Analysis by Ultrasound of the Behavior of Carbon Nanotubes on Cementitious Composites

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Abstract: Nanotechnology has brought significant innovations in science and engineering. Nanomaterials could change the face of modern construction because they are more resistant, more durable and have notable features. Concrete is a material widely used in construction industry worldwide. Carbon nanotube has been considered a new and outstanding material in nanoscience field with great potential application in the construction industry. The study presented in this paper, aims at assessing how carbon nanotubes can affect cement composites and so the concrete, in terms of microstructure and physical-mechanical properties. Three different ratios of carbon nanotubes have been searched: 0.20%, 0.40% and 0.60%. Tests were carried out with the ultrasound technique, measuring the propagation delay of the signal thought the specimens of cementitious materials with and without CNT, to reach the dynamic modulus of elasticity.

1. INTRODUCTION

The mechanical behavior of cementitious materials as concrete and mortar depends on structural elements and phenomena occurring in micro and nanoscale. The nanotechnology may change the molecular structure of material and thus improve its properties, such as performance physic-mechanical, the volumetric stability, durability and sustainability [2][3][11].

The revolutionary effects, performed by nanotechnology, allow the development of cementitious products of low cost, high performance and long duration which may lead to uses unprecedented of these materials in the construction industry [5][9][19][20].

The quality and durability of cementitious materials are directly linked with the ability to absorb deformations. One way to evaluate these characteristics is through the searching of the modulus of elasticity and the degree of compaction of the structure. The modulus of elasticity can provide good information about the deformity and stiffness of a material. These mechanical properties are of great interest, because they are straightly related with pathological phenomena such as structural cracks [6][14].

The dynamic modulus of elasticity (MOEd) determined by the method of ultrasound is equivalent to the initial tangent modulus of elasticity in origin, as illustrated in Figure 1. It is an approximate manner to evaluate the mechanical behavior of a material in relation to their ability to resist deformation [10].
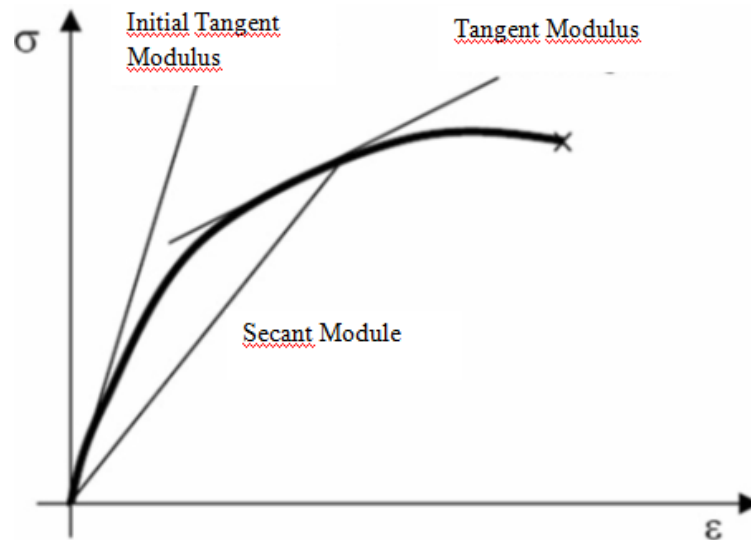
Figure 1: Diagram of deformation and modules of elasticity.
Source: http://www.abece.com.br/web/download/pdf/Eventos.pdf

The well-known "Non Destructive Testing methods – NDT" have been object of several researches in laboratories of excellence, worldwide for a long time. Good reasons for adopt these methods may be observed given that they don't affect the appearance or performance of the structure being analyzed. In addition these tests can be performed in the same place or in a place very close to it, and enable a constantly monitoring of the structure, to identify possible variations over time [8] [10].

Among the NDT methods available, the ultrasound technique may be considered as the most promising one for the evaluation of concrete structures, given that it allows performing homogeneity test of the material. Through it is possible to perform a total control of the structure, including eventual change of its parameters over time. For example, by analyzing the variation in the propagation speed of an ultrasonic wave one can obtain the degree of compactness of the structure or even detect heterogeneous regions inside the material [16][17].

