



High-Performance Cementitious Matrix using Carbon Nanofibers

Muhammad Maqbool Sadiq Awan¹, Parviz Soroushian², Arshad Ali¹, Muhammad Yousaf Saqid Awan

¹CE Wing, Military College of Engineering, National University of Sciences and Technology, Islamabad 44000, Pakistan

²Department of Civil and Environmental Engineering, Michigan State University, Engineering Building 428 S. Shaw Lane, Room 3546 East Lansing, MI 48824, US

* Correspondence: arshadali@mce.nust.edu.pk

ABSTRACT

Graphite nanomaterials would realize their reinforcement potential within cement-based materials when they are thoroughly dispersed and effectively bonded to cement hydrates. Thorough dispersion of graphite nanomaterials in the fresh cementitious matrix encounters challenges associated with the hydrophobic nature of nanomaterial surfaces and their strong tendency towards agglomeration via attractive van der Waals forces. Effective interfacial interactions with cement hydrates are further challenged by the relatively inert nature of nanomaterial surfaces. An experimental program was conducted with the objective of effectively utilizing both acid-oxidized and pristine carbon nanofibers towards reinforcement of high-performance cementitious pastes. Hybrid reinforcement systems comprising optimum volume fraction of carbon nanofibers and micro-scale fibers were also evaluated in cementitious matrices. The improvements in nanofiber dispersion and interfacial interactions resulting from acid-oxidation and use of proper dispersion techniques were found to bring about significant gains in the engineering properties of high-performance cementitious materials.

© 2017 Tim Pengembang Jurnal UPI

ARTICLE INFO

Article History:

Submitted/Received 13 Dec 2016

First revised 15 Jan 2017

Accepted 29 Mar 2017

First available online 01 Apr 2017

Publication date 01 Apr 2017

Keyword:

*Cementitious
Nanocomposites,
Carbon Nanofibers,
High Performance.*

1. INTRODUCTION

Cementitious materials are generally characterized as brittle materials with relatively low tensile strength and strain capacity, which are susceptible to early-age cracking due to restraint of shrinkage movements. (D'Ambrosia, 2012) These problems tend to be more pronounced in the case of high-performance cementitious materials with high compressive strengths. (Bui *et al.*, 2005) Fibers (with micro-scale diameters) are incorporated into cementitious matrices to overcome these drawbacks. The micro-scale diameters and relatively low aspect (length-to-diameter) ratios of these fibers, and their viable volume fractions in cementitious materials; however, yield relatively large fiber-to-fiber spacing and relatively small specific surface area of fibers. (Peyvandi *et al.*, 2013) These features limit the effectiveness of micro-scale fibers in controlling the flaw (microcrack) size and propagation in cementitious materials. (Peyvandi & Soroushian, 2015) Slender nanomaterials (e.g. carbon nanofibers) with nano-scale diameters and relatively high aspect ratios offer the potential to overcome these drawbacks of micro-scale fibers in cementitious materials. (Chen *et al.*, 2011) The relatively close spacing and high specific surface area of nanomaterials provide them with the potential to effectively control the flaw size and propagation in cementitious materials. (Peyvandi & Soroushian, 2015) The close spacing of nanomaterials could also enhance the moisture barrier qualities and thus the durability characteristics of cementitious materials by forcing tortuous diffusion paths of moisture (and aggressive solutions) into cementitious materials. (Peyvandi *et al.*, 2013)

Previous research on high-performance cementitious materials reinforced with multiwall carbon nanotubes (MWCNTs) has shown that, as far as the uniform dispersion

and effective interfacial interactions of nanotubes within cementitious paste are achieved, important gains in diverse engineering properties of cementitious materials can be realized at nanotube volume fractions in less concentration of the cementitious paste. (Sbia *et al.*, 2015). The work reported herein examines the potential of carbon nanofibers (CNFs), which are of substantially lower cost when compared with carbon nanotubes, to bring about balanced gains in engineering properties of high-performance cementitious materials.

Carbon nanofibers have a unique hybrid grapheme sheet structure based on conical and tubular elements. Their diameters range from 50 to 200 nm (which are greater than typical nanotube diameters). CNFs provide high mechanical properties (e.g., 25 to 200 GPa elastic modulus depending on their diameter), (Lawrence *et al.*, 2008) specific surface areas and aspect ratios, which are below those of carbon nanotubes. Their electrical and thermal conductivity as well as thermal and chemical stability are also relatively high. When compared to carbon nanotubes, carbon nanofibers provide more active sites on their surfaces for bonding to cementitious materials. The desired combination of performance and cost of carbon nanofibers suits applications in the field of nanocomposites. Past research efforts have focused on development of CNF-polymer nanocomposites. (Shofner *et al.*, 2003; Hammel *et al.*, 2004; Lafdi *et al.*, 2008) Limited work has been conducted on the use of carbon nanofibers in cementitious matrices. The prerequisites for successful use of CNFs in cementitious materials include thorough dispersion and effective interfacial interactions of CNFs within the cementitious matrix. (Xie *et al.*, 2005) Past research efforts have examined the effects of 0.005, 0.02, 0.05, 0.5, and 2% CNF by

weight of cementitious materials on the microstructure and mechanical properties of a cementitious matrix with 10% of cement replaced with silica fume. (Sanchez & Ince, 2009) The effects of surface treatment of CNFs with nitric acid on their reinforcement efficiency (at 0.5% by weight of cementitious materials) were also evaluated. It was found that the use of silica fume and surface treatment of CNFs facilitated their dispersion, and improved their interfacial interactions with the cementitious paste. The gains in engineering properties (splitting tensile strength and compressive strength) of cementitious matrix with introduction of carbon nanofibers were, however, insignificant. Other investigations involving microscopic observations have indicated that CNFs can control cracking in cementitious materials by bridging across fine cracks, yielding improvements in flexural strength of cementitious materials at weight fractions of about 0.048%. (Metaxa *et al.*, 2010)

In this study, the effects of surface functionalization of carbon nanofibers (CNFs) through introduction of carboxyl groups and use of refined dispersion techniques on the reinforcement efficiency of nanotubes at different volume fractions within a high-performance cementitious (densified with small particles – DSP) matrix were evaluated. Scanning electron microscope observations of fractured surfaces pointed at successful dispersion of nanofibers within the cement-based matrix. An investigation of hybrid reinforcement systems comprising CNFs and micro-scale fibers (CMFs) indicated that selected hybrid systems offer a cost-effective approach for realizing balanced gains in performance characteristics of high-performance cementitious matrices.

2. MATERIALS AND METHODS

2.1. Materials

The carbon nanofibers (CNFs) used in this investigation had outer diameters in the 60-150 nm range, lengths ranging from 30 to 100 μm , specific surface area of 50-60 m^2/g , true density of $\sim 1.95 \text{ g/cm}^3$, and >95% purity. They were either pristine (NF, see **Figure 1a**) or oxidized via acid-functionalized (NF-OX, see **Figure 1b**). These nanofibers were purchased from Pyrograf Products, Inc. Carbon microfibers (TT 143, obtained from Toho Tenax America, Inc.), shown in **Figures 1c**, were 6 mm long, with 6-7 μm diameter. Deionized (DI) water was used for all solution preparations.

