 2010, doi: 10.1016/j.msea.2009.09.039.

[5] A. Anvari, "The Influence of CNT Structural Parameters on the Properties of CNT and CNT-Reinforced Epoxy," *Int. J. Aerosp. Eng.*, 2020, doi: 10.1155/2020/4873426.

[6] C. Redondo-Gómez, R. Leandro-Mora, D. Blanch-Bermúdez, C. Espinoza-Araya, D. Hidalgo-Barrantes, and J. Vega-Baudrit, "Recent Advances in Carbon Nanotubes for Nervous Tissue Regeneration," *Adv. Polym. Technol.*, 2020, doi: 10.1155/2020/6861205.

[7] Ö. Güler, Ö. Başgöz, S. H. Güler, C. A. Canbay, Ş. Açıkgöz, and M. Boyrazlı, "The synergistic effect of GNPs + CNTs on properties of polyester: comparison with polyester–CNTs nanocomposite," *J. Mater. Sci. Mater. Electron.*, 2021, doi: 10.1007/s10854-021-06275-w.

[8] A. Nieto, A. Agarwal, D. Lahiri, A. Bisht, and S. R. Bakshi, "Mechanics of CNT-MMCs," in *Carbon Nanotubes*, 2021.

[9] R. Hamzaoui, S. Guessasma, B. Mecheri, A. M. Eshtiaghi, and A. Bennabi, "Microstructure and mechanical performance of modified mortar using hemp fibres and carbon nanotubes," *Mater. Des.*, 2014, doi: 10.1016/j.matdes.2013.10.084.

[10] V. C. Khed, B. S. Mohammed, and M. F. Nuruddin, "Effects of Nano-Silica modified Self-Compacted, High Volume Fly Ash Mortar on Slump Flow and Compressive Strength," *Madridge J. Nanotechnol. Nanosci.*, 2016, doi: 10.18689/mjnn-1000104.

[11] L. Jiang and Y. Guan, "Pore structure and its effect on strength of high-volume fly ash paste," *Cem. Concr. Res.*, 1999, doi: 10.1016/S0008-8846(99)00034-4.

[12] F. U. A. Shaikh and S. W. M. Supit, "Mechanical and durability properties of high volume fly ash (HVFA) concrete containing calcium carbonate (CaCO3) nanoparticles," *Constr. Build. Mater.*, 2014, doi: 10.1016/j.conbuildmat.2014.07.099.

[13] "Standard Specification for Portland Cement C150/C150M," 2019.

[14] ASTM, "Standard Specification for Standard Sand C778 − 17."

[15] A. A. K. F. K. I. K. Z. Nasser, "Effect the Local Fly Ash on Cement Mortar Properties," *J. Univ. Babylon, Eng. Sci.*, vol. 26, no. 5, pp. 11–12, 2018.

[16] S. W. M. Supit, F. U. A. Shaikh, and P. K. Sarker, "Effect of ultrafine fly ash on mechanical properties of high volume fly ash mortar," *Constr. Build. Mater.*, 2014, doi: 10.1016/j.conbuildmat.2013.11.002.

[17] M. S. Amin, S. M. A. El-Gamal, and F. S. Hashem, "Fire resistance and mechanical properties of carbon nanotubes - Clay bricks wastes (Homra) composites cement," *Constr. Build. Mater.*, 2015, doi: 10.1016/j.conbuildmat.2015.08.074.

[18] S. Musso, J. M. Tulliani, G. Ferro, and A. Tagliaferro, "Influence of carbon nanotubes structure on the mechanical behavior of cement composites," *Compos. Sci. Technol.*, 2009, doi: 10.1016/j.compscitech.2009.05.002.

[19] R. Siddique and A. Mehta, "Effect of carbon nanotubes on properties of cement mortars," *Construction and Building Materials*. 2014, doi: 10.1016/j.conbuildmat.2013.09.019.