Original Research Article

Mechanical Behavior of Concrete with High Absorption Limestone Aggregate and Multi-Walled Carbon Nanotubes

ABSTRACT

Carbon nanotubes have demonstrated their versatility in the manufacture of various devices such as molecular probes, pipes, cables, fibers and springs. Recently, they have been used in cement composites to improve their physical and mechanical properties, but there are still many questions regarding the physical-mechanical behavior that can be achieved in structural concrete. In view of this, the present work aimed at the designing of concrete mixtures with multi-walled carbon nanotubes additions, in order to minimize the unfavorable conditions caused by high absorption limestone aggregates and to improve the mechanical properties compared to regular concretes. Results showed improvements in the microstructural development, compressive strength (7 -11%), splitting tensile strength (14-16%) and modulus of elasticity of the concrete (8-12%). However, some issues related to the functionalization and dispersion of the nanotubes in the mixtures remain to be solved to advance their utilization.

Keywords: Carbon nanotubes, compressive strength, splitting tensile strength, modulus of elasticity.

1. INTRODUCTION

Concrete made with high absorption limestone aggregates is limited in its mechanical properties compared to other types of concrete in which aggregates from igneous rocks or from natural deposits such as rivers are used. Therefore, in order to achieve favorable mechanical properties, the cement content must often be increased, a practice that generates important environmental impacts, from global to local.

Carbon nanotubes (CNTs) may be able to positively modify the properties of the cement paste. The use of CNTs as a concrete addition represents a significant potential utility because they can improve the mechanical properties and help in the control of micro cracks in the matrix.

Nanotubes can be classified as single-walled or multi-walled [1, 2], they are Carbon allotropes belonging to the fullerene structural family, consisting of cylindrical structures with at least one closed end, they have few nanometers in diameter and reach high tensile strengths. Discharge arc, laser ablation and chemical vapor deposition are the major used techniques for the production of CNTs; they have demonstrated their versatility in the manufacture of devices such as molecular probes, pipes, cables and springs [1] and they have a potential use as reinforcement in the form of fibers because they provide better ductility and increase fracture energy [3].

Recently, CNTs have been studied as an addition in mortars to improve the mechanical properties by increasing compactness [4-6]. However, the lack of effective knowledge on

CNTs properties, the difficulties for achieving functionalization in concrete mixtures, as well as their relatively high cost compared to cement, have limited their applications in the construction industry. Functionalization consists in the modification of the surface physical properties by adsorbing atoms or molecules to achieve solubility and dispersion in the cement paste, which can be problematic [7, 8]. In addition, the acquisition cost can be very high depending on the purity degree and on the manufacturing process.

On the other hand, the most important mechanical properties defining a concrete's quality are compressive strength (Fc), splitting tensile strength (Ft) and modulus of elasticity (Ec), which depend on the water/cement ratio (w/c) and are key inputs for the structural elements design. In laboratory conditions, these properties can be determined by following the ASTM C 39-05 [9], ASTM C 496-04 [10] and ASMT C 469-02 [11] standards, respectively.

Based on all of the above mentioned, the present work aimed at the designing of concrete mixtures with high absorption limestone aggregates, incorporating multi-walled carbon nanotubes (MWCNTs), in order to improve their performance in terms of Fc, Ft and Ec to fulfill structural requirements, without increasing cement consumption, which is justified from a sustainable perspective.

2. METHODOLOGY

The experimental procedure consisted, first of all, in obtaining both the aggregates and the MWCNTs. Subsequently, the physical characterization of materials, the design of concrete mixtures and the manufacturing process of the test specimens were carried out. Finally, samples were cut and prepared for the scanning electron microscope (SEM) and the tests for the assessment of the mechanical properties, central point of the present work object, were performed.