2.2. Dispersion of Nanofibers in Water

The steps involved dispersion of carbon nanofibers in the mixing water of cementitious matrix. In short, first, we added the required amount of pristine or oxidized nanofibers to the mixing water. Then, we stirred the mix overnight (12 to 15 h) using a magnetic stirrer (**Figure 2a**). Next, the mix was sonicated using a probe as follows (**Figure 2b**):

1. Sonicate for ten minutes at each of the 30, 45, 65, and 75% amplitudes, with 1-minute breaks between different amplitudes;
2. Pulse (sonicate over 1 minute and rest for 30 seconds) over a period of 10 minutes at 85% amplitude;
3. Turn off the sonic probe for 2 minutes, and repeat the pulse cycle two more times;
4. Repeat steps i through iii.

Finally, we added the required amount of carbon microfibers (for hybrid mixes only) to the aqueous dispersion of nanotubes prior to adding them to the remaining ingredients of the cementitious matrix in mixer.

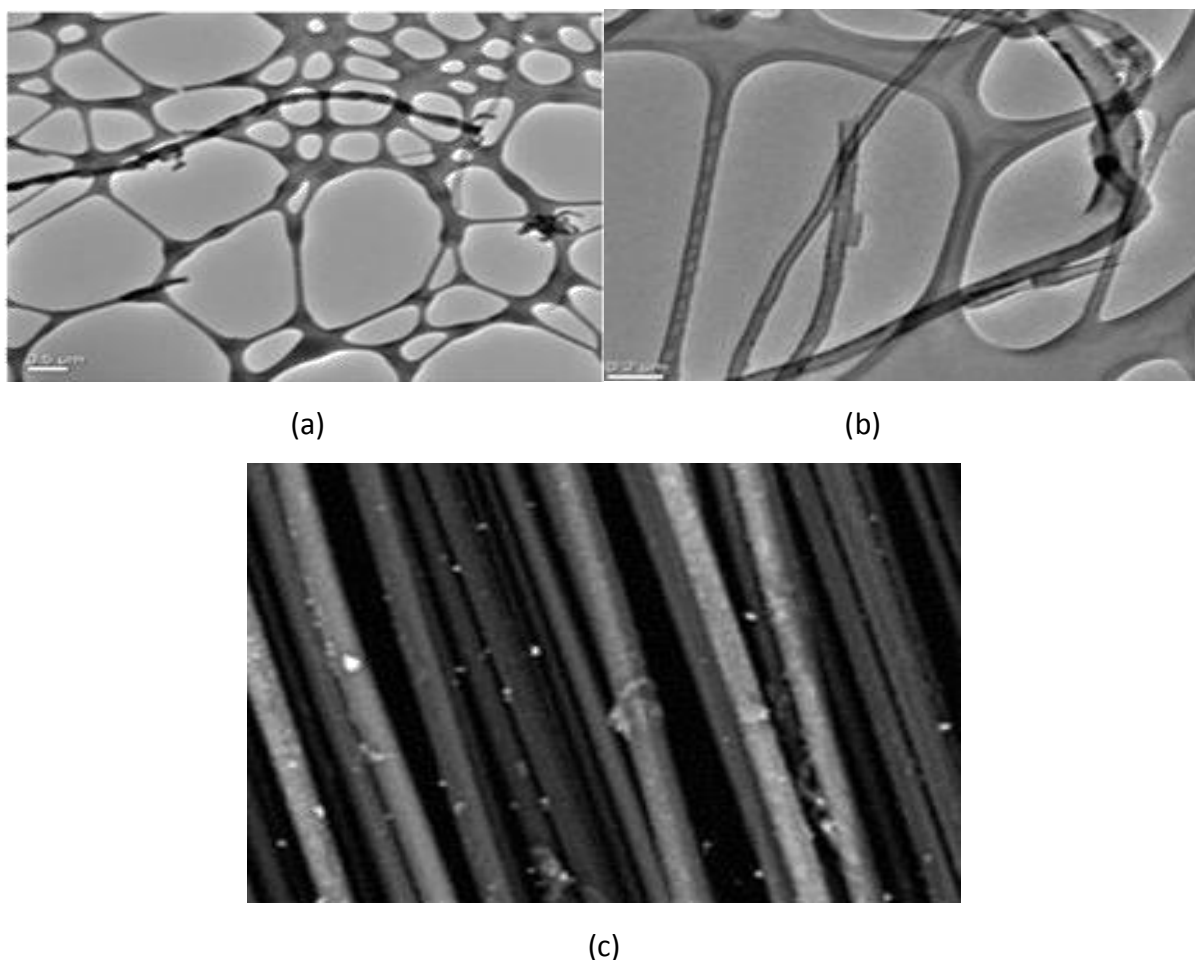


Figure 1. Microscope images of carbon nanofibers and microfibers: (a) TEM micrograph of non-functionalized nanofibers with 60-150 nm outer diameter and lengths up to 100 µm; (b) TEM micrograph of oxidized nanofibers with 60-150 nm outer diameter and lengths up to 100 µm ; (c) SEM micrograph of carbon microfibers (TT 143) with 6 mm length.

2.3. Cementitious Matrices

A dense cement-based matrix with a smooth particle size gradation covering nano- to micro-scale range was used to ensure effective interfacial interactions which help mobilize the tremendous mechanical qualities of graphite nanomaterials within cementitious nanocomposites. The high-performance cement-based matrix used here is generally referred to as densified with small particles (DSP). DSP cement-based materials

comprise micro-scale cement and nano-scale silica fume particles, dispersed and densified using superplasticizer (**Figure 3**). This cementitious matrix, when used with other high-quality ingredients (e.g., high-quality aggregates and discrete reinforcement) can yield highly desired combinations of mechanical and durability characteristics suiting demanding fields of application.



Figure 2. Dispersion equipment: (a) Magnetic Stirrer and (b) Sonication horn

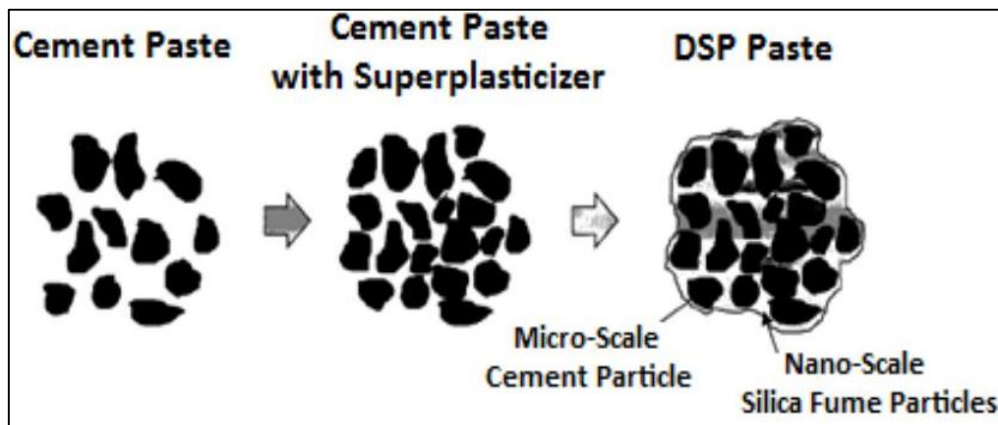


Figure 3. Schematic depiction of high-performance Densified with small particles (DSP) cementitious paste

The microstructure and thus engineering properties of high-performance (DSP) cementitious materials can be improved by steam or high-pressure steam curing, which benefit the pozzolanic reactions of reactive micro-scale fillers; this sub-category of DSP cementitious materials is generally referred to as reactive powder concrete (RPC).