The ultrasound method is based on the propagation of high frequency sound waves through the material analyzed. The speed of these waves varies depending on the amount of pores and voids in the material, enabling the detection of structural discontinuities. The method is performed injecting sound into the material and measuring its propagation time when reaching any other point of choice. Knowing the distance between the delimited points it is possible to determine the average signal speed propagation in the section, which will depend on various factors, such as the nature of the material, its porosity, the presence or absence of water in the pores, among others. Depending on the sensitivity on these factors, the ultrasound test may also serve to characterize a material, as well as its integrity and other physical properties, making it a technique widely used for quality control, fault detection, measurement of the thicknesses of the constituent of cementitious materials, etc., according to American Standard ASTM E 114-95 [1].

2. EXPERIMENTAL WORK

The study was oriented to obtain essentially comparative results between mortar samples with and without carbon nanotubes, with no concern with maximization or process improvement. Therefore, it was used in the experiment commercial materials frequently applied in construction, always maintaining the relationship between the components in the preparation of the mortar mixtures and following the same methodology for samples manufacturing and testing [13].

The main objective of this study is to evaluate, through an experimental procedure using the ultrasound test, performed in the laboratory of Universitat Politècnica de Catalunya (UPC) – Barcelona- Spain, how carbon nanotubes affect the physic-mechanical properties of samples cementitious materials, measuring the propagation time of ultrasound wave in the specimens, to reach the dynamic modulus of elasticity of the composites.

2.1 Test profile

Tests were carried out with mortar samples of cylindrical shape, of dimensions 4.4 x 8.0 cm, with contents of carbon nanotubes of 0.20%, 0.40% and 0.60% on the weight of cement, to compare their physic-mechanical properties to the equivalent properties of plain mortar, without nanotube. Tests were made in the ages of 3 days, 7 days and 28 days, using a replication factor equal to 3 for each blend.

The ultrasound test was performed according to was established in the Spanish standard UNE-EN 14579. The test of each specimen consisted in passing through the material a wave of frequency of 55 kHz produced by an ultrasound generator and measuring the corresponding propagation time in microseconds (μs). Figure 2 shows the test.

Figure 2: Using the method of ultrasound.

Using the propagation time, the value of dynamic modulus of elasticity may be obtained by the following expression:

$$MOEd = [\rho\ (1+\mu)\ (1-2\mu)\ (L/Tp)2]\ /\ 106\ (1-\mu) \tag{1}$$

Were MOEd is the Dynamic Modulus of Elasticity, ρ – density, μ = 0, 16 - Poisson coefficient, L - length of the specimen and Tp - propagation time.
The presentation and analysis of the results of the tests was based on the theory of Design of Experiments (DOE), and using MINITAB program [18].

2.2 Characterization of the Materials

Cement - was used cement type Portland CEM I 52, 5 R UNC-EM 197-1, manufactured by Cimento Molins Industrial S.A. from Barcelona – Spain;
Sand – fine sand provided by ÀRIDS CATALUNYA S.A, from Barcelona– Spain;
Water - potable water supplied by Water and Sanitation Company of Barcelona – Spain;
Additive - additive super plasticizer polycarboxylate ADVA Flow 401, produced by GRACE Construction Products, according to European Standard EN934-2;
Carbon Nanotubes - the nanotubes were manufactured and supplied by the Nanomaterials Laboratory of Physics Department of Universidade Federal de Minas Gerais – UFMG, Brazil. They were produced by the method of chemical deposition in vapor phase identified by MWCNT HP2627 and have the following characteristics [12]:
Type: multiple walled carbon nanotubes (MWCNT);
Weight: 60 g
Purity: > 93%
Other carbon structures: < 2%
Contaminants: < 5% of catalyst powder type MgO-Co-Fe
Dimensions: 99% of the CNT external diameter between 5 nm and 60 nm and a length estimated from 5 μm e 30 μm.

