

Thermal Stability of Latex Modified Mortars Containing CNTs

Ahmed Abdel-Mohti¹⁾ , Eslam Soliman²⁾, and Hui Shen^{3),*}

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Abstract: Durability of concrete and cementitious materials has been of a great concern to the construction industry in the last two decades due to the deterioration of large number of concrete structures which were built in the 60 and 70 s. Among different environmental conditions, the continuous exposure to freeze–thaw and thermal fatigue cycles remains one of the most aggressive conditions to concrete structures and bridges. On the other hand, the use of nanomaterials, such as carbon nanotubes, has shown promising results in improving the properties of cementitious materials. In this paper, the role of using carbon nanotubes (CNTs) in the thermal stability and durability of latex modified mortars (LMM) is examined. CNTs contents of 0.5 wt%, 1.0%, and 1.5 wt% of latex were added prior to mixing the latex modified mortar components and the resulting LMM specimens were subjected to freeze–thaw and thermal fatigue cycles. The mechanical properties and dimensional stability of LMM specimens were then evaluated. In general, it was observed that the addition of CNTs improve the compressive strength of LMM specimens. On the contrary, CNTs have limited or no influence in the tensile strength, development of shrinkage strains, and flexural capacity of LMM specimens under same thermal conditions.

Keywords: CNT, freeze and thaw, thermal fatigue, durability.

1. Introduction

Introduced almost 50 years ago, nanotechnology represents a relatively new and very important research field with numerous current and potential future applications in different industrial sectors. Currently, the use of nanotechnology extends to cover several mechanical, electrical, and medical applications (Gasman 2006). Of the mechanical applications, the use of nanomaterials as additives to construction materials has been seldom introduced in industry compared to other mechanical applications. Torgal (2013) attributed this slow progress due to the lack of research on the use of the nanomaterials in construction industry. Applications of nanomaterials in construction industry include concrete, steel, coatings and paintings, solar cells, and structural health monitoring (Lee et al. 2009). Since concrete and cementitious materials represent the most construction materials that are widely used in construction industry, research on using nanomaterials in concrete mixtures have grown rapidly in the last few years showing

promising results for enhancing their mechanical, electrical, and thermal properties. Among all nanomaterials, carbon nanotubes (CNTs) appear to be the strongest nano-sized reinforcement for concrete so far.

A number of investigations have addressed the effect of adding nanomaterials such as CNTs on the performance of the mortar or concrete mixture. For example, Kumar et al. (2012) investigated the effect of adding multi-walled CNTs on mechanical properties of cement paste. For compressive strength, CNTs were found to affect the early stage of concrete. 0.50% CNT content seemed to be the optimum content for the cement mix. Siddique and Mehta (2014) investigated effect of CNTs on properties of cement mortars. As CNTs content rose, compressive strength increased with a maximum observed strength at 1% content. Under high strain loading rate, the compression strength, flexural strength, and Young's modulus were also improved with the addition of CNTs. A low-cost pyrolysis technology that produced CNTs and have hydrogen as the only byproduct without carbon dioxide was developed. It was reported that making mixes with 0.5 wt% CNTs increased the compressive strength of the concrete by up to 30%. Compared to other common admixtures, CNTs seemed to provide more benefits with the addition of a smaller amount of material.

Two major challenges have been reported that typically limits the use of nanomaterials in cementitious materials. First is the difficulty in obtaining uniform dispersion of the nanomaterials in cementitious matrix. To address this, some studies suggested the use of ultra sonication as a suitable method for obtaining fair dispersion of the nanomaterials in the mixtures (Tyson et al. 2011; Sobolkina et al.

¹⁾College of Engineering and Computer Science, McNeese State University, 4205 Ryan St., Lake Charles, LA 70605, USA.

²⁾College of Engineering, Assiut University, Assiut 71516, Egypt.

³⁾College of Engineering, Ohio Northern University, 525 S Main St, Ada, OH 45810, USA.

*Corresponding Author; E-mail: h-shen@onu.edu

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2012). Second challenge arises from the need for creating strong chemical bonding between the nanomaterials and surrounding matrix. The presence of chemical coupling agents between the CNTs and the cement hydration products is necessary to transfer the loads between the mixture constituents. Recently, Soliman et al. (2011) obtained fair dispersion of CNTs in latex modified mortar specimens through creative methods of mixing CNTs with surfactants in polymer latex before adding the cement components. Adding CNTs improved the properties of Latex modified mortars (LMMs) such as compressive and tensile strengths, failure strain, and toughness. In addition, early age compressive strength was not affected by the amount of CNTs. Soliman et al. (2012) have also shown that the addition of CNTs to Styrene butadiene rubber (SBR) latex increases the polymer cross-linking resulting in stronger and stiffer latex membranes. Konsta-Gdoutos et al. (2010) used ultrasonication, aided by surfactant treatment, to disperse CNTs with different lengths in cement paste. It was found that fracture properties of cement were enhanced with the proper distribution.

Durability of concrete and cementitious materials has been of a great concern to the construction industry as well as research institutes in the last two decades. Large number of concrete infrastructures which was built in the 60 and 70 s has been deteriorated due to poor durability and the exposure to aggressive environments. Several studies investigated the deterioration of ordinary concrete due to freeze and thaw cycles. Cai and Liu (1998) explained the mechanism of concrete deterioration due to the presence of frozen water inside the concrete pores. The frozen water causes high internal hydraulic pressure, which in turn damages the concrete. Sun et al. (1999) concluded that the applied stress/strength ratio and the grade of concrete are the most important parameters that affect the concrete durability when exposed to freeze and thaw cycles. Mu et al. (2002) has shown that concrete deterioration was further accelerated when freeze–thaw cycles, loading, and chloride salt attacks all acted simultaneously.

Limited number of studies investigated the freeze and thaw resistance of concrete mixtures containing nanoparticles (Cwirzen and Habermehl-Cwirzen 2013; Salemi et al. 2014; Wang et al. 2014; Li et al. 2015). It was concluded in many studies that CNTs can retain more strength and less cracking after being exposed to freezing and thawing tests. While ordinary concrete suffers significantly when exposed to freeze and thaw cycle, polymer modified concretes, such as latex modified concrete, have been introduced to the construction industry as a more durable class of construction material to serve several structural applications such as bridge deck overlays, water tanks, and swimming pools (Ohama 1995, ACI 548.3R 2009). In this study, the durability of polymer modified mortar (PMM) mixes containing CNTs has been investigated. Different contents of CNTs were dispersed in latex modified mortar (LMM) mixtures and the durability of LMM mixes was evaluated through freeze–thaw and thermal fatigue tests as discussed later.