Based on a review of the literature on DSP (and RPC) high-performance

cementitious materials, the cementitious paste matrix introduced in **Table 1** was selected for evaluation of the merits of graphite nanomaterials in cement-based matrices. The materials selected for use in this high-performance (DSP) cement-based matrix include: Type I Portland cement (Lafarge-North America), undensified silica fume (Norchem, Inc.) with 200 nm average particle size, and Glenium 7700 polycarboxylate-based Type F ASTM C 494 superplasticizer (BASF).

Tabel 1. Mix proportions of the high-performance (densified with small particles – DSP) cementitious matrix selected for evaluation of the reinforcement efficiency of carbon nanofibers and/or microfibers.

Component	Information
Silica Fume/Binder	0.20
Water/Binder	0.185
Superplasticizer/Binder	Adjusted for different reinforcement Conditions

Cementitious materials (with and without functionalized graphite nanomaterials dispersed in the mixing water) were prepared following ASTM C192 and C305 procedures. The specimens were moist-cured inside molds after casting (ASTM C 192) over a 24-hour period, and were then demolded and subjected to 48 hours of steam curing at 70°C. The samples were subsequently conditioned at 50% relative humidity for seven days prior to testing. At least two mixes were prepared for each reinforcement condition, and at least two specimens from each mix were tested for evaluation of each engineering property.

2.4. Experimental Methods

The test procedures employed to determine the engineering properties of cement-based materials are described in this section. *Compression* tests (ASTM C 109) were performed on 50 mm cube specimens. *Flexure* tests (ASTM C 1185) were performed on 12.5x50x150 mm specimens by center-point loading on a span of 125 mm using a deflection-controlled mechanical test system, with load and deflection data collected throughout the test using a data acquisition system. *Impact* tests (ASTM D 7136) were performed on 12x150x150 mm specimens. These specimens were subjected to the impact of a fixed weight (with 1.5 mm in diameter tip)

dropped from heights increasing sequentially by 2.5 mm until the specimen exhibited visible cracking. *Abrasion* tests (ASTM C 944) were conducted on the surface of cylindrical specimens with 100 mm diameter (and 50 mm height). The specimens were subjected to six 2-minute periods of abrasion.

2.5. Analysis

The following experimental methods were also employed to gain further insight into the structure and failure mechanisms of cement-based nanocomposites: (i) scanning electron microscopy (SEM); and (ii) Energy Dispersive Spectroscopy (EDS). The experimental results were subjected to statistical analysis using the analysis of variance (ANOVA) and pair-wise comparison methods. The failed surfaces of flexure and compression test specimens were evaluated under a high-precision SEM (JEOL 7500F and JEOL JM-6300F, Japan). All samples were coated with Osmium (Using Osmium Coater Neoc-AN, Meiwa Shoji, Japan) prior to SEM observations.

3. RESULTS AND DISCUSSION

3.1. Effects of Carbon Nanofiber Surface Functionalization on Engineering Properties

3.1.1. Flexural Performance

Typical flexural load-deflection curves for cementitious (DSP paste) matrices

reinforced with 0 and 0.24% volume fractions of acid-functionalized and non-functionalized nanofibers are shown in **Figure 4**. Volume fraction is calculated here with respect to the volume of cement and silica fume. The mean values of flexural strength, maximum deflection and energy

absorption capacity (area underneath the flexural load-deflection curve) are summarized in **Table 2**. The mean values and standard deviations of the flexural strength and energy absorption capacity test results are presented in **Figure 5**, respectively.

Table 2. Mean values of the flexural strength, maximum deflection and energy absorption capacity test results for high-performance cementitious pastes with 0 and 0.24% (by volume of cement plus silica fume) of non-functionalized and acid-functionalized carbon nanofibers.

Reinforcement Condition	Flexural Strength (MPa)	Maximum Deflection (mm)	Energy Absorption (N.mm)
Plain	10.30	0.40	62
Acid-functionalized nanofiber (NF-OX), 0.24 vol.%	15.70	1.18	245
Non-functionalized nanofiber (NF), 0.24 vol.%	9.09	0.79	102

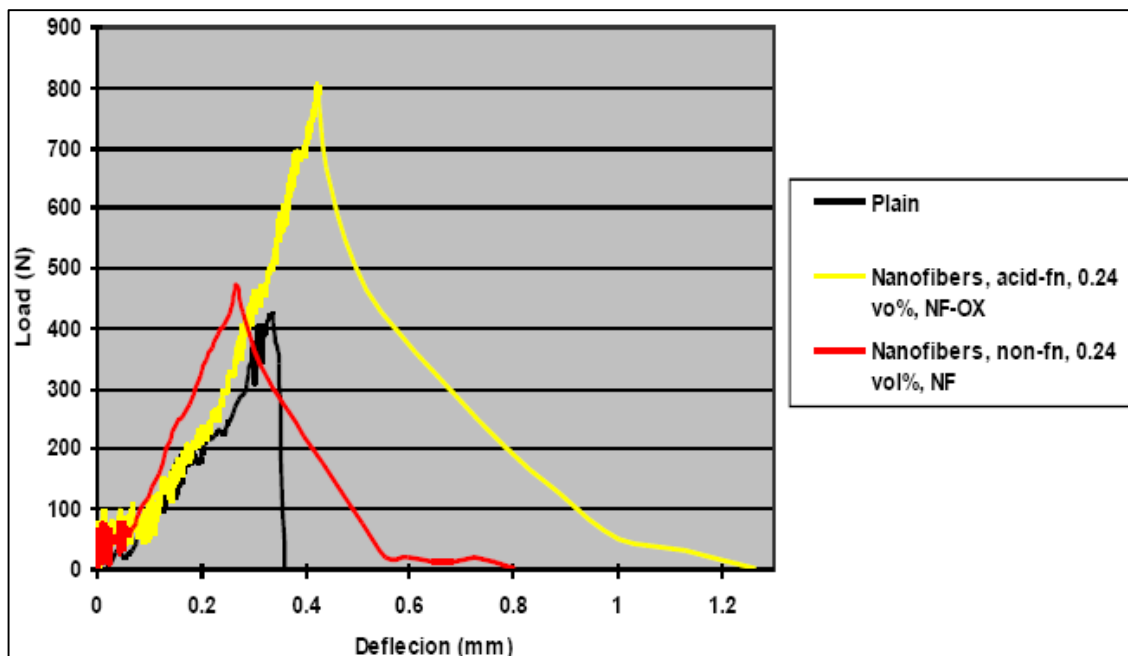


Figure 4. Representative flexural load-deflection curves of high-performance cementitious pastes with 0 and 0.24% (by volume of cement plus silica fume) of non-functionalized and oxidized nanofibers per volume of cement plus silica fume.

