Pakistan Journal of Engineering and Technology, PakJET
Multidisciplinary & Peer Reviewed
Volume: 04, Number: 01, Pages: 212- 217, Year: 2021

Evaluation of Mechanical and Microstructural Properties of Mortar Reinforced with Carbon Nanotubes at Elevated Temperatures

Raja Wajahat Zahoor Khan[1*], Muhammad Yaqub[1], Muhammad Noman[2], Rana Muhammad Waqas[1]

[1]Department of Civil Engineering, University of Engineering and Technology, 47050 Taxila, Pakistan.
[2]Department of Civil Engineering, International Islamic University, 44000 Islamabad, Pakistan.
Corresponding author: Raja Wajahat Zahoor Khan (email: wajahat.zahoor@students.uettaxila.edu.pk)

ABSTRACT: An experimental study was performed to analyze the effect of multi-walled carbon nanotubes (MWCNT's) on preheated and post heated mechanical properties of cement mortar. Cement was replaced with 0.125%, 0.25%, 0.375%, and 0.5 wt.% MWCNT's and mortar cubes were then subjected to 25°C, 400°C, and 800°C after 90 days of curing to determine the residual compressive strength. Microstructural analysis was performed on pre-heated and post-heated samples to identify changes in hydration products and decomposition phases by using scanning electron microscopy (SEM). Mortar samples heated at 400°C showed slight changes in microstructure but became more evident at 800°C. Tests performed on pre-heated samples show that the addition of 0.125% in cement as an optimum dosage can increase mortar strength up to 53.4% due to the bridging effect of CNT's which improve load distribution, however higher dosages of CNT's lead to a decrease in strength as compared to optimum mix. It has been determined that higher dosages of CNT's (0.375% and 0.5%) enhanced relative compressive strength of mortar up to 26.3% and 66.9% respectively at 400°C. Similarly, the addition of 0.375% and 0.5% CNT's improved residual compressive strength by 23.64% and 61.4% respectively at 800°C due to reduction in the size of cracks and formation of compact and stable microstructure as observed from SEM images. Besides, an increase in the dosage of CNT's provide sufficient resistance against spalling and reduction in mass of mortar at elevated temperatures.

Keywords - Carbon Nanotubes, Mortar mass loss, Fire resistance, Mechanical properties, Microstructural properties

I. INTRODUCTION

The use of carbon nanotubes (CNTS) as a multifunctional cementitious material has got special attention due to its unique physical and chemical properties. These are hollow cylindrical tubes obtained from single or multiple walls of graphite sheets named single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) having a diameter of about 0.4 nanometers [1]. Due to the high aspect ratio ranging from 30 to many thousands and small size (1nm to tens of nm), carbon nanotubes improve bonding and reduce micro-cracking [2]. The addition of optimum dosage of CNT's (0.01 wt.%) can increase compressive strength and flexural strength of cement composites by 10% and 24% respectively [3]. When concrete or mortar is exposed to high temperatures for a long time, it results in a decrease in mechanical properties like strength, volume stability, and modulus of elasticity[4]. Theoretically, the fire resistance characteristic of mortar and concrete depends on the composition and microstructure of the matrix [5]. At high temperatures, the physical and chemical changes lead to the degradation of mechanical properties [6]. The study has revealed that the bilayer material interface in the composite system is the most vulnerable part which is susceptible to external conditioning. Due to the outstanding physical and mechanical characteristics of CNT's, they can be mixed with cement-based materials to enhance their heating characteristics [7]. Study shows that CNT's can form a shield-like layer that slows down the thermal degradation of polymer nanocomposite [8]. It has been reported that the optimum dosage of MWCT's is 0.08wt% of binder, which firmly binds the components in the matrix [9]. Other studies also suggest that the addition of CNT's in cement paste significantly improves resistance against high temperatures [10].