2. Experimental Program

2.1 Mix Design

Ordinary ASTM C 150 Type I portland cement was used in all mortar specimens along with natural sand, water, and commercial SBR-Latex. Multi-walled carbon nanotubes (MWCNTs) were obtained from Cheap Tubes, Inc. According to the manufacturer's specifications, the MWCNTs had outer diameter of 8 nm, inner diameter of 2–5 nm, length of 10–30 μm , specific surface area of 500 m^2/g , and bulk density of 0.27 g/cm^3 . In addition to the control LMM specimens which had no MWCNTs, three MWCNTs contents were added as a percentage of the weight of latex: 0.5, 1.0, and 1.5%. Table 1 shows the mix proportions of all LMM specimens examined in the study. Sand-to-cement, water-to-cement, and latex-cement ratios of 2.7, 0.38, and 0.15 were utilized in this study. This mix proportions conform to range for the conventional LMM mix proportions reported by Ohama (1978). The LMM specimens with no MWCNTs were considered the control specimens in this investigation.

2.2 CNTs Dispersion

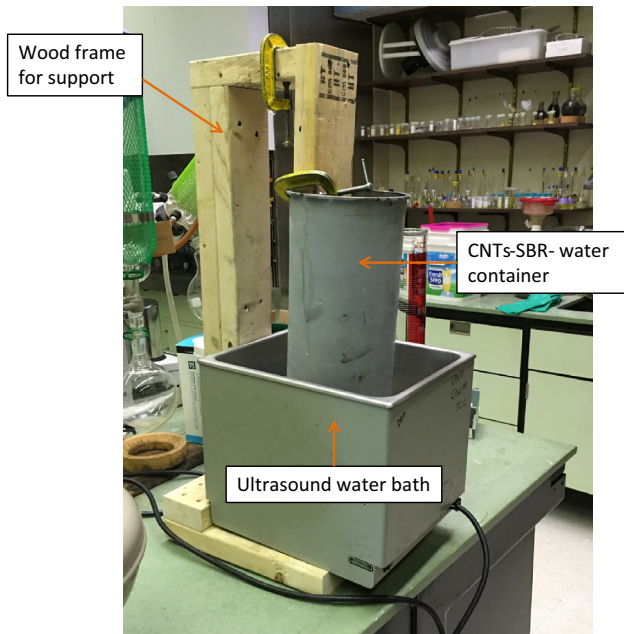
To incorporate MWCNTs in LMM mixtures, a combination of mechanical and chemical dispersion techniques was implemented. The mechanical techniques involved the development of ultrasonic waves (e.g. ultrasonication) or high shear mixing forces (e.g. extrusion, ball milling) needed to disentangle the nanotubes. In this study, ultrasonication was implemented as a relatively cheap and effective method for the mechanical dispersion. Ultrasonic bath Model B-52, supplied by Branson[®], was used to perform the ultrasonication in this study. The ultrasonic bath has a basket dimensions of 292 mm \times 230 mm \times 150 mm and operates on frequency of 50–60 Hz. Approximately, 70% of the ultrasonic bath tank capacity was filled with distilled water to perform the ultrasonication. On the other hand, the chemical techniques involved the formation of weak (i.e. non covalent) or strong (i.e. covalent bond) to promote the dispersion process. In SBR latex, the presence of surfactants in the ingredients of the latex facilitated the dispersion through the formation of noncovalent Van der Waal bond between the surfactants and the CNTs. The MWCNTs were used first dispersed in deionized water using ultrasonication for 30 min. The resulting MWCNTs–water mixture was added to the SBR latex and the suspension was ultrasonicated for 2 h. The ultrasonication setup is shown in Fig. 1. The dispersion procedures were utilized previously by Soliman et al. (2012) who showed a fair distribution of the CNTs in LMM.

2.3 Casting and Curing LMM Specimens

Two mechanical mortar mixers, supplied by Hobart, Inc. (Fig. 2), were used to prepare all the mixes. Cement and sand were first added in the mixer and were mixed for 5 min at a rotational speed of 261 r.p.m. This is followed by adding the CNTs-SBR-water suspension and mixing the composite

Table 1 Mix proportions.

Mix ID	Portland cement (kg/m ³)	Sand (kg/m ³)	Water (kg/m ³)	SBR-Latex (kg/m ³)	CNT (kg/m ³)
LMM-0%	530.2	1457.7	203.4	79.5	0
LMM-0.50%	530.2	1457.7	203.4	79.5	0.4
LMM-1.00%	530.2	1457.7	203.4	79.5	0.8
LMM-1.50%	530.2	1457.7	203.4	79.5	1.2

**Fig. 1** Ultrasonic bath setup for dispersion CNTs in SBR latex.**Fig. 2** Two mechanical mixers used to prepare LMM mixes.

for 10 min. The LMM specimens were then cast in 50.8 mm wide × 50.8 mm high × 279.4 mm long prisms, 50.8 mm diameter × 101.6 mm high cylinders, and 50.8 mm ×

50.8 mm × 50.8 mm cubes. Specimens were then cured following ACI 548.3R, 2009 for 28 days. The curing regime included water curing for 2 days, followed by air curing for 5 days, and finally water curing for the remainder of 28 days. The specimens were submerged in lime water for 48 h before they were subjected to 300 cycles of two types of tests: thermal fatigue and freeze–thaw tests. The LMM prisms were used to examine shrinkage and flexural response of different LMM mixes while the cylinders and cubes were used to examine the tension and compression strengths respectively. At least three replicas were tested at any given time, exposure, and loading conditions.

2.4 Thermal Exposure

The thermal exposure in this investigation consisted of freeze–thaw cycling and thermal fatigue cycling tests. The freeze–thaw and thermal fatigue tests were proposed in this study to simulate the outdoor temperature changes during the winter and summer times respectively. For the two tests, the thermal cycles were applied directly after the curing of specimens following ASTM C-666B (2015) standard. In the freeze–thaw test, the temperature varied between $(-18 \pm 2 \text{ }^\circ\text{C})$ and $(4 \pm 2 \text{ }^\circ\text{C})$ for 300 cycles. The duration for a single cycle was selected three hours following the ASTM standards recommendations, which suggest duration between 2 and 5 h for each cycle during freeze–thaw testing. Mechanical testing and shrinkage measurements were applied at specified intervals to monitor the damage evolution throughout the test. The test was performed by first cooling the air around the specimens to $(-18 \pm 2 \text{ }^\circ\text{C})$ then thawing the specimens by pumping water at a temperature of $(4 \pm 2 \text{ }^\circ\text{C})$. On the other hand, similar procedures were followed in conducting the thermal fatigue test by altering the specimen's temperature between $(16 \pm 2 \text{ }^\circ\text{C})$ and $(40 \pm 2 \text{ }^\circ\text{C})$.