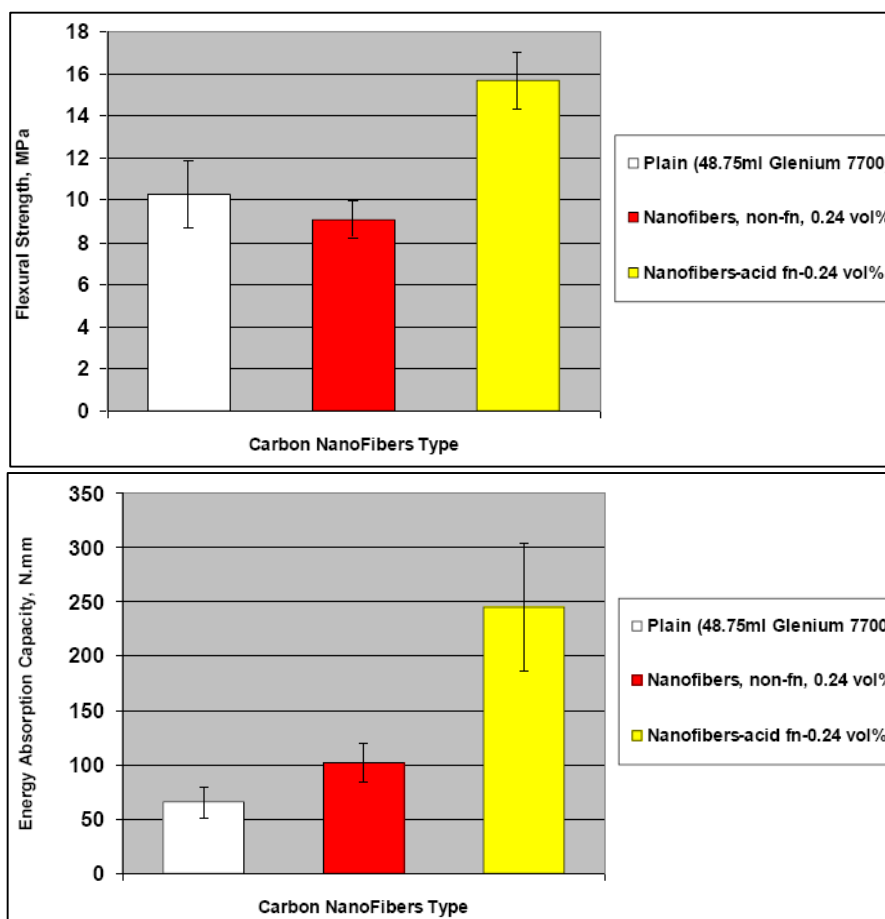


Figure 5. Mean values and standard errors of the flexural strength (top) and energy absorption capacity (down) of high-performance cementitious pastes reinforced with 0 and 0.24% (by volume of cement plus silica fume) of non-functionalized and acid-functionalized carbon nanofibers.

Acid-oxidized Nanofibers produced significant gains in the flexural strength and especially energy absorption capacity of the cementitious matrix. The improvements in flexural strength and energy absorption capacity were 52 and 296%, respectively. The relatively large length of carbon nanofibers benefits their contributions to energy absorption capacity via extended frictional pullout at cracks. The contributions of oxidized carbon nanofibers to the flexural energy absorption capacity and strength of the high-performance cementitious paste were confirmed through statistical analysis (ANOVA) of test results at 0.001 of

significance level. Non-oxidized Nanofibers produced a drop in flexural strength, although they contributed to the flexural energy absorption capacity and maximum deflection of the cementitious matrix. The drop in flexural strength can be attributed to the potential for clumping of non-functionalized nanofibers in the cementitious matrix. This observation was confirmed by SEM observations, see **Figure 6**. The contributions of carbon nanofibers to the flexural performance characteristics of high-performance cementitious materials are attractive, given their relatively low cost when compared with other nanomaterials.

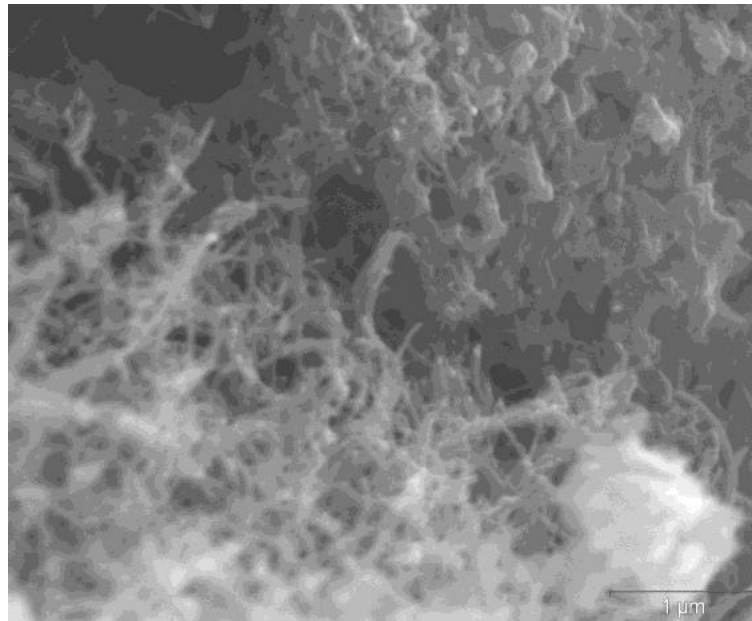


Figure 6. Clumping of non-functionalized carbon nanofibers in the high-performance cementitious paste at 0.24% by volume of cement plus silica fume.

3.1.2 Compressive Strength

The compressive strength test results (means and standard deviations) are summarized in **Figure 7**. The compressive strength of the high-performance cementitious matrix is observed to be either

preserved or improved with the addition of nanofibers. Analysis of variance of test results indicated that, at 0.05 significance level, the high compressive strength of the cementitious matrix was preserved after introduction of nanofibers.

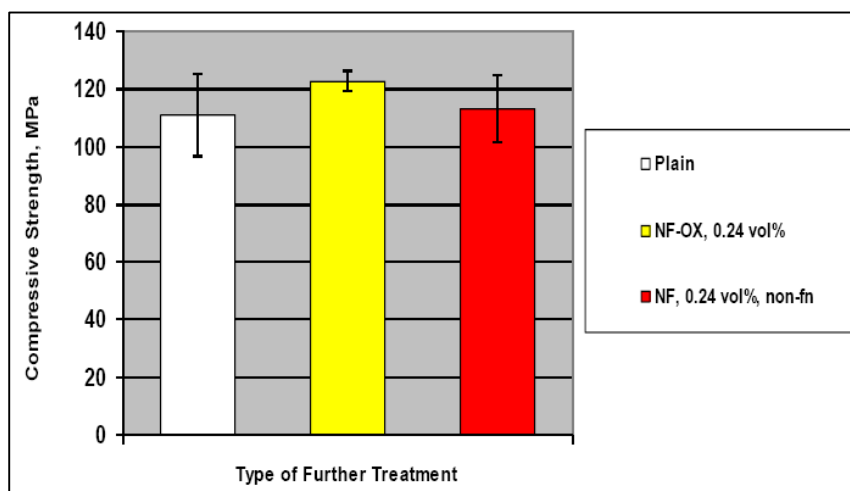


Figure 7. Mean values and standard errors of the compressive strength test results for high-performance cementitious paste reinforced with 0 and 0.24% (by volume of cement plus silica fume) of non-functionalized and acid-functionalized carbon nanofibers.

3.1.3 Impact Resistance

Examples of failed impact test specimens are shown in **Figure 8**, whereas the mean values of impact test results are presented in **Figure 9**. The impact resistance of cementitious materials is observed to increase with introduction of 0.24% in volume fraction of both non-functionalized and acid-functionalized Nanofibers.

The test results suggest that functionalization of nanofibers benefits their contributions to the impact resistance of the cement-based matrix. The functionalized and non-functionalized nanofibers, at 0.24% (with respect to cementitious materials), yielded about 73.6 and 44.7% gains, respectively, in impact resistance, which can be attributed to the arrest and deflection of microcracks, pullout of nanofibers, and multiple cracking phenomena in the presence of nanofibers. Cementitious materials reinforced with oxidized nanofibers exhibited more pronounced

multiple cracking as compared to those with pristine nanofibers (**Figure 8**).