2.3   Molding of Samples

The specimens for testing were prepared using mortar with different percentages of carbon nanotubes. Four different blends were used to evaluate the behavior of mortars with and without nanotubes:

MIX 1 (CN0): cement + sand + water + 1,0% additive;
MIX 2 (CN2): cement + sand + water + 1,0% additive + 0.20% CNT;
MIX 3 (CN4): cement + sand + water + 1,0% additive + 0.40% CNT;
MIX 4 (CN6): cement + sand + water + 1,0% additive + 0.60% CNT.

The European standard EN 196-1 (2005) establishes the standard composition between the components for the manufacture of mortar in the following ratios: cement / sand, 1:3 and cement / water 1:1/2. Based on these ratios, plus the CNT and additive, the blends were prepared for manufacturing the specimens for test in the cylindrical shape with dimensions of 4.4 cm x 8.0 cm. As well as was done with the sand and water, the additive and the percentage of carbon nanotubes in the mixture were taken based on the weight of cement.

The specimens had to be manufactured in batches of six due to the small capacity of the mixer for preparation of mortars, associated to the plan of the test in the ages of 3, 7 and 28 days and the shared use of the laboratory of the UPC. The production of mortar and molding of the specimens were performed on the materials laboratory of the "Escola Politècnica Superior d' Edificació of UPC", following the methodology outlined below.

1. Initially cement and sand were weighed on a precision balance Gram brand, model ST-4000, maximum capacity of 4,000 g, and accuracy of $\pm$ 0.1 g. Then the two materials were mixed manually until they reached a homogeneous appearance;
2. Then, water and additive were weighed on the same balance;
3. The additive and water were mixed manually in a plastic container for about 5 minutes;
4. Next the nanotube was weighed on the same balance, for the blends that include this material;
5. The nanotube was added to water with the additive and mixed by hand for 5 minutes. Then this whole was submitted to the sonication for 60 minutes to obtain a dispersion of nanotubes and a better homogenization of the mixture [4][7][15]. For this purpose, we used the equipment ultrasonic P2000 clining qteck Gmbh;
6. The cement and sand (previously mixed) were accommodated within the mixer, brand Matest model E93, with maximum capacity of 3 kg together with the mixture of the water, additive and CNT;
7. After a mixing time of 15 minutes, the mortar was removed from the mixer for molding the samples. The densification of the samples was made in two layers, using a manual vibrating platform. The surface finish of the samples was performed with the aid of a spatula;
8. After molding, the specimens were kept for 24 hours in a chamber at a temperature of 21.4 C and 99% relative humidity;
9. After 24 hours, the specimens were demoulded and then were returned to the greenhouse, where they were kept until the test date. Figure 3 shows a batch of six samples ready for testing.

Fig. 3 - Specimens demoulded and ready for testing

3. RESULTS & DISCUSSION

The ultrasound test provides a good approximation of the investigated parameters and so achieves the goal of this work, which is basically a comparison between the parameters of the mortar samples, with and without CNT. Table 1 shows the average values of dynamic modulus of elasticity (MOEd), the material density and propagation velocity of the waves in the specimens, obtained with three test samples of each trace and age [16].

Table 1: Results of ultrasound test.

Trace	Age (day)	Vol. (mm3)	Density (g/cm3)	MOEd (Gpa)	V.usound (m/s)
CN0	3	126,36	2,164	21,635	3262,82
	7	123,35	2,110	21,806	3317,42
	28	128,01	2,129	23,065	3396,38
CN2	3	125,37	2,139	21,905	3302,31
	7	127,24	2,130	22,231	3300,51
	28	126,28	2,137	22,466	3345,56
CN4	3	127,24	2,164	27,042	3647,96
	7	129,74	2,166	27,374	3668,14
	28	124,36	2,162	28,712	3760,38
CN6	3	129,71	2,104	22,275	3356,61
	7	126,54	2,114	24,533	3515,52
	28	127,70	2,126	25283	3558,30

The scientific treatment model that was applied to the results obtained from the tests and used in the MINITAB is summarized in table 2:

Table 2 - Multilevel Factorial Design	
Factors: 2	Replicates: 3
Base runs: 12	Total runs: 36
Base blocks: 1	Total blocks: 1
Number of levels: 4,3	

Table 3, obtained with the processing of the program "MINITAB" shows the sequence of the events on the combination of variables (%) of nanotubes and age of the samples, and even the results of tests, where MOEd (GPa) represents the values of the dynamic modulus of elasticity.