The thermal cycles were applied to LMM specimens in the environmental chamber facility available at Ohio Northern University. The temperature varying processes were controlled by a DirectLOGIC D4-450 PLC (programmable logic controller). The controller enabled setting the upper and lower temperature limits, the water fill time, the delay before draining time, and the drain time before putting the PLC in automatic or manual control mode. User input and process output was displayed on a C-more EA7-T8C 8-inch touchscreen. The touch screen displayed the current temperatures of the two thermocouples used, along with indicators for the current operation in progress. Current water fill, freezer run,

and water drain times along with the current cycle and last cycle times and cycle count were also displayed on the touch screen.

2.5 Testing

The effect of thermal exposure on the mechanical and dimensional stability of different LMM specimens was evaluated through mechanical testing and shrinkage measurements. In order to determine the effect of shrinkage on the LMM specimens, the length of the LMM was measured after every 30 cycles (i.e. almost every 4 days) using a digital comparator. The change in length was then used to compute the shrinkage strains induced due to the application of freeze–thaw and thermal fatigue cycles. The prisms were later tested in flexure according to ASTM C348 (2014) standards using three point bending test after the completion of the 300 cycles, which corresponds to concrete age of 66 days (Fig. 3). In the flexural test, the load was applied at the mid-span of each specimen with a supported length of 228.6 mm. The load and mid-span deflection was recorded and the load–deflection curves for different LMM specimens were presented and discussed. In addition, compressive and tensile strengths were determined for cubes and cylinders after 28 days, after the exposure to 150 thermal cycles, and after the exposure to 300 thermal cycles, which correspond



Fig. 3 Three-point bending test setup.

to concrete age of 47 days and 66 days respectively. The strength of each specimen was determined and the average of the three replicas was calculated and presented. The compression test was performed in accordance with ASTM C39 (2016), whereas the splitting tensile test was performed in accordance with ASTM C496 (2004). The same standard testing machine was used to conduct both of the compression and tensile tests.

3. Results and Discussions

3.1 Effect of CNTs Content on Compressive and Tensile Strengths

Figures 4 and 5 presents the compressive strength of LMM samples due to the freeze–thaw and thermal fatigue cycles, respectively. In addition, statistical analysis using student *t* test is conducted and presented in Tables 2 and 3 to study the statistical significance of the compressive strength test results due to changing CNTs content and number of thermal cycles, respectively. For freeze–thaw testing, after 150 cycles, the LMM control samples experienced a drastic drop in compressive strength; however, it gained part of the lost strength (about 50%) after 300 cycles. The student *t*-test shows the drop and the regain in the compressive strength is statistically significant (Table 3). Similarly, LMM specimens with different CNTs contents exhibited similar drop in strength after the first 150 cycles. However, they regained almost all the strength after 300 cycles. The student *t*-test also shows that the drop and regain in compressive strength for all CNTs contents is statistically significant. The drop in strength in the first 150 cycles could be attributed to the early development of microcracks due to the exposure to freeze–thaw cycles, which in turn reduced the compressive strength. As the LMM specimens were subjected to more freeze–thaw cycles, no further development of microcracks occurred. In addition, the low permeability of LMM helped reduce the water loss from the mixtures and therefore contributed to the late curing of cement and latex films. The late curing resulted in a regain in the compressive strength (Sprinkel 1993). The role of CNTs is evident in increasing the regain

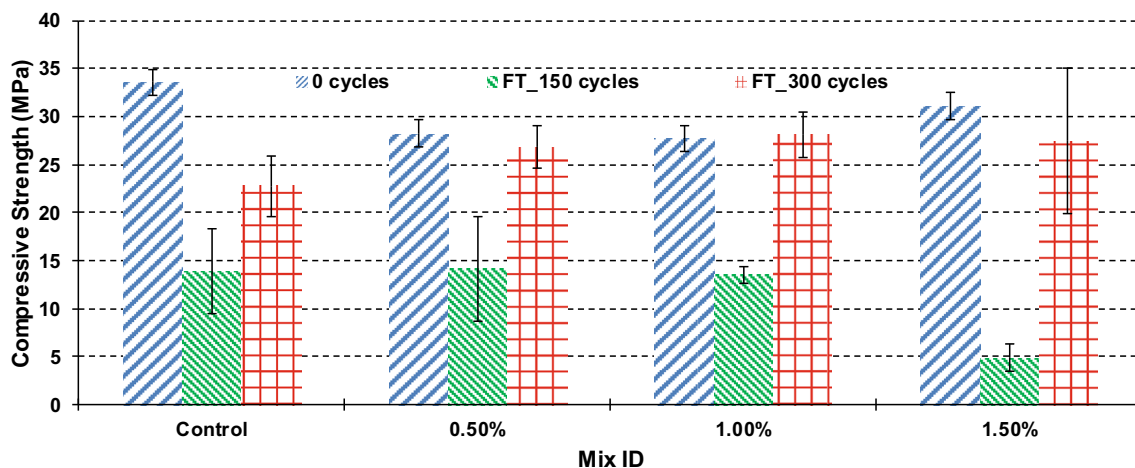


Fig. 4 Compressive strength results due to freeze and thaw cycles.