In recent years, an increase in incidents of building fires have not only damaged lives and property but also caused significant damage to buildings. When a building is subjected to high temperature, the protecting layers of concrete such as mortar starts to deteriorate which leads to the failure of the entire structure. Recent studies show that even though a lot of research has been carried out to address the fire resistance of concrete, however, structures made with both high and low strength concrete are vulnerable to high temperatures [11] [12]. An un-protected structure becomes more susceptible to fire when the finishing layers such as mortars become weak. Study shows that there is no literature available on the performance of nano-modified matrices that could address the behavior of cement mortar at elevated temperatures [13]. Experimental studies on the high-temperature behavior of mortar are limited, therefore the evaluation of new materials such as multiwalled carbon nanotubes is extremely important that could protect mortar at elevated temperatures. In this study cement was replaced with 0.125%, 0.25%, 0.375% and 0.5% CNT's in mortar to investigate:

- Mechanical properties such as post-heated residual compressive strength.
- Microstructural properties of pre-heated and post-heated cement mortar by using SEM images.
- The changes in hydration products due to the incorporation of CNT's after exposing mortar to 400°C and 800°C.
- The loss in mass of mortar at different temperatures.
- The surface characteristics such as color change and pattern of cracking due to elevated temperatures.

II. EXPERIMENTAL PROGRAM

A. MATERIALS

The cement (ASTM Type I) used in this research follows the requirements of (ASTM C150) [14] and has a specific gravity of 3.14. Black-colored multi-walled carbon nanotubes having outer diameter 20-40nm and length 5-15nm were used in this study. The specific surface area of CNTS used was 90-120 m^2g^{-1} having 97% purity. The dosage of the plasticizer was kept as 0.1% of the binder. The maximum and minimum nominal sizes of fine aggregates were recorded as 4.75 and 0.075mm respectively. Sieve analysis of fine aggregates was done according to guidelines of ASTM C136/C136M-19 [15].

B. MIX PROPORTIONS

Mix	w/c	water	cement	sand	plasticizer	CNTS	
		kg/m^3	kg/m^3	kg/m^3	kg/m^3	kg/m^3	%
Control	0.5	234	468	1440	-	-	-
C1 0.125	0.5	234	467.4	1440	2.82	0.6	
C2	0.5	234	466.8	1440	2.82	1.2	0.25
C3	0.5	234	366.2	1440	2.82	1.8	0.375
C4	0.5	234	365.6	1440	2.82	2.3	0.5

C. DISPERSION OF CNTS

CNT's were dispersed in water along with plasticizer by using the process of sonication. In the process of sonication, the pressure waves are created in the liquid due to mechanical vibrations which result in the formation and collapse of microscopic bubbles [16]. In this study, the liquid was sonicated for 30 minutes to obtain a better dispersion of CNT's before mixing with mortar.

D. HEATING AND COOLING REGIMES

After 28 days of curing, the mortar samples were dried in an electric oven at a constant temperature of 100±5 C° to obtain their dry weight. Afterward, the test specimens were subjected to elevated temperatures of 400°C and 800°C. The variation of temperature is shown in Fig.1. In the first stage, the furnace was heated at an approximate rate of 10±25°C/min to obtain the desired temperature across the cross-section of the furnace. Mortar specimens after subjected to 400°C and 800°C are shown in Fig.2. In the second stage, the samples were allowed to remain in the furnace for 2 hours at a constant temperature. Afterward, the furnace was allowed to cool down slowly, with an approximate rate of cooling of 2±1°C/min.

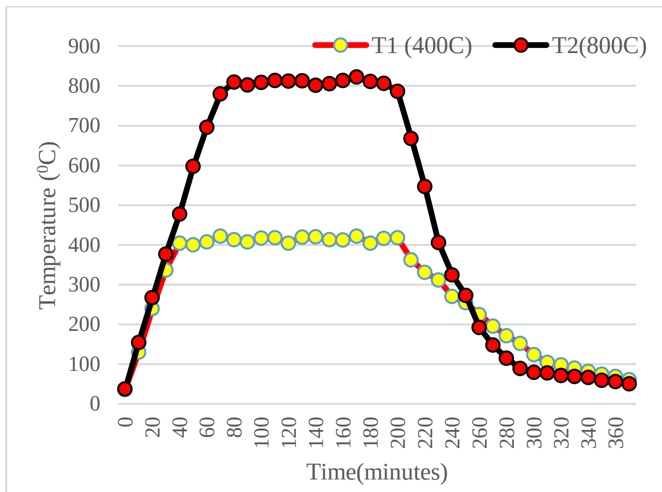

FIGURE 1: Variation of furnace temperature for 400°C and 800°C.