2.1. Materials

The used materials were Ordinary Portland Cement (OPC), crushed limestone aggregates (fine and coarse), water and commercial MWCNTs kindly provided by Yurui (Shangai) Chemical Co., LTD, which were employed for this work as an addition, with an estimated yield of 6.45 kg of MWCNTs per m3 of concrete. The aggregates were extracted from a quarry in the study area, located on the southern region of Quintana Roo, Mexico. The physical properties, indicated in Table 1, showed a low unit weight and high absorption, which is explained by its geological origin. Likewise, the characteristics of the MWCNTs are presented in Table 2.

Table 1. Aggregates physical properties

Properties	Coarse aggregate	Fine aggregate
Loose unit weight, kg/m^3	1265	1462
Compact unit weight, kg/m^3	1423	-
Specific gravity	2.3	2.6
Absorption, %	3.3	4.7
Abrasion, %	26	-
Fineness modulus, %	-	2.9

Table 2. MWCNTs characteristics

Characteristic	Value
Outer diameter	10-30 nm
Length	0.5-500 µm
Ash	0.2%
Purity	95%

Specific surface area	40-300 m^2/g
Amorphous carbon	3.0%
Electrical conductivity	10^2-10^{-4} s/cm

MWCNTs elemental chemical analysis was conducted by means of Energy Dispersive X-Ray Spectrometry, where it could be verified that the predominant element was Carbon (98.20%). Other elements were detected at low concentrations, such as Oxygen (1.40%), Aluminum (0.17%), Iron (0.13%) and Sulfur (0.10%), as shown in Figure 1.

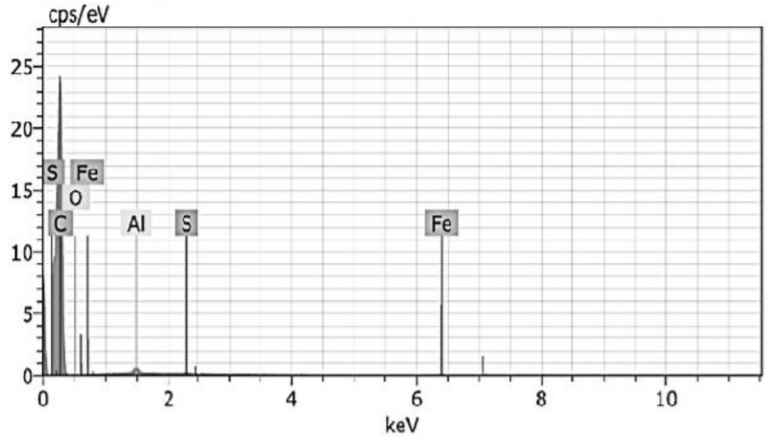


Figure 1. Elemental chemical analysis of MWCNTs

2.2. Mixtures design and manufacture of test specimens

Mixture design was performed according to the ACI method [12]. Two w/c ratios were set (0.5 and 0.7) and then, the aggregates amount were determined. Effective absorption of 80% for the mixing water correction was considered. The MWCNTs quantity for each w/c were 0, 0.5 and 1% weight of cement. The relative amounts of the materials for each mixture, before daily moisture corrections, are presented in Table 3.

Table 3. Mixture design (kg/m^3)