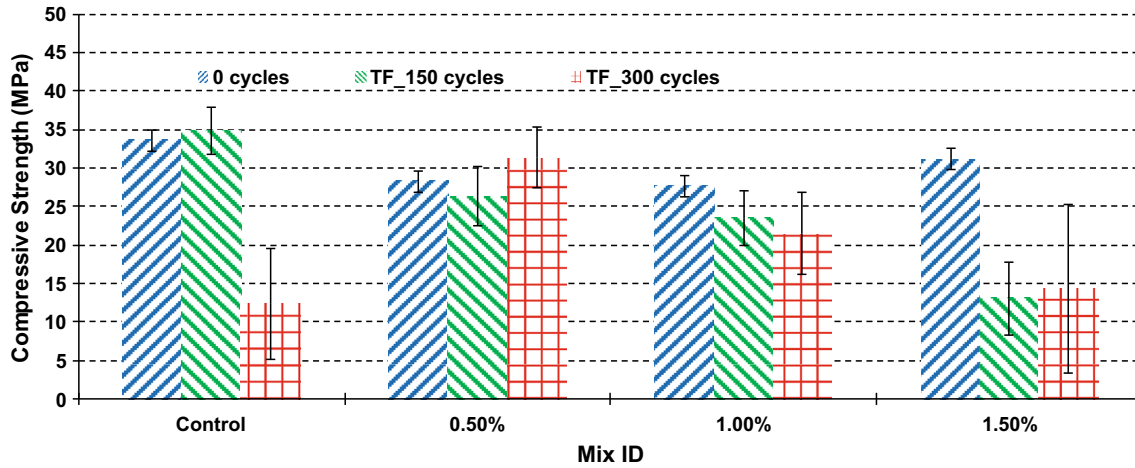


Fig. 5 Compressive strength results due to thermal fatigue cycles.

Table 2 Student t test analysis for compressive strength test results based on different CNTs contents.

Test	Sample type	t Test results	Level of difference
FT_150 cycles	Control	1.00	No difference
	0.50%	0.95	No difference
	1.00%	0.90	No difference
	1.50%	0.06	Significant difference
FT_300 cycles	Control	1.00	No difference
	0.50%	0.33	No difference
	1.00%	0.17	No difference
	1.50%	0.33	No difference
TF_150 cycles	Control	1.00	No difference
	0.50%	0.04	Significant difference
	1.00%	0.01	Significant difference
	1.50%	0.00	Significant difference
TF_300 cycles	Control	1.00	No difference
	0.50%	0.25	No difference
	1.00%	0.18	No difference
	1.50%	0.79	No difference

in compressive strength as shown in Fig. 4. The mechanism of CNTs in improving the compressive strength is due to their reinforcing effect on the cured SBR latex, which yields an integrated network of latex membrane that limits water loss from the LMM mixtures. The reduced water loss encourages late curing of cement and contributes significantly on the regain in compressive strength. This mechanism is in line with the observation reported by Soliman et al. (2012) in which the cured SBR latex films reinforced by CNTs showed superior mechanical response when compared to cured plain SBR latex films (Soliman et al. 2012).

For thermal fatigue testing (Fig. 5), no regain was observed in compressive strength after 300 cycles, instead a drastic drop was observed. For the control specimen, the

drop in the compressive strength reached of 70%. Similar drop in compressive strength of 60% was observed with LMM specimen with high CNTs content of 1.5%. The difference between the effect of freeze–thaw and thermal fatigue tests on compressive strength is attributed to the difference in the temperature exposure range. In freeze–thaw cycles, the temperature was altered between -18 to 4 °C, which helped maintain water in the mixture for late curing. On the other hand, the temperature in the thermal-fatigue test was altered between 18 and 40 °C which promoted water loss from the mixture and prevented the late curing and the regain in compressive strength. It can also be noted that LMM specimens with the moderate and low CNTs contents (i.e. 0.5 and 1.0%) were more stable under thermal fatigue

Table 3 Student *t* test analysis for compressive strength test results based on the exposure to different number of cycles.

Sample type	Type of testing	No. of cycles	<i>t</i> Test results	Level of difference
Control	F_T	0 cycles	1.00	No difference
		150 cycles	0.02	Significant difference
		300 cycles	0.04	Significant difference
	T_F	0 cycles	1.00	No difference
		150 cycles	0.54	No difference
		300 cycles	0.03	Significant difference
0.5% CNTs	F_T	0 cycles	1.00	No difference
		150 cycles	0.05	Significant difference
		300 cycles	0.04	Significant difference
	T_F	0 cycles	1.00	No Difference
		150 cycles	0.49	No difference
		300 cycles	0.99	No difference
1.0% CNTs	F_T	0 cycles	1.00	No difference
		150 cycles	0.00	Significant difference
		300 cycles	0.01	Significant difference
	T_F	0 cycles	1.00	No difference
		150 cycles	0.17	No difference
		300 cycles	0.96	No difference
1.5% CNTs	F_T	0 cycles	1.00	No difference
		150 cycles	0.06	Significant difference
		300 cycles	0.00	Significant difference
	T_F	0 cycles	1.00	No difference
		150 cycles	0.02	Significant difference
		300 cycles	0.93	No difference

cycles as they demonstrated statistically insignificant or no drop in compressive strength after 300 cycles. It can therefore be deduced from the compressive strength testing that the addition of low-to-moderate CNTs contents to LMM mixtures yields more thermally stable and more durable mortar specimens. The inefficiency of adding high contents of CNTs might be attributed to the poor dispersion and/or increased surface area of the CNTs, which may slow down the cement hydration and the latex curing. The adverse effect of high content of CNTs (i.e. 1.5%) on LMM subjected to thermal fatigue cycles is also evident from the high variability of the compressive strength data, represented by the high error bars for 1.5% CNTs case, as shown in Fig. 5, relative to other CNTs contents.

Figures 6 and 7 show the tensile strength results of LMM specimens subjected to freeze–thaw and thermal fatigue tests, respectively. Unlike compressive strength, tensile strength of LMM specimens showed much higher thermal stability with almost no loss in tensile strength due to 150 or

300 cycles of freeze–thaw or thermal fatigue cycles. This might be attributed to the difference in the failure mechanisms of LMM between compression and tension. The compression failure is typically governed by the formation of multiple cracks which increase in numbers and intensity till complete failure. In this case, the overall condition of the treated LMM specimens contributes in the compressive strength of the specimens. On the other hand, the tensile fracture is governed by single critical crack in which the local condition around the crack surface affects the tensile strength and therefore, experience less effect due to thermal treatment. Of interest in Fig. 7 is the fair improvement in tensile strength after 300 cycles of thermal fatigue with the use of 1.5% CNTs. The improvement in the tensile strength could be attributed to the bridging effect of CNTs on the crack surface. However, such improvement in tensile strength is less than the regain observed in the compressive strength observed in Fig. 4 given its lower magnitude and relatively high variability.