FIGURE 2. Mortar specimens after subjected to 400°C and 800°C.

III. TESTING PROCEDURE

A. COMPRESSIVE STRENGTH TEST

The pre-heating and post-heating compressive strength of cubes having a size of 70mm were found according to the guidelines of ASTM C109 [17]. The load was transferred uniformly over cube through rubber pad at top of the cylinder.

B. MICROSTRUCTURAL ANALYSIS

The mineralogical characterization of mortar samples was carried out by using X-ray diffraction and microstructural analysis was performed by scanning electron microscopy (SEM) to determine the structure of hydration products. Cubical specimens having sizes of 20mm from different samples were obtained to obtain SEM images at different resolutions ranging between 5-50 µm.

C. MASS LOSS TEST

The mass loss of mortar samples was recorded before and after exposure to heat in terms of percentage. The damage that occurred to mortar due to different temperatures was visually inspected and recorded in photographs.

IV. RESULTS AND DISCUSSIONS

A. PRE HEATING COMPRESSIVE STRENGTH

The compressive strength test was conducted for cement mortars containing various dosages of CNT's before subjected to fire. The microstructural analysis of control specimens shows the formation of C-S-H gel and $Ca(OH)_2$ crystals as shown in Fig.5 (a). Study shows that mortar specimens containing different dosages of CNT's exhibited higher compressive strength as compared to control sample. Experimental results show that replacement of cement with 0.125% of MWCNT's as an optimum dosage has increased the compressive strength of mortar by 53.4% at 90 days. Similarly, the addition of 0.25%, 0.375%, and 0.5% CNT's also led to an increase in compressive strength of mortar by 38.5%, 24.5%, and 0.5% respectively, showing significant improvement in compressive strength of mortar cubes as compared to the control sample, however, a decreasing trend in mortar compressive strength has been noticed in specimens containing higher dosages of CNT's as compared to the optimum mix of mortar. The improvement in compressive strength of mortar containing different dosages of CNT's is due to the bridging action of CNT's which helped to distribute load among cement matrix. The presence of a small amount of CNT's produced well crystalline hydrates that were bridged with fibers of CNT's which contributed towards the improvement of compressive strength of mortar as evident from the SEM study presented in Fig.5 (b). An increase in compressive strength of mortar is due to adequate adhesion of nano-fibers from CNT's with cement interface [18]. A recent study conducted by Y. Gao et al. [19] shows that the addition of 0.1% CNT's in mortar has improved the mechanical properties and modulus of elasticity of mortar. Similarly, V. Rocha [20] reports that the addition of 0.05% CNT's can increase the compressive strength of mortar up to 34%. Similar results were reported in research carried out by [21] showing that the replacement of composite cement with 0.1% MWCNTS gives higher compressive strength and 0.2% MWCNTS leads to a decrease in strength. The reduction in compressive strength is regarded due to the formation of agglomerates of CNT with cement paste which produced local stress raisers that reduced the strength of mortar [22]. The microstructural study carried out in a recent study also suggests that the addition of 0.35-0.5 wt.% CNT's form congested areas of CNT's in the cement matrix which results in strength loss [23].