3.1.4 Abrasion Resistance

Examples of photograph images of abrasion test specimens after performance of abrasion tests are shown in **Figure 10**. The abrasion test results presented in **Figure 11** indicates that cementitious materials with oxidized and pristine nanofibers, 0.24% of volume fraction (with respect to the cement and silica fume volume) showed superior abrasion resistance when compared when compared with the plain cementitious matrix. The significant increase in abrasion resistance with oxidized nanofibers can be attributed to their thorough dispersion and effective interfacial interactions in the high-performance cementitious matrix. Analysis of variance of test results indicated that the contributions of nanofibers to the abrasion resistance of high-performance cementitious matrix were statistically significant at 0.05 of significance level.

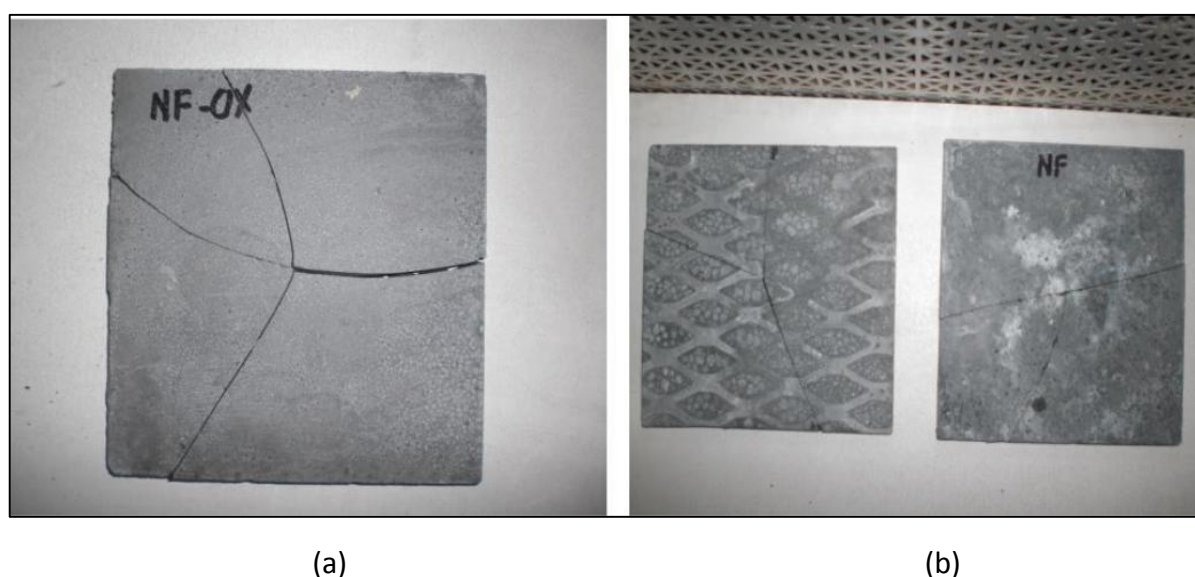


Figure 8. Failed impact test specimens in low (a) and high magnification (b).

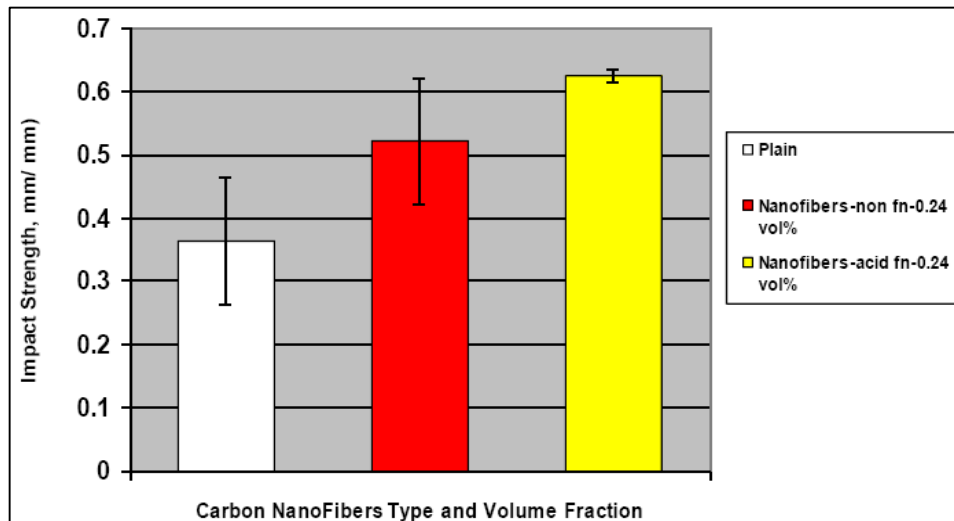


Figure 9. Mean values and standard errors of the impact resistance test results for high-performance cementitious paste reinforced with 0 and 0.24% (by volume of cement plus silica fume) of non-functionalized and acid-functionalized carbon nanofibers.

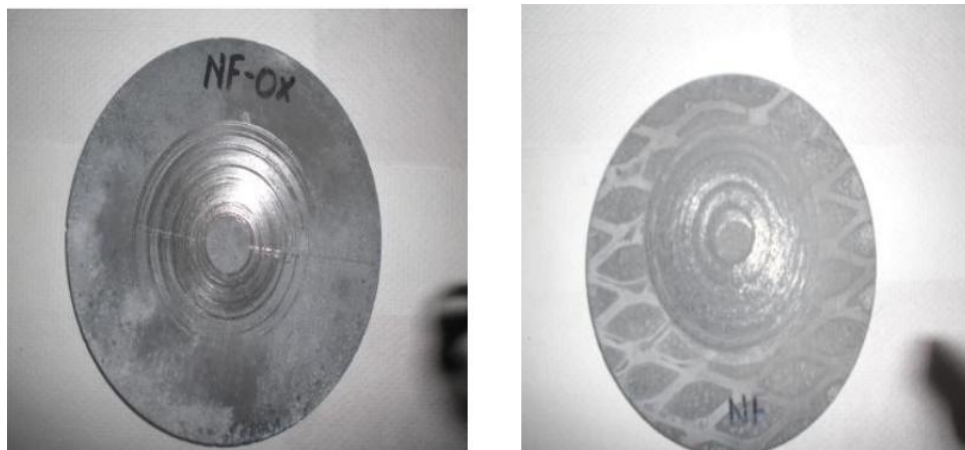


Figure 10. Abrasion test specimens after test.

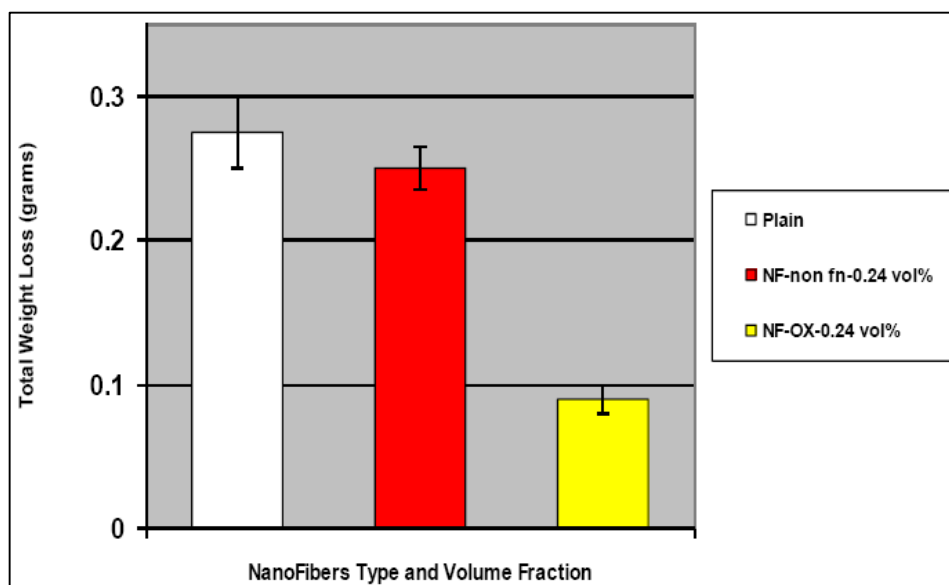


Figure 11. Mean values of abrasion weight loss for high-performance cementitious pastes reinforced with 0 and 0.24% (by volume of cement plus silica fume) of non-functionalized and acid-functionalized carbon nanofibers.