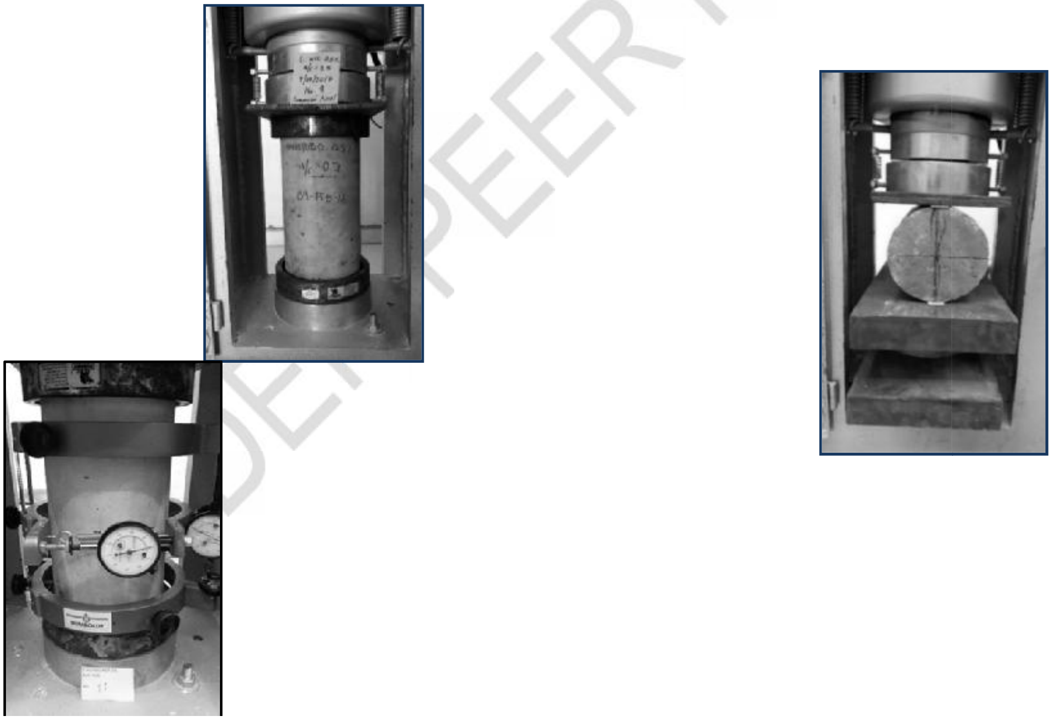
Mixture	Water	Cement	Coarse	Fine	MWCNTs
1	205	410	868	649	0
2	205	410	868	649	2.1
3	205	410	868	649	4.2
4	205	292	868	739	0
5	205	292	868	739	1.2
6	205	292	868	739	2.3

In several studies, the dispersion of MWCNTs is achieved by applying different sonication conditions [13]. Nevertheless, in this research, as an exploration of an alternative procedure, the mixture was made manually using a blender, incorporating them directly into the cement paste, prior to the concrete mixing (Figure 2). Concrete casting was carried out in an electric motor rotary drum mixer. For each concrete mixture, fifteen cylindrical specimens of 15 x 30 cm were manufactured, which were subjected to a process of moist curing by immersion for 28 days, before the obtaining of the micrographs and performing the mechanical tests.

Figure 2. Dispersion of MWCNTs

2.3. Physical and Mechanical Tests

Physical tests were performed in concrete fresh, such as unit weight and slump by ASTM C 143 [14], and trapped air with ASTM C 231 [15]. Subsequently, mechanical tests were made in hardened concrete: Fc, Ft and Ec, same that are illustrated in Figure 3.



(a) (b) (c)

Figure 3. Mechanical tests in hardened concrete: *Fc* (a), *F*t (b) and *Ec* (c)

3. RESULTS AND DISCUSSION

In the fresh concrete tests, a slight difference was observed between the values for both the mixtures with and without MWCNTs. However, when increasing the amount of MWCNTs, there is also an increase in the unit weight and a decrease in the slump and trapped air content, because the mixtures became denser. These results are correlated with the microstructure observed in the SEM analysis where a greater degree of compaction was observed in the samples with MWCNTs additions. The average results for fresh concrete are shown in Table 4.

Table 4. Fresh concrete properties

Mixture	Unit weight kg/m^3	Slump cm	Trapped air %
1	2406	11.0	4.5
2	2418	10.5	4.3
3	2423	10.2	3.9
4	2329	12.5	4.1
5	2336	12.4	3.6
6	2353	12.3	3.5

Results of the mechanical tests are presented in Figures 4 to 6, where it is observed that the mixtures with MWCNTs presented better performances than the control mixtures in all the studied mechanical properties.