B. POST HEATING COMPRESSIVE STRENGTH

The residual strength of mortar specimens was determined after exposing mortar specimens to 400^{o}C and 800^{o}C. The relative strength of the mortar specimen was also calculated by comparing the strength of preheated and post heated specimens. As shown in Fig.3. Study shows that mortar specimens containing higher dosages of CNT's performed very well when exposed to 400^{o}C and 800^{o}C, however significant amount of strength reduction was noticed to the specimens containing a small dosage of CNT's. It was found that mortar specimen containing 0.125% CNT's has lost 26.4% and 36.16% of their compressive strength as compared control sample which lost 32.2% and 43% of its compressive strength when specimens were exposed to 400^{o}C and 800^{o}C respectively. Similarly, the mortar specimen containing 0.25% CNT's lost 6.2% and 13.2% of its compressive strength after exposure of 400^{o}C and 800^{o}C. Higher reduction in compressive strength is due to the decomposition of calcium hydroxide when the mortar was heated between 400^{o}C and 500^{o}C. However, it was observed that the presence of small dosages of CNT's (0.125% and 0.25%) can improve the residual strength of mortar up to 67% and 97% as compared to the control sample at 800^{o}C respectively. The improvement in residual strength is ascribed due to the bridging action of CNT's. The reinforcing action of CNT's was studied through microstructural showing that the presence of CNT's has contributed towards the formation of stable microstructure. Microstructural study of control samples of mortar subjected to 800^{o}C induced concentration of thermal stresses which resulted in the formation of cracks as shown in Fig.4 and Fig.6 (a). An enhancement in compressive strength up to 26.35% and 23.64% was observed when mortar specimens containing 0.137% CNT's were heated at 400^{o}C and 800^{o}C respectively. A similar study conducted by [24] suggests that the compressive strength of mortar specimens containing different dosages of CNT's continued to increase when subjected to high temperature. The improvement in compressive strength is attributed due to the continuation of the hydration process of cement and the ability of CNT's to create microscopic channels in the matrix for releasing high-pressure steam resulted from the evaporation of water which induced less damage and cracking [25]. Similarly, the incorporation of multi-walled carbon nanotubes resulted in less cracking due to the distribution of thermal stresses which led to an increase in thermal conductivity and reduction of specific heat. The improvement in the fire resistance of mortar is due to the contribution of carbon nanotubes where it helped to reduce the pore size between ettringite and calcium silicate hydrates (C-S-H) which led to the denser structure as shown in Fig.6 (b). The results obtained in this study recommend the potential use of carbon nanotubes in construction of structures that are vulnerable to fire.

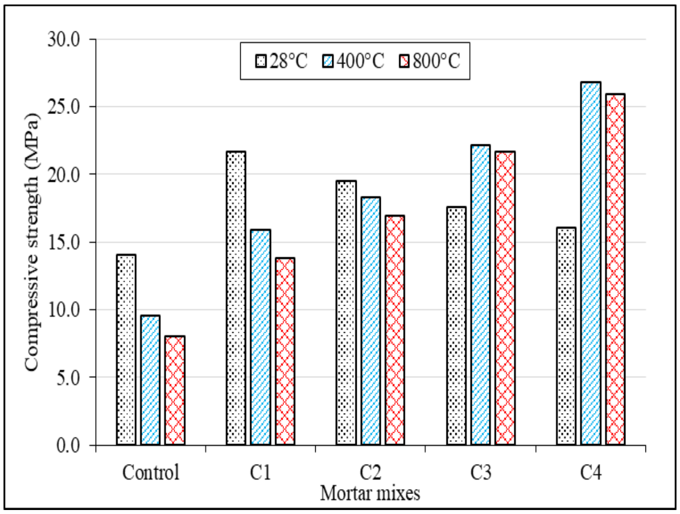

FIGURE 3. Pre-heating and post-heating compressive strength of mortar specimens containing CNTS.

FIGURE 4. Post heated failure pattern of mortar cubes containing CNTs subjected to the compressive test.

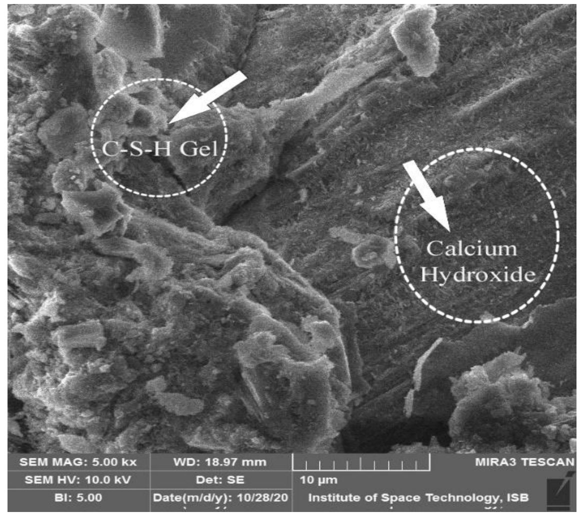

FIGURE 5 (a). Control specimen of mortar at 25°C.