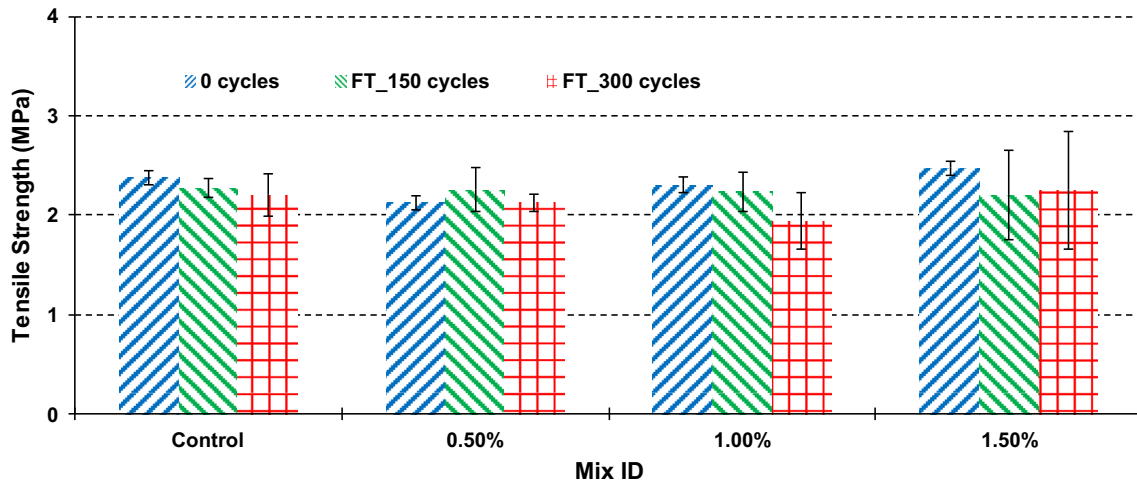


Fig. 6 Tensile strength results due to freeze and thaw cycles.

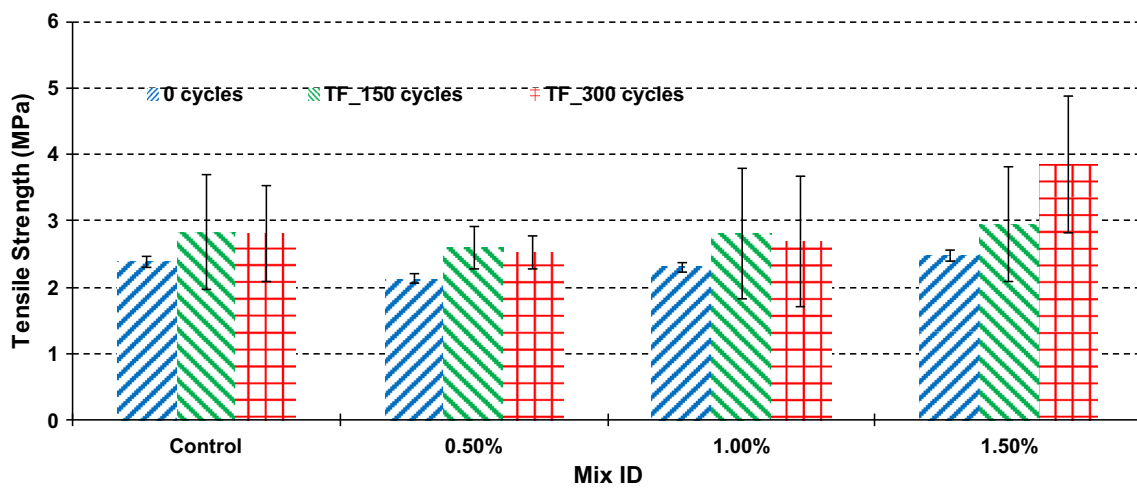


Fig. 7 Tensile strength results due to thermal fatigue cycles.

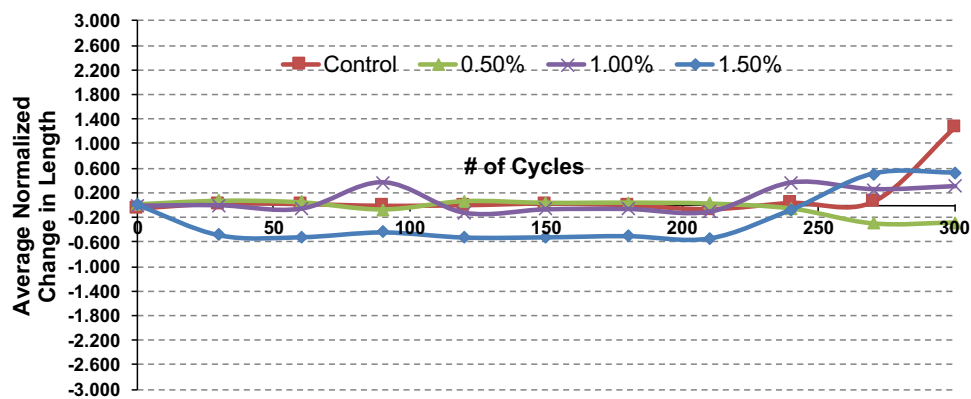


Fig. 8 Shrinkage/expansion strains due to freeze–thaw cycles.

3.2 Effect of CNTs Content on Shrinkage Strains

The development of shrinkage/expansion strains due to freeze–thaw and thermal fatigue cycles are examined in Figs. 8 and 9 respectively. Average normalized change in length were calculated every 30 cycle from the change in the specimen length in order to reduce uncertainties due to

precision in measurements, change in humidity, and materials' microstructure variability. Figure 8 shows that for freeze–thaw cycles, all specimens observed average normalized change in length within ± 0.6 , except for the control specimen which observed a maximum change in length of 1.3 at the 300th cycle only. In addition, the LMM specimen with 1.5% observed a constant and continuous

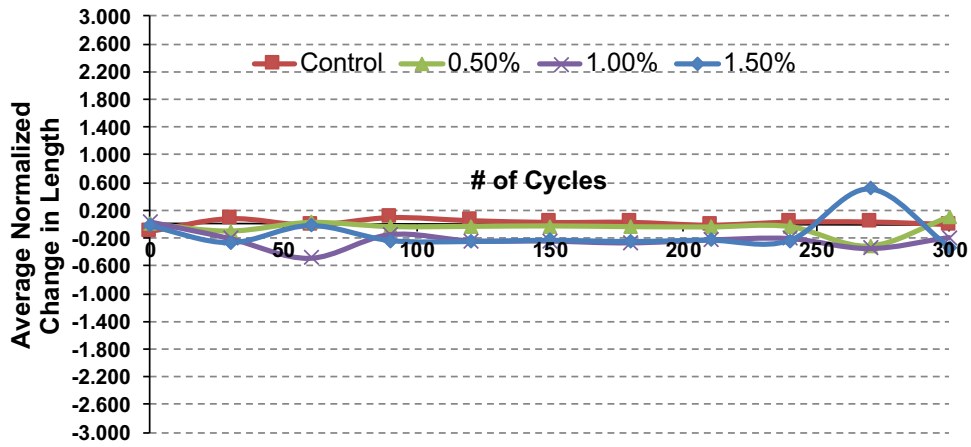


Fig. 9 Shrinkage/expansion strains due to thermal fatigue cycles.