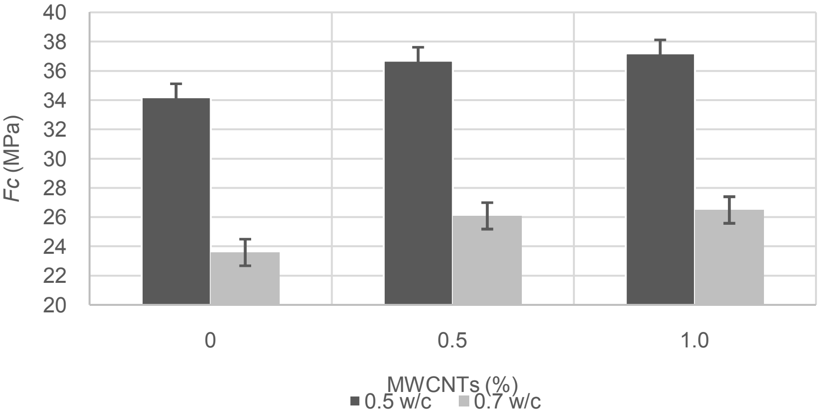


Figure 4. *Fc* according to MWCNTs and w/c

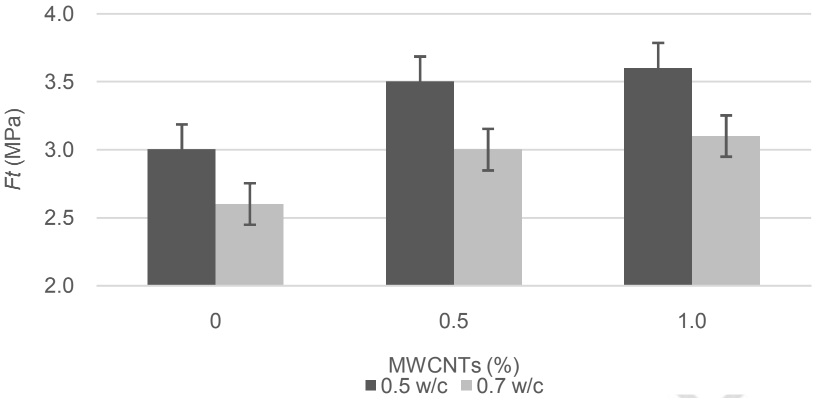


Figure 5. *Ft* according to MWCNTs and w/c

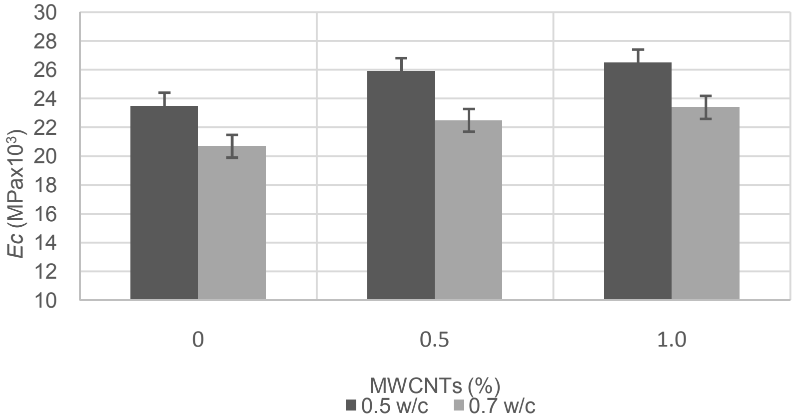


Figure 6. *Ec* according to MWCNTs and w/c

The obtained results in the present study can be compared with the results of other recent papers that can be found in the literature (see Table 5), where the percentage of improvement reached is reported.

Table 5. Percentage of improvement in the mechanical properties

Improvement in mechanical properties (%)			Experimental details	Reference
Fc	***Ft***	***Ec***		
7 a 11	14 a 16	8 a 12	Additions of 0.5 and 1.0% MWCNTs in concrete samples	Actual data
10	--	--	Additions of 0.15 and 0.25% MWCNTs in cement mortars	[5]
20	--	--	Additions of 0.1% MWCNTs in high performance mortars	[6]
10 a 20	--	--	Additions of 0.5% MWCNTs in cement mortars	[16]
15	23 a 40	--	Additions of 0.01, 0.05 y 0.025% MWCNT in cement composites with moderate and high sonication	[13]
7.5	--	15 a 27	Additions of 0.1, 0.2 y 0.3% MWCNT in	[7]

cement composites without sonication

In all cases, improvements in mechanical properties were reported. In cement composites better results were observed because there was no influence of the aggregates on the mechanical properties, which in turn depend on the adhesion with the cement paste.