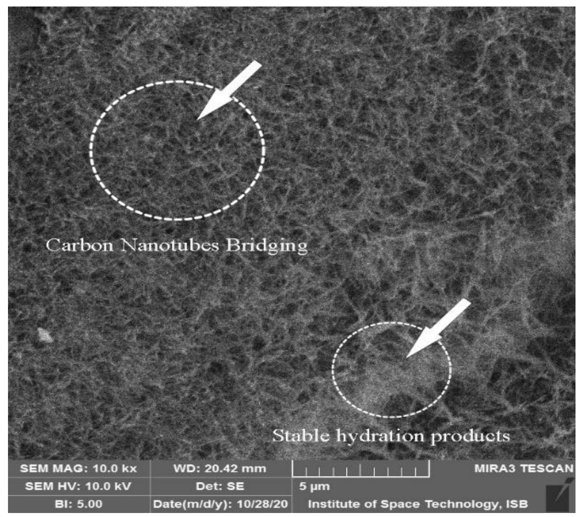

FIGURE 5 (b). Mortar specimen containing CNT's at 25°C.

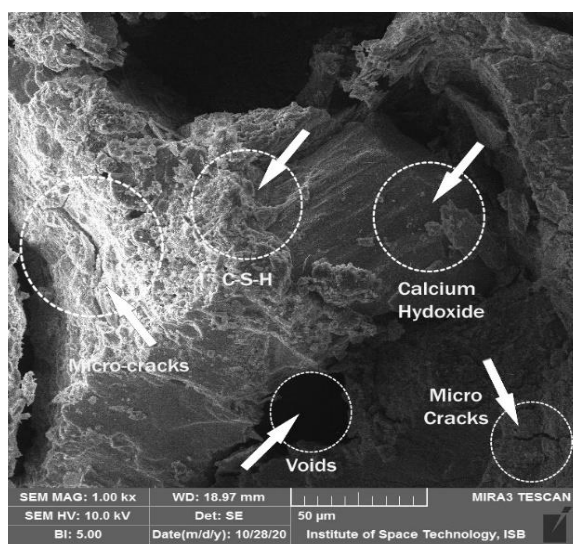

FIGURE 6 (a). Control specimen of mortar at 800°C.

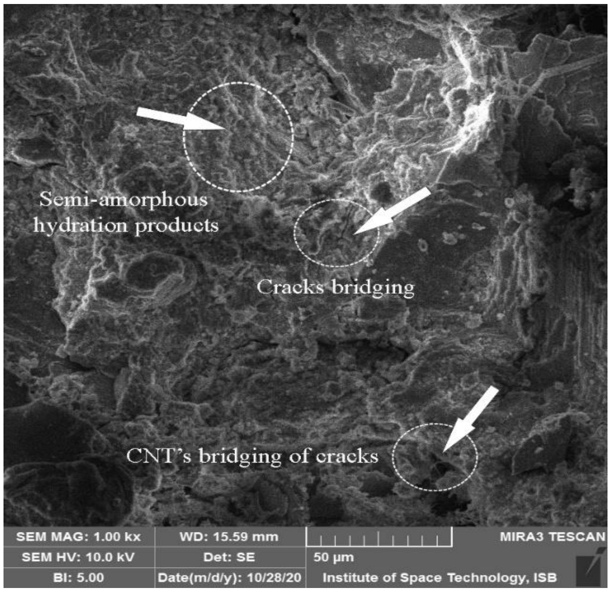

FIGURE 6 (b). Mortar specimen containing CNT's at 800^{o}C.