3.1.5 Scanning Electron Microscope Evaluation

The SEM images presented in **Figure 12** indicate that the refined sonication and mixing steps developed in the project were successful in dispersion of individual oxidized nanofibers within the cementitious matrix at 0.24 vol% of cement and silica fume. These images also point at the low porosity of the high-performance cementitious matrix used here; the

introduction of nanofibers does not seem to have compromised the high density (low porosity) of this matrix. SEM observations verified the uniform dispersion of oxidized nanofibers; evidences of crack suppression and crack bridging were also found in all specimens examined under SEM. Oxidized nanofibers, which provided higher levels of reinforcement efficiency, were found to be more uniformly dispersed within the cementitious matrix, as some clumping was found for pristine nanofibers.

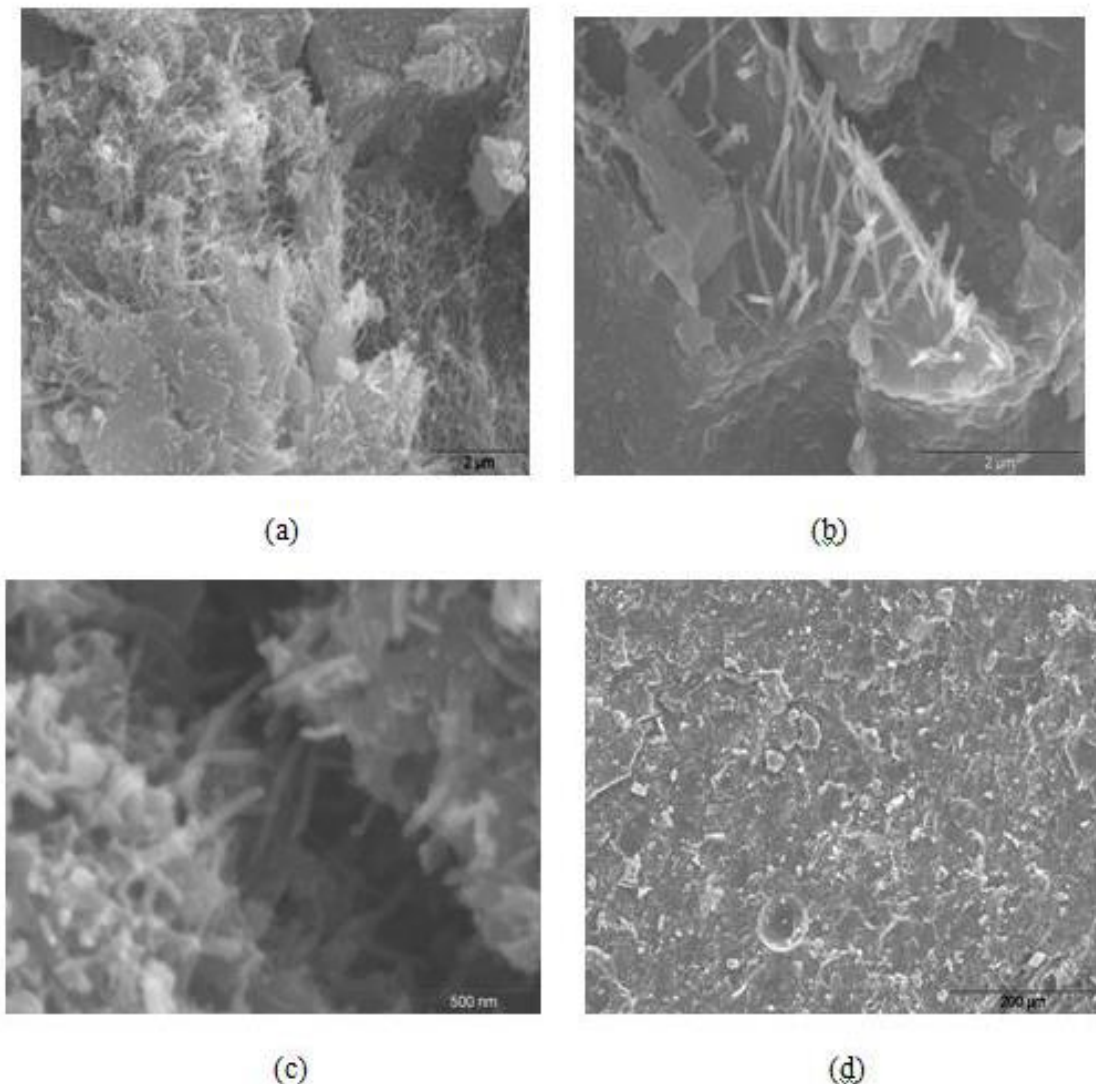


Figure 12. Typical SEM images of high-performance pastes reinforced with 0.24% (by volume of cement plus silica fume) of carbon nanofibers: (a) uniform dispersion of nanofibers in matrix; (b) and (c) micro-crack-bridging action of nanofibers; (d) dense DSP matrix.

3.1.6 Energy-Dispersive Spectroscopy (EDS)

Elemental analyses were performed on 2.54x12x12 mm samples of high-performance cementitious paste with 0 and 0.24 vol% pristine and oxidized carbon nanofibers. The specimens were coated with carbon (using Carbon String Evaporator, Ernest F. Fullam) to make them more conductive for the purpose of EDS analysis. Elemental and Quantitative analyses of these samples indicated that all

cementitious materials exhibit similar elemental compositions, except for the (expected) higher carbon content in materials incorporating carbon nanofibers.

3.2. Effects of Hybrid (Nano- and Micro-Scale) Reinforcement Systems

Hybrid reinforcement systems comprising oxidized carbon nanofibers (NF-OX) and carbon fibers with micro-scale diameter (CMF) were evaluated in DSP paste. Exploratory studies of carbon

nanofiber and carbon microfiber reinforcement indicated that, for the cementitious matrix and processing conditions considered here, the nanofiber volume fraction (of cement plus silica fume) should be lowered below 0.24% before benefits can be realized from introduction of carbon microfibers. Hence, a nanofiber volume that was 0.16% that of cement plus silica fume was considered for development of hybrid reinforcement systems, which also incorporated carbon microfiber at 0.24 vol% of cement plus silica fume.