Figure 7 shows results of Ft above the expected values according to equation 1, suggested by ACI 318 [17] and equation 2 by CEB-FIB [18]:

$$Ft = 0.56\sqrt{Fc} \quad (1)$$
$$Ft = 0.3(Fc)^{0.66} \quad (2)$$

Likewise, a comparison from experimental data of concretes with MWCNTs and limestone aggregates obtained of the same study area is made [19], in which similar performance was observed. On the other hand, in Figure 8, the results of Ec have been compared with equations 3 and 4, suggested by ACI 318 [17] and Centeno et al. [20], respectively. The latter, obtained with experimental data of concretes with limestone aggregates from the Yucatan Peninsula:

$$Ec = 0.043\,(W)^{1.5}\sqrt{Fc} \quad (3)$$

Where W corresponds to the unit weight of the concrete (1440 to 2480 kg/m^3).

$$Ec = 3.757\sqrt{Fc} \quad (4)$$

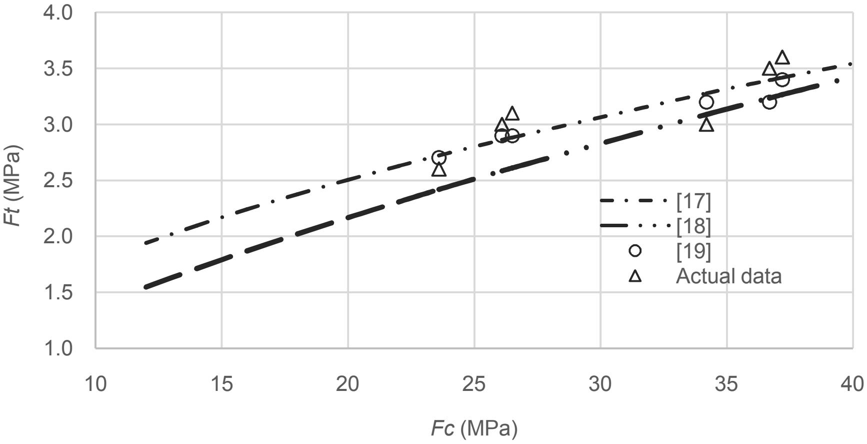


Figure 7. *Ft* versus *Fc*

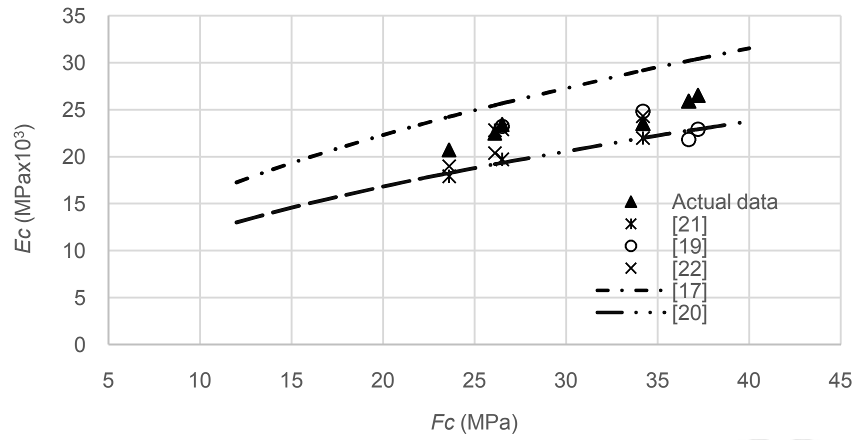


Figure 8. *Ec* versus *Fc*

For Ec, the experimental results in this investigation, and other unpublished [19, 21 and 22], obtained from concretes with high absorption limestone aggregates, were below what was predicted by ACI 318 [17], but above expected for concrete in the region [20].