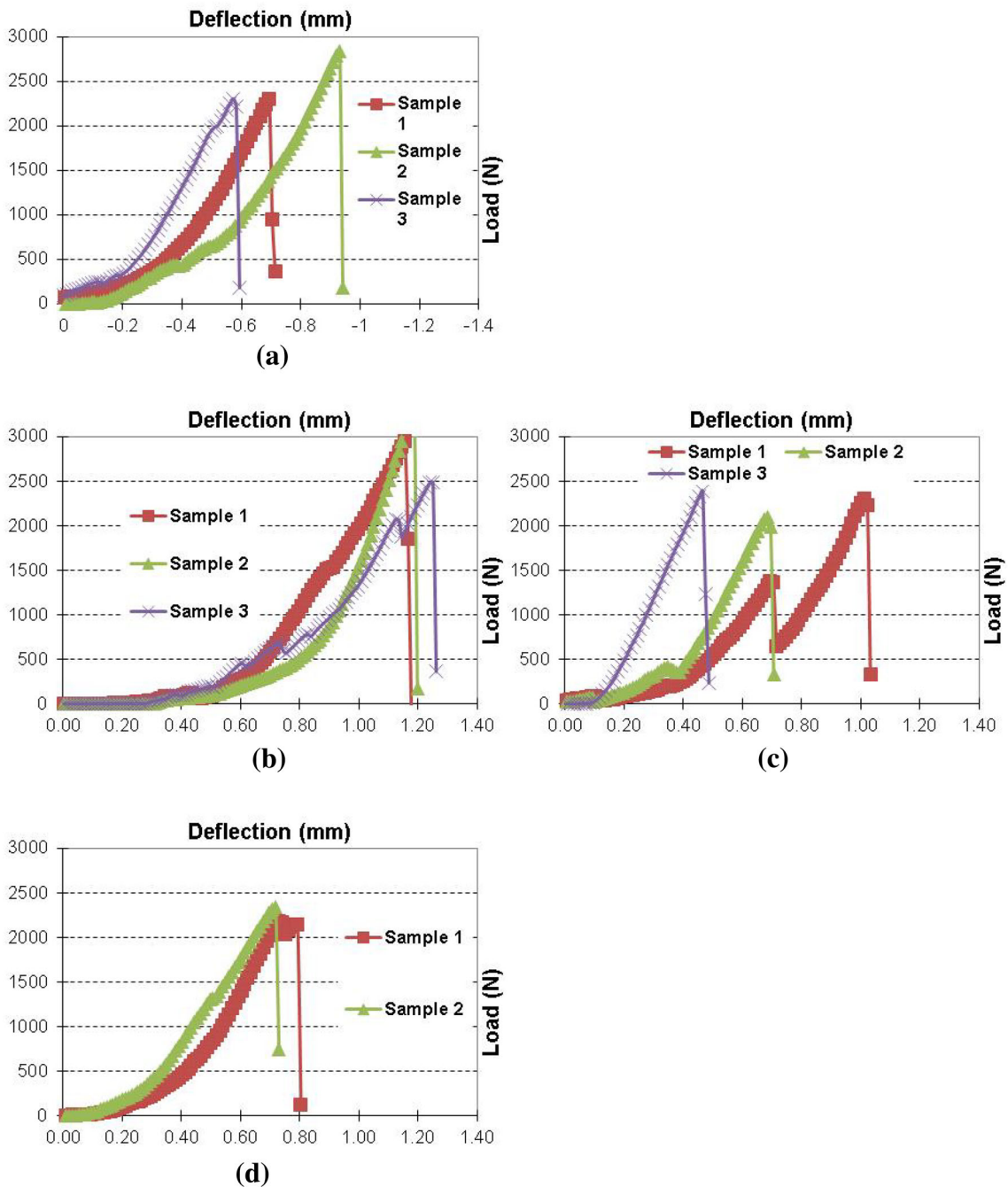


Fig. 10 Load-deflection relationships due to freeze and thaw cycles. a Control, b 0.5%, c 1.0%, and d 1.5%.

decrease in length from the 30th cycle to the 200th cycle. Such decrease may be attributed to the fact that incorporating high contents of CNTs reduces the mixture workability, which in turn would introduce relatively high void content. The high voids content will enable high shrinkage and expansion under freeze–thaw cycles. The role of high contents of CNTs in reducing the workability and increasing the voids content of cementitious materials has been reported by Van Tonder and Mafokoane (2014). Figure 8 also shows that the moderate contents of CNTs (e.g. 0.5 and 1.0%) are slightly more thermally stable under freeze–thaw cycles than the control LMM specimens and LMM specimens with high CNTs content specimens. Lower shrinkage/expansion strains would reduce the development of shrinkage microcracks and yields LMM with better tensile and compressive strength as discussed in some cases in the previous section.

Thermal fatigue test results showed more stable behavior for All LMM specimens under thermal cycles than that observed for the freeze–thaw cycles as shown in Fig. 9. A maximum average normalized expansion and shrinkage strains of + 0.6 and – 0.6 were observed in a single

measurement for LMM specimens with 1.5% CNTs and 1.0% respectively. In addition, similar to the freeze–thaw cycles, the LMM specimens with 1.5% CNTs observed constant and continuous shrinkage between the 90th cycle and the 240th cycle, which can be attributed to the decreased workability and increased void contents. Overall, CNTs are found to have little or no influence on the thermal stability of LMM subjected to either freeze–thaw or thermal-fatigue cycles. It is well known that LMC and LMM mixture have good thermal stability (ACI 548.3R 2009) and therefore the role of CNTs in improving the thermal stability shall not be evident. However, previous research work has reported that CNTs might improve the thermal stability of ordinary Portland concrete due to its negative coefficient of expansion (Veedu 2010).