3.2.1 Flexural Performance

The flexural performance of high-performance cementitious paste was assessed following ASTM C293 - 08 Standard Test Method for Flexural Strength of Concrete (Simple Beam with Center-Point Loading), using 150x50x12.5 mm rectangular specimens. The flexural strength, maximum deflection and energy absorption capacity test results for the high-performance (DSP)

cementitious paste reinforced with different volume fractions of carbon nanofibers and microfibers are shown in **Table 3** and **Figure 13**. Carbon nanofibers and microfibers, and especially their combination, are observed to yield important gains in the flexural strength, energy absorption capacity and maximum deflection of DSP cementitious paste. The hybrid (carbon nanofiber and microfiber) reinforcement system produced 64.9, 356, and 288% gains in the flexural strength, energy absorption capacity and maximum deflection, respectively, of DSP paste. These benefits could be attributed to the multi-scale reinforcing action of the hybrid reinforcement system. Statistical analysis (of variance) of flexure test data confirm, at 0.00 significance level, that the contributions of nano- and/or micro-scale reinforcement effects to the flexural performance of this high-performance cementitious paste are statistically significant.

Tabel 3. Mean values of the flexural strength, maximum deflection and energy absorption capacity test results for high-performance cementitious paste with carbon nanofiber and/or microfiber reinforcement systems

Reinforcement Condition	Flexural Strength (MPa)	Maximum Deflection (mm)	Energy Absorption (N.mm)
Plain	10.3	0.401	61.8
Carbon microfiber, 0.24%	16.1	1.13	251
Carbon nanofiber, 0.16%	14.9	1.05	213
Mixed (Carbon microfiber, 0.24% and Carbon nanofiber, 0.16%)	17.0	1.55	282

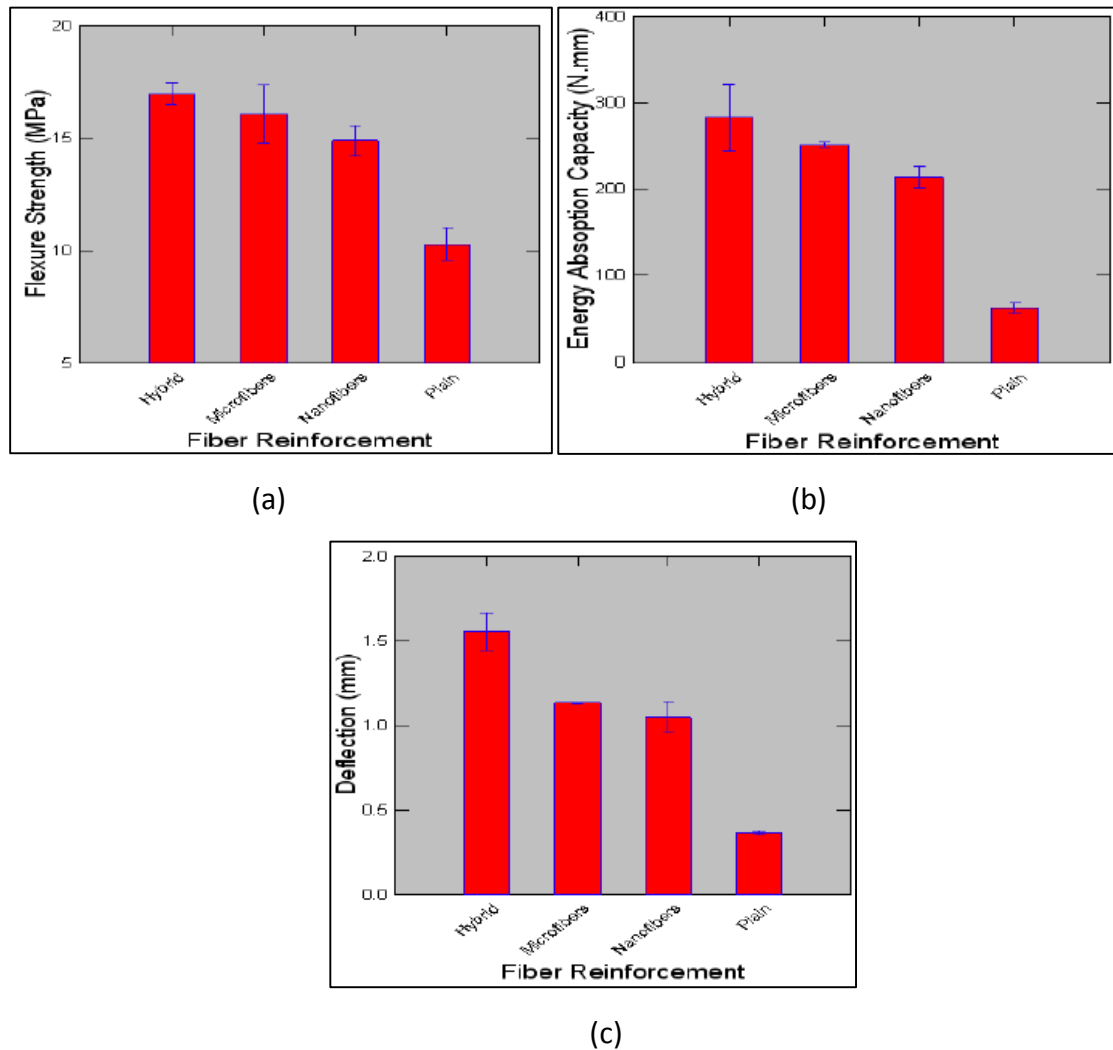


Figure 13. Mean values and standard errors of the flexural performance attributes of the high-performance pastes with different reinforcement systems, including flexural strength (a), energy adsorption capacity (b), and maximum deflection (c).

3.2.2 Compressive Strength

While fiber reinforcement tends to lower the compressive strength of concrete, mainly due to the introduction of interfacial stress rise and structural defects, nano-scale (and hybrid) reinforcement systems are observed in **Table 4** to produce a slight rise in the compressive strength of the high-performance cementitious paste. This

effect, however, is not statistically significant. The somewhat positive effects of nano-scale reinforcement on compressive strength could be attributed to: (i) the reduced interfacial stress concentration and structural defects due to the nano-scale dimensions and spacing of the reinforcement; and (ii) effective arrest of microcrack propagation by the closely spaced nanofibers.

Tabel 4. Mean values and standard errors of the compressive strength test results for high-performance cementitious paste reinforced with carbon nanofibers and/or microfibers.

Reinforcement Condition	Mean (MPa)	Standard Error (MPa)
Plain	111	14.3
Carbon microfiber, 0.24 vol%	117	28.0
Carbon nanofiber, 0.16 vol%	113	17.9
Mixed (Carbon microfiber, 0.24 vol% and Carbon nanofiber, 0.16 vol%)	117	15.3

3.2.3 Impact Resistance

The impact resistance test results presented in **Table 5** indicate that carbon microfibers, carbon nanofibers and the hybrid reinforcement systems enhance the impact resistance of DSP paste by 42.7%, 71.2, and 92.9%, respectively, which can be attributed to the arrest and deflection of microcracks by nanofibers, frictional pullout of nanofibers, the multiple cracking induced by nanofibers, and control of microcrack size by the closely spaced nanofibers. The particularly significant contribution of the hybrid reinforcement to impact resistance could be attributed to the multi-scale interaction of the nano- and micro-scale reinforcement within the matrix with microcracks. The contributions of nano- and/or micro-scale reinforcement to the impact resistance of the high-performance cementitious paste were found to be statistically significant (at 0.01 of significance level).

Tabel 5. Mean values of the impact resistance test results for high-performance cementitious pastes with carbon nanofiber and/or microfiber reinforcement systems.