Table 3: Table design, generated by MINITAB.

MINITAB - Design Table

StdOrder	RunOrder	PtType	Blocks	%CNT	Age	MOE$_d$ (GPa)
1	1	1	1	0.0	3	21,821
2	2	1	1	0.0	7	21,759
3	3	1	1	0.0	28	22,713
4	4	1	1	0.2	3	22,238
5	5	1	1	0.2	7	22,051
6	6	1	1	0.2	28	22,904
7	7	1	1	0.4	3	26,821
8	8	1	1	0.4	7	26,809
9	9	1	1	0.4	28	28,626
10	10	1	1	0.6	3	20,989
11	11	1	1	0.6	7	23,956
12	12	1	1	0.6	28	25,685
13	13	1	1	0.0	3	21,743
14	14	1	1	0.0	7	22,046
15	15	1	1	0.0	28	23,521
16	16	1	1	0.2	3	21,470
17	17	1	1	0.2	7	22,729
18	18	1	1	0.2	28	22,611
19	19	1	1	0.4	3	27,045
20	20	1	1	0.4	7	27,274
21	21	1	1	0.4	28	28,613
22	22	1	1	0.6	3	22,377
23	23	1	1	0.6	7	24,975
24	24	1	1	0.6	28	25,011
25	25	1	1	0.0	3	21,341
26	26	1	1	0.0	7	21,612
27	27	1	1	0.0	28	22,960
28	28	1	1	0.2	3	22,008
29	29	1	1	0.2	7	21,914
30	30	1	1	0.2	28	21,883
31	31	1	1	0.4	3	27,259
32	32	1	1	0.4	7	28,040
33	33	1	1	0.4	28	28,897
34	34	1	1	0.6	3	23,460
35	35	1	1	0.6	7	24,669
36	36	1	1	0.6	28	25,152

3.1 Evaluation of the dynamic modulus of elasticity (MOEd)

Table 4 summarizes the statistical parameters representing the result of experiment conducted for obtaining the dynamic modulus of elasticity of the samples.

Table 4: Dynamic Modulus of Elasticity

Age	Parameters	CN0	CN2	CN4	CN6	Average
3 days	Average MOE$_d$ (GPa)	21,635	21,905	27,042	22,275	23,214
	Standard Deviation	0,25758	0,39416	0,21902	1,23863	
	Variance	0,06635	0,15536	0,04797	1,53421	
	% gain/(reduction)	-	1,24	24,99	2,96	
7 days	Average MOE$_d$ (GPa)	21,806	22,231	27,374	24,533	23,986
	Standard Deviation	0,22073	0,43640	0,62160	0,52287	
	Variance	0,04872	0,19045	0,38639	0,27339	
	% gain/(reduction)	-	1,95	25,53	12,50	
28 days	Average MOE$_d$ (GPa)	23,065	22,466	28,712	25,283	24,882
	Standard Deviation	0,41404	0,52572	0,16035	0,35549	
	Variance	0,17143	0,27638	0,02571	0,12637	
	% gain/(reduction)	-	(2,59)	24,48	9,62	
Average		22,168	22,201	27,709	24,030	

The average values of MOEd were generated directly by MINITAB, whereas the standard deviation (Dp) and the variance (Var) were calculated, respectively, by the equations (2) and (3):

$$Dp = [\Sigma \ (Xi - Xm) \ / \ (n-1)]1/2 \qquad (2)$$
$$Var = Dp2 \qquad (3)$$

Where xi represents the value of the readings, obtained during the test, Xm is the average of readings and n, the number of samples used in the test. In this table, the percentage of gain or reduction was taken in relation to the reference sample CN0.