3.3 Effect of CNT Content on Flexural Load–Deflection Relationships

Figures 10 and 11 depict the load–deflection curves of LMM samples tested after the completion of all the freeze–thaw and thermal fatigue cycles. For freeze–thaw test, an

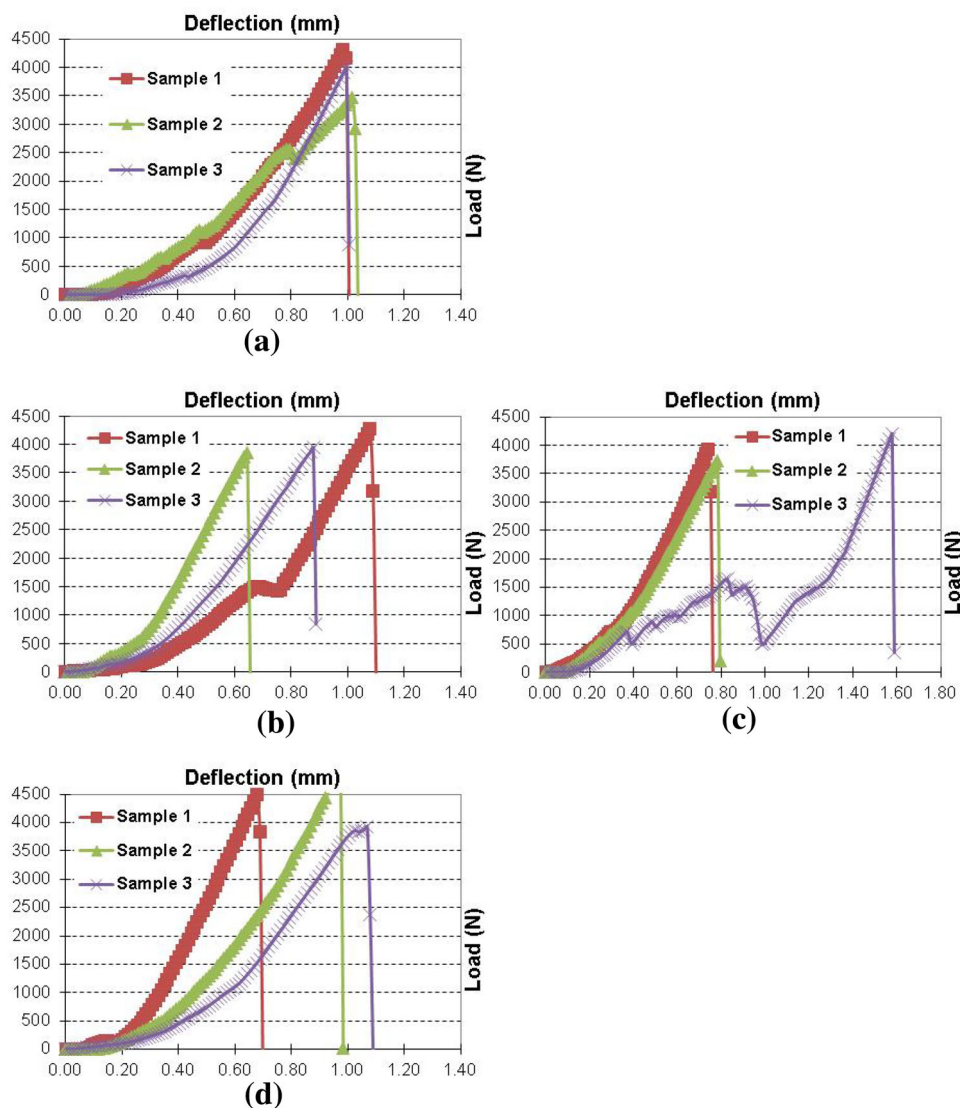


Fig. 11 Load-deflection relationships due to thermal fatigue cycles. a Control, b 0.5%, c 1.0%, and d 1.5%.

average load capacity of 2500 N was observed for the control specimens as shown in Fig. 10a. By adding 0.5% CNTs to LMM specimens, the load capacity improved by 15% (Fig. 10b) whereas the load capacity reduced by 10% with the addition of 1.0 or 1.5% CNTs (Fig. 10c and d). The change in load capacity between the control specimens and other groups are found within the acceptable single laboratory coefficient of variation precision 1 s % of 14.4%. Furthermore, statistical analysis using student t-test with 95% confidence level reveals no significant statistical difference in the load capacity between the control specimens and other CNTs reinforced specimens. Therefore, no effect of the adding CNTs on the load capacity of flexural specimens subjected to freeze–thaw cycles can be deduced from Fig. 10.

Thermal fatigue test results in Fig. 11 observed higher flexure capacity for all LMM specimens as compared to freeze–thaw cycles. For instance, the control specimens observed average flexural capacities of 2500 and 4000 N due to the application of 300 cycles of freeze–thaw and thermal fatigue respectively. Such reduction in the flexural capacity reflects the significant effect of freeze–thaw cycles on the durability of LMM specimens. Moreover, similar to the freeze–thaw testing, the addition of CNTs does not seem to have any effect on the flexural capacity of thermal fatigue treated specimens. This observation is in agreement with most of the observed trend for the splitting tension strength results of LMM specimens with various CNTs contents as reported earlier in Figs. 6 and 7.

4. Conclusion

In this study, the effect of adding various contents of CNTs on the thermal stability of SBR LMM was investigated. Freeze–thaw and thermal fatigue cycles were subjected to different LMM specimens to assess their shrinkage, compressive, tensile and flexural performance. In general, noticeable effect in compressive strength was observed with the addition of 0.5 to 1.5% CNTs to LMM. However, limited or no effect was observed on tensile strength, shrinkage strains, and flexural behavior due to the addition of same amounts of CNTs. Considerable loss in the compressive strength was associated with the application of 150 cycles of freeze–thaw, which could be attributed to the development of microcracks. This was followed by relative regain in compressive strength in the second 150 freeze–thaw cycles. The role of adding CNTs to LMM specimens is evident by regaining almost 100% of the loss in compressive strength while on the control specimens; only 50% of the loss in compressive strength was regained. For thermal fatigue test, the addition of low-to-moderate CNTs contents maintained the compressive strength unaffected by the thermal cycles whereas a drastic drop of 70% in compressive strength was observed in the control specimen. Unlike compressive strength, the freeze–thaw or thermal fatigue cycles did not influence the tensile strength of most of LMM specimens. Of great interest is the addition of 1.5% CNTs which improved

the tensile strength of LMM specimens after the exposure to 300 cycle of thermal fatigue by 52% relative to no exposure to thermal-fatigue cycles. This trend was not observed in the control specimens or the LMM specimens with low and moderate CNTs contents. Moreover, unlike other LMM specimens, LMM specimens with 1.5% CNTs exhibited little but constant and continuous shrinkage due to freeze–thaw and thermal fatigue cycles. The shrinkage of such high content of CNTs could be attributed to the reduced workability of the LMM mixture and the corresponding increase in voids content.