Reinforcement Condition	Impact Resistance (mm/mm)
Plain	0.365
Carbon microfiber, 0.24 vol%	0.521
Carbon nanofiber, 0.16 vol%	0.625
Mixed (Carbon microfiber, 0.24 vol% and Carbon nanofiber, 0.16 vol%)	0.704

3.2.4 Abrasion Resistance

The abrasion test results presented in **Table 6** indicate that carbon microfibers and especially hybrid reinforcement, and (to a lesser extent) carbon nanofibers enhance the abrasion resistance of the high-performance (DSP) cementitious paste. These benefits were found to be statistically significant at 0.000 significance level.

3.2.5. SEM results

Figure 14 shows SEM images which are indicative of the uniform dispersion of nanofibers within the cementitious paste (**Figure 14a**), and a combination of carbon fiber rupture and pullout at fracture surfaces (**Figures 14b and c**). The change of the morphology was found clearly.

Tabel 6. Mean values and standard errors of the abrasion test results for high-performance cementitious pastes with carbon nanofiber and/or microfiber reinforcement systems.

Reinforcement Condition	Loss of Mass (g)
Plain	0.275
Carbon microfiber, 0.24 vol%	0.150
Carbon nanofiber, 0.16 vol%	0.250
Mixed (Carbon microfiber, 0.24 vol% and carbon nanofiber, 0.16 vol%)	0.125

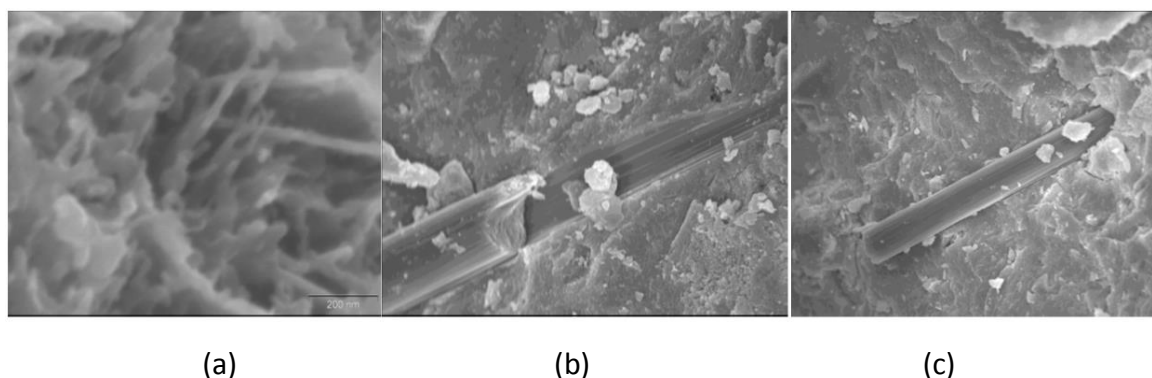


Figure 14. Typical SEM images of DSP cementitious paste reinforced with carbon microfibers and/or oxidized carbon nanofibers: dispersion of oxidized carbon nanofibers within the matrix (a); and failure mechanism of micro-scale fibers at fracture surfaces (b & c). All figures have similar scale bar (200 nm) as displayed in Figure 14(a)

4. CONCLUSIONS

Results of experiments conducted on cementitious pastes reinforced with non-functionalized and functionalized carbon nanofibers as well as their hybrids with carbon microfibers yielded the following conclusions. Acid-oxidation of carbon nanofibers benefited their dispersion and reinforcement efficiency in a high-performance cementitious matrix. The high specific surface area and the nano-scale spacing of dispersed nanofibers benefit their control of defect (microcrack) size and mitigation of microcrack growth, thus improving the nanofiber contributions to

the strength, energy absorption capacity and ductility of high-performance cementitious materials. Properly functionalized and well-dispersed carbon nanofibers with desired interfacial interactions brought about balanced gains in the flexural strength, energy absorption and ductility, impact and abrasion resistance of high-performance cementitious paste, while preserving its high compressive strength. For the cementitious matrix and processing conditions considered in this investigation, the nanofiber volume fraction should be lowered below 0.24% before benefits can be realized from introduction of carbon microfibers. Hence, a nanofiber volume

fraction of 0.16% was considered for development of hybrid reinforcement systems. A hybrid reinforcement comprising carbon nanofibers and microfibers at 0.16 and 0.24% of the volume of cement plus silica fume produced distinct gains in the engineering properties of the high-performance cementitious paste, which could not be matched by nano- or micro-scale reinforcement used alone. This finding points at the synergistic effects offered by nano- and micro-scale reinforcement systems.

7. REFERENCES

- Bui, D. D., Hu, J., & Stroeven, P. (2005). Particle size effect on the strength of rice husk ash blended gap-graded Portland cement concrete. *Cement and concrete composites*, 27(3), 357-366.
- Chen, S. J., Collins, F. G., Macleod, A. J. N., Pan, Z., Duan, W. H., & Wang, C. M. (2011). Carbon nanotube–cement composites: A retrospect. *The IES journal part a: Civil & structural engineering*, 4(4), 254-265.
- D'Ambrosia, M. (2012). *Early age creep and shrinkage of emerging concrete materials* (Doctoral dissertation, University of Illinois at Urbana-Champaign).
- Hammel, E., Tang, X., Trampert, M., Schmitt, T., Mauthner, K., Eder, A., & Pötschke, P. (2004). Carbon nanofibers for composite applications. *Carbon*, 42(5), 1153-1158.
- Lafdi, K., Fox, W., Matzek, M., & Yildiz, E. (2008). Effect of carbon nanofiber-matrix adhesion on polymeric nanocomposite properties: Part II. *Journal of nanomaterials*, 2008, 5.
- Lawrence, J. G., Berhan, L. M., & Nadarajah, A. (2008). Elastic properties and morphology of individual carbon nanofibers. *ACS nano*, 2(6), 1230-1236.
- Metaxa, Z., Konsta-Gdoutos, M., & Shah, S. (2010). Carbon nanofiber-reinforced cement-based materials. *Transportation research record: Journal of the transportation research board*, (2142), 114-118.
- Peyvandi, A., & Soroushian, P. (2015). Structural performance of dry-cast concrete nanocomposite pipes. *Materials and structures*, 48(1-2), 461-470.
- Peyvandi, A., Soroushian, P., Balachandra, A. M., & Sobolev, K. (2013). Enhancement of the durability characteristics of concrete nanocomposite pipes with modified graphite nanoplatelets. *Construction and building materials*, 47, 111-117.

5. ACKNOWLEDGEMENTS

This project was sponsored by the National Science Foundation Grant No. IIP-1142455. The authors are thankful to Norchem, Inc and BASF Construction Chemicals for contributing materials for use in the project.

6. AUTHORS' NOTE

The author(s) declare(s) that there is no conflict of interest regarding the publication of this article. Authors confirmed that the data and the paper are free of plagiarism.

- Sanchez, F., & Ince, C. (2009). Microstructure and macroscopic properties of hybrid carbon nanofiber/silica fume cement composites. *Composites science and technology*, 69(7), 1310-1318.
- Sbia, L. A., Peyvandi, A., Soroushian, P., Balachandra, A. M., & Sobolev, K. (2015). Evaluation of modified-graphite nanomaterials in concrete nanocomposite based on packing density principles. *Construction and building materials*, 76, 413-422.
- Shofner, M. L., Lozano, K., Rodríguez-Macías, F. J., & Barrera, E. V. (2003). Nanofiber-reinforced polymers prepared by fused deposition modeling. *Journal of applied polymer science*, 89(11), 3081-3090.
- Xie, X. L., Mai, Y. W., & Zhou, X. P. (2005). Dispersion and alignment of carbon nanotubes in polymer matrix: A review. *Materials science and engineering: R: Reports*, 49(4), 89-112.