With the values of MOEd inserted in table 3, the MINITAB program, using the technique of regression analysis, generated the statistical profile model to the ultrasound test, represented by the graphs on figure 4.
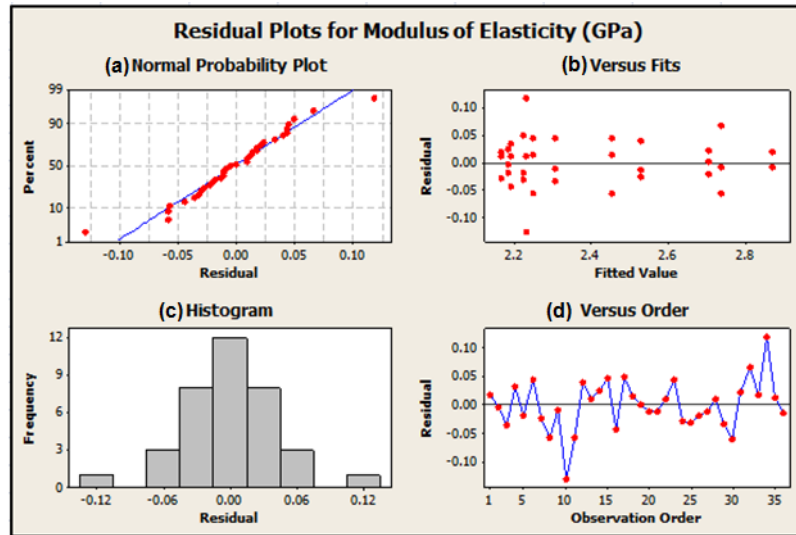
Figure 4: Regression Analysis to the MOEd search.

The validation of a model is possibly the most important step in the sequence of model building. The residual plots are used to ensure that the assumptions associated with the ANOVA model are not violated. The ANOVA model assumes that the random errors are independent and normally distributed with the same variance for each treatment.

The Normal Probability Plot is a graphical technique for testing a data distribution model of an experiment. It is estimated, thereby whether a data set presents or not a Gaussian distribution profile. It's possible to see from the graph 4-a, that the values of MOEd are distributed on concentrated form, almost entirely along of the straight line, which leads us to conclude that the model performed by the test has the profile of a normal distribution. This fact is ratified by the histogram (graph 4-c), it is configured with a symmetry bell-shaped, which is evenly distributed around zero, showing that the assumption of normality is likely to be true.

Graphs 4-b and 4-d depict an experiment with consistent methodology, since the residues are randomly distributed around zero, on a band within ± 5%, meaning that there is no deviation in the process. The divergences found on these graphs, are the values corresponding the inputs 10 and 34 of Table 2 reported from MINITAB as "Unusual Observations for Emod". These values correspond to the two samples CN6, tested in the age of 3 days, with results of MOEd far from the average. This may be due to an error in the reading process or the poor quality of the specimens.

Figure 5 shows the variation of the average value of the dynamic modulus of elasticity with the percentage of carbon nanotubes and the age of the samples of mortar.

According to the results, we can see that the samples CN4 and CN6 exhibited MOEd values higher than for samples CN0 and CN2, at all ages. The CN4 composite showed the most significant increasing to MOEd in relation to the reference sample, reaching a peak value at the age of 28 days and the highest gain, of 25.53% on the age of 7 days.
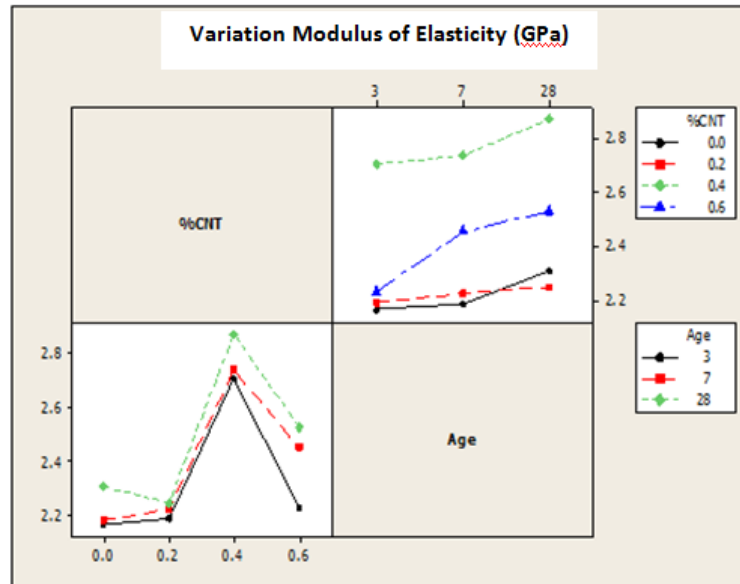
Figure 5: Variation of dynamic modulus of elasticity.