For the microstructural performance study, three samples of each concrete specimen were cut and prepared for SEM analysis. In concrete without MWCNTs it was possible to identify high porosity and micro-cracks, as shown in Figure 9. On the other hand, samples with MWCNTs presented a better microstructural development (Figure 10), probably due to the filler effect and the formation of bond bridges in hydrates and nano-cracks [23].

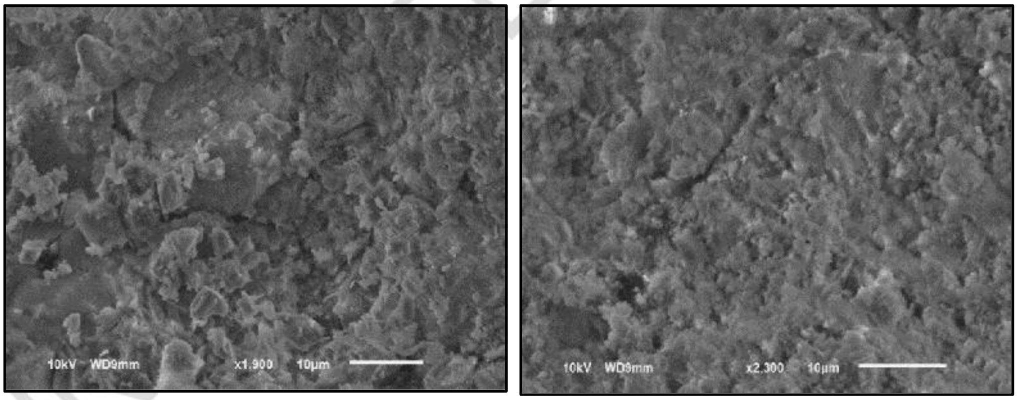


Figure 9. SEM micrographs of concrete without MWCNTs at 1500x and 2300x

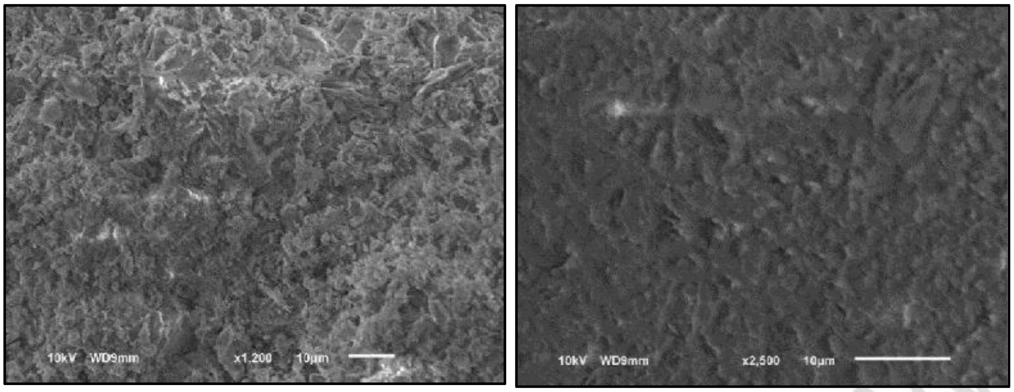


Figure 10. SEM micrographs of concrete with MWCNTs at 1200x and 2500x

4. CONCLUSION

The implementation of carbon nanotubes in concrete mixtures implies the opening of a new and promising research avenue for the construction industry. Compressive strength and splitting tensile strength of concrete improved significantly with the addition of MWCNTs, even above the expected values according to international codes. Modulus of elasticity increased with the addition of MWCNTs without reaching predicted values by the ACI 318, but above expected values for concretes with limestone aggregates from the study area. Finally, the use of MWCNTs improved the microstructural development of the concrete, which in turn influenced the mechanical properties.

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