C. MASS LOSS TEST

The relative loss in mass of mortar specimens subjected to various temperatures is shown in Fig.7. Three specimens from each mix were weighted to determine the reduction in their mass before and after heating. Results show that exposing mortar specimens to high temperatures resulted in a significant reduction in their mass, however, the addition of CNT's increased the resistance against a reduction in mass. Mortar specimens containing higher dosages of CNT's also performed very well in the fire while maintaining their masses. It was observed that the control sample of mortar lost 18.66% and 12.4% of its mass at 400^{o}C and 800^{o}C respectively, however, the specimens containing 0.125% and 0.25% CNT's lost 11.70 and 7% of their mass when exposed to 800^{o}C. Similarly, mortar specimens containing 0.375% and 0.5% CNT's lost only 6.9% and 5.7% of their mass as compared to the control sample showing that higher dosages of CNT's have significantly improved fire resistance which provided stability to mortar. Heating mortar specimens between 50-200^{o}C resulted in the evaporation of interlayer water which led to a reduction of mortar mass due to the decomposition of C-S-H gel [26]. However, the presence of CNT's contributed significantly to confining mesopores and nanopores which lead to the formation of stiff C-S-H gel [27], [28]. Also, the inclusion of CNT's in mortar helped in the formation of stable hydration products that significantly contributed towards the retention of mass even up to 800^{o}C as evident from SEM images. It is established that the addition of carbon nanotubes in mortar can enhance mortar resistance against mass loss which could help in protecting different types of concrete that are vulnerable to fire. Also, inclusion of CNT's can help to provide sufficient resistance against spalling and cracking.

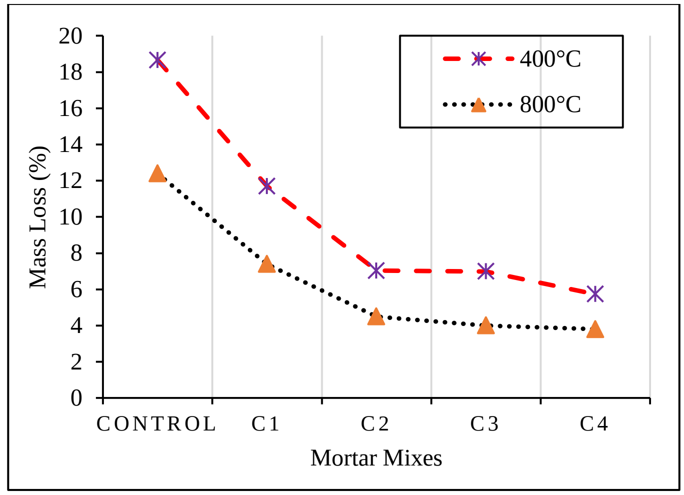

FIGURE 7. Mass loss of mortar specimens at 400^{o}C and 800^{o}C.

V. CONCLUSION

This research program was carried out to evaluate the mechanical properties and fire resistance behavior of mortar containing optimum dosages of multi-walled carbon nanotubes. The following conclusions are made from this study.

1. The study performed on preheated mortar specimens shows that the addition of 0.125% CNTS as an optimum dosage can increase the compressive strength of mortar up to 53.4% at 90 days. Similarly higher dosages of CNT's also enhance the compressive strength of mortar as compared to control specimen, however, the improvement is less as compared to optimum mix.
2. The addition of CNT's reduced cracking and enhanced the load-carrying capacity of mortar. It has been determined that mixing 0.5% CNT's in cement can improve the relative strength of mortar up to 66.9% and 61.44% respectively as 800^{o}C.
3. SEM images show that the introduction of CNT's refines the microstructure of mortar by bridging cracks which results in significant improvement in fire resistance and residual strength or mortar.
4. Mortars exposed to 800^{o}C revealed a reduction in the amount of calcium hydroxide and calcium silicate hydrate gel, however, the study also evidenced bridging of hydration products and cracks due to the presence of nano-reinforcements of CNT's which improved the thermal stability of mortar even at high temperatures.
5. The addition of 0.25% and 0.5% CNT's can enhance the resistance of mortar against mass loss up to 62.5% and 69.28% respectively at 800^{o}C. The

presence of CNT’s prevents the cracking and spalling of mortar.

6. The findings obtained in this study recommend the potential use of carbon nanotubes in cement mortar to protect buildings from fire, however, further analysis on flexural and deformation behavior of mortar is recommended.

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