The blend with 0.2% of nanotubes did not show significant change, and even had the value of MOEd reduced at the age of 28 days.

Therefore, the sample with 0.40% of nanotube showed the best performance at all ages analyzed. The fact that, this mix had the best performance may indicate that there is a band considered "optimal" to insertion of nanotubes in cementitious product which should be close to the value quoted. It's still observed that, outside of this range, there is no significant gains, and may even result in the loss of resistance.

The graphics called 'Main Effects Plot and Interaction Plot", shown respectively in Figures 6-a and 6-b provide a statistical view more general of what goes on with the experiment, due to the interference of the variables in the process of evaluating the dynamic modulus of elasticity.

Figure 6-a, shows the evolution of the average of MOEd with each value of each variable, combining the effect of the other variables as if they were independent. In this graph, we may see, for example, that the average of MOEd is around 28 GPa, for the percentage of nanotube 0,4% and of 24 GPa on the age of 7 days.

In Figure 6-b, one may see the interaction of the variables on the process, plotting the average of MOEd for the combination of each level of a variable, with the levels of other variables. In this experiment there is only interaction between the curves of 0.0% and 0.2% of NTC, in the ages ranging between 7 and 28 days, when the average value of the modulus of elasticity of the specimens achieves a value around 22 GPa.
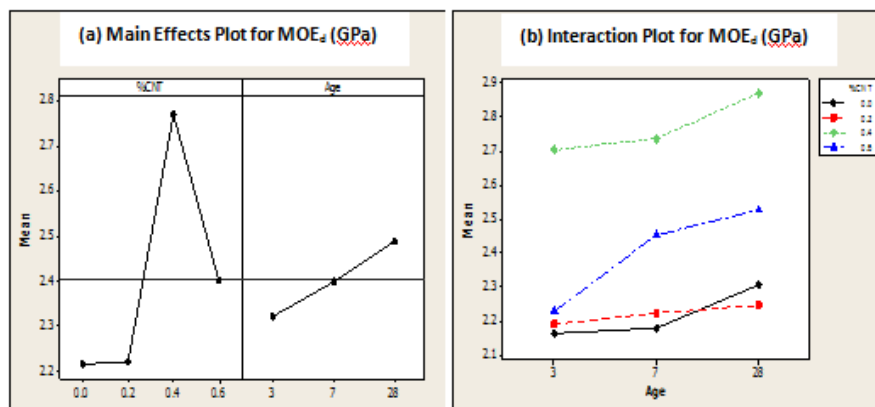

Figure 6: Main effects and interaction between the variables of MOEd.

3.2 Consideration on the density of the samples

The density of the mortar mixtures with and without carbon nanotubes, evaluated here, is simply the ratio of the mass and volume for each specimen. Table 5 presents the statistical parameters of the test results to the density ρ, as well as the percentage of gain/reduction in density of the samples with the addition of CNT, in relation to the reference sample CN0.