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References

- ACI 548.3R-09. (2009). *Report on polymer-modified concrete*. ACI Committee 548, Farmington Hills, Michigan, USA.
- ASTM C348-14. (2014). *Standard test method for flexural strength of hydraulic-cement mortars*. West Conshohocken, PA: ASTM International.
- ASTM C39/C39M-16b. (2016). *Standard test method for compressive strength of cylindrical concrete specimens*. West Conshohocken, PA: ASTM International.
- ASTM C496/C496M-11. (2004). *Standard test method for splitting tensile strength of cylindrical concrete specimens*. West Conshohocken, PA: ASTM International.
- ASTM C666/C666M-15. (2015). *Standard test method for resistance of concrete to rapid freezing and thawing*. West Conshohocken, PA: ASTM International.
- Cai, H., & Liu, X. (1998). Freeze-thaw durability of concrete: Ice formation process in pores. *Cement and Concrete Research*, 28, 1281–1287.
- Cwirzen, A., & Habermehl-Cwirzen, K. (2013). The effect of carbon nano- and microfibers on strength and residual, cumulative strain of mortars subjected to freeze-thaw cycles. *Journal of Advanced Concrete Technology*, 11(3), 80–88.
- Gasman, L. (2006). *Nanotechnology applications and markets*. Norwood, MA: Artech House Inc.

- Konsta-Gdoutos, M. S., Metaxa, Z. S., & Shah, S. P. (2010). Highly dispersed carbon nanotube reinforced cement based materials. *Cement and Concrete Research*, 40(7), 1052–1059.
- Kumar, S., Kolay, P., Malla, S., & Mishra, S. (2012). Effect of multiwalled carbon nanotubes on mechanical strength of cement paste. *Journal of Materials in Civil Engineering*. [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000350](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000350).
- Lee, J., Mahendra, S., & Alvarez, P. J. J. (2009). Potential environmental and human health impacts of nanomaterials used in the construction industry. In *Nanotechnology in Construction 3* (pp. 1–14). Berlin: Springer.
- Li, W.-W., Li, W.-M., Yang, W.-C., Liu, Y., Shen, R.-Y., & Xing, F. (2015). Investigation on the mechanical properties of a cement-based material containing carbon nanotube under drying and freeze-thaw conditions. *Materials*, 8(12), 8780–8792. <https://doi.org/10.3390/ma8125491>.
- Mu, R., Miao, C., Luo, X., & Sun, W. (2002). Interaction between loading, freeze-thaw cycles, and chloride salt attack of concrete with and without steel fiber reinforcement. *Cement and Concrete Research*, 32(7), 1061–1066.
- Ohama, Y. (Oct. 1978). *Proceedings of the Second International Congress on Polymers in Concrete*, Austin, Texas, p. 125.
- Ohama, Y. (1995). *Handbook of polymer-modified concrete and mortars: Properties and process technology*. Norwich: William Andrew Inc.
- Salemi, N., Behfarnia, K., & Zaree, S. A. (2014). Effect of nanoparticles on frost durability of concrete. *Asian Journal of Civil Engineering (BHRC)*, 15(3), 411–420.
- Siddique, R., & Mehta, A. (2014). Effect of carbon nanotubes on properties of cement mortars. Effect of carbon nanotubes on properties of cement mortars. *Construction and Building Materials*, 50, 116–129.
- Sobolkina, A., Mechtcherine, V., Khavrus, V., Maier, D., Mende, M., Ritschel, M., et al. (2012). Dispersion of carbon nanotubes and its influence on the mechanical properties of the cement matrix. *Cement and Concrete Composites*, 34(10), 1104–1113.
- Soliman, E. M., Kandil, U. F., & Reda Taha, M. M. (2011). *A new latex modified mortar incorporating carbon nanotubes: Preliminary investigations* (Vol. 278). Michigan: ACI Special Publications.
- Soliman, E. M., Kandil, U. F., & Taha, M. M. R. (2012). The significance of carbon nanotubes on styrene butadiene rubber (SBR) and SBR modified mortar. *Materials and Structures*, 45(6), 803–816.
- Sprinkel, M. M. (1993). Twenty-year performance of latex-modified concrete overlays. In *Polymer-modified hydraulic-cement mixtures*. West Conshohocken: ASTM International.
- Sun, W., Zhang, Y. M., Yan, H. D., & Mu, R. (1999). Damage and damage resistance of high strength concrete under the action of load and freeze-thaw cycles. *Cement and Concrete Research*, 29, 1519–1523.
- Torgal, F. P. (2013). Introduction to nanotechnology in eco-efficient construction. In *Nanotechnology in eco-efficient construction* (pp. 1–6).
- Tyson, B. M., Abu Al-Rub, R. K., Yazdanbakhsh, A., & Grasley, Z. (2011). Carbon nanotubes and carbon nanofibers for enhancing the mechanical properties of nanocomposite cementitious materials. *Journal of Materials in Civil Engineering*, 23(7), 1028–1035.
- Van Tonder, P., & Mafokoane, T. T. (2014). Effects of multiwalled carbon nanotubes on strength and interfacial transition zone of concrete (pp. 718–727). In *Proceedings of the First International Conference on Construction Materials and Structures*, 2014, South Africa.
- Veedu, V. P. (2010). Multifunctional cementitious nanocomposite Materials and methods of making the same. U.S. Patent 7,666,327, issued February 23, 2010.
- Wang, X., Rhee, I., Wang, Y., & Xi, Y. (2014). *Compressive strength, chloride permeability, and freeze-thaw resistance of MWNT concretes under different chemical treatments*. Cairo: Hindawi Publishing Corporation.