Table 5: Density of the samples

Age	Parameters	CN0	CN2	CN4	CN6	Average
3 days	Average ρ (g/cm³)	2,134	2,139	2,164	2,104	2,135
	Standard Deviation	0,00700	0,00700	0,00987	0,01389	
	Variance	0,00005	0,00005	0,00010	0,00019	
	% gain/(reduction)	-	0,23	1,40	(1,42)	
7 days	Average ρ (g/cm³)	2,110	2,130	2,166	2,114	2,130
	Standard Deviation	1,01473	0,01212	0,00794	0,01664	
	Variance	0,00022	0,00015	0,00006	0,00028	
	% gain/(reduction)	-	0,95	2,65	0,19	
28 days	Average ρ (g/cm³)	2,129	2,137	2,162	2,126	2,138
	Standard Deviation	0,02409	0,01758	0,01124	0,01212	
	Variance	0,00058	0,00031	0,00013	0,00015	
	% gain/(reduction)	-	0,37	1,55	(1,41)	
Average		2,124	2,135	2,164	2,115	

As can be seen in the graph of Figure 7, the values of the densities for the four samples are too close. The sample CN6 was the one showing worst result, below the reference sample, for the ages of 3 days and 28 days.
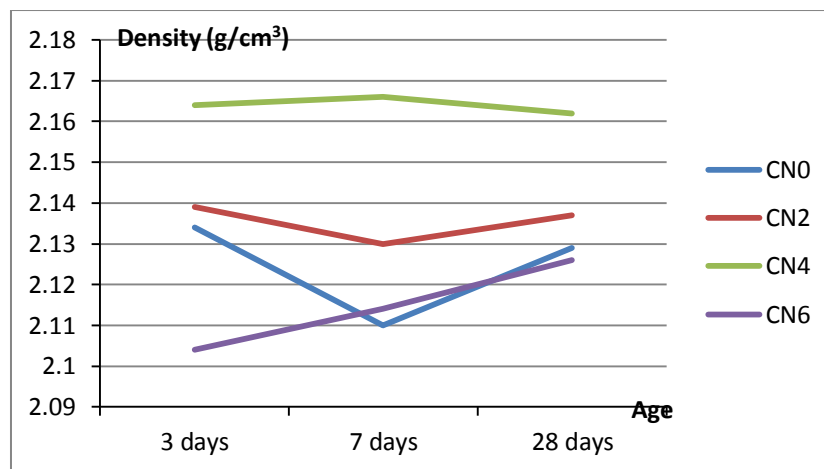

Figure 7: Density evolution.

The density of the mixture CN4 showed a performance slightly better, reaching a peak value at the age of 7 days indicating the presence of a denser structure, probably caused by filling the pores and better linkage between the grains, through the presence of the nanotubes.

4. CONCLUSIONS

Traditional materials employed in the construction industry, such as concrete, steel, asphalt coatings, glass, etc., are used in large scale and produced in large quantities. To give just one example, the cementitious materials exist for over 2000 years, and currently more than two tons of concrete per person on average, are used annually worldwide. Historically, the evaluation of the properties of these materials has only been possible in a macro scale.

The understanding of nanoscale behavior of the cement matrix and its interaction with other components used in the built environment can provide a powerful approach to develop superior concrete, with better properties and more effective control of the degradation process.

Carbon nanotubes, when incorporated into cementitious materials, present a remarkable characteristic, producing the best results with low levels of adding and behavior of Gaussian distribution, i.e., identifies a range considered "optimal" for insertion of nanotubes, out of this range, the properties of the composites have worse results.

In the experiment reported in this study, we found that the mixture of 0.4% of carbon nanotubes (CN4) was the mortar that showed the best performance in relation to the reference sample, reaching an increase of about 25% in the dynamic modulus of elasticity and a higher rate of structural compaction. The composites with addition of 0.2% and 0.6% of CNT did not show significant results for these same characteristics.

It's noteworthy that this experiment had a character purely of exploration comparative, where the characteristics of the composites with nanotubes were compared with the equivalent characteristics of the pure mortar. Different results could be obtained for the same phenomena investigated, if we changed, for example, the properties of materials such as nanotube type, the type of additives, granulometry of sand, etc. But we believe that the results, in qualitative terms, will be the same.

The results derived from this research and from other studies in the literature leave no doubt of the benefits received by inserting carbon nanotubes in cementitious products. Besides the increments obtained on microstructure and mechanical properties of the composites, the use of nanomaterials in construction can represent savings and greater profitability in the enterprises, as well as a positive step toward preserving the environment, when using Portland cement in a more efficient and durable, in concrete structures.

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