THE INFLUENCE OF CARBON NANOTUBES ON THE FRACTURE ENERGY, FLEXURAL AND TENSILE BEHAVIOUR OF CEMENT BASED COMPOSITES

Vanessa Vilela Rocha (1), Péter Ludvig (1), Flávio de Andrade Silva (2), Ana Carolina Constâncio Trindade (2)

(1) Department of Civil Engineering, Federal Centre for Technological Education of Minas Gerais, Belo Horizonte, Brazil

(2) Department of Civil and Environmental Engineering, Pontifícia Universidade Católica do Rio de Janeiro, Brazil

https://doi.org/10.21452/bccm4.2018.02.16

Abstract

Due to the necessity to improve the mechanical properties of cement-based materials, carbon nanotubes (CNTs) have been studied to prepare cement composites. Once they present high tensile strength, if well dispersed and well adhered to the cement hydration products, they can improve the mechanical properties of a cement paste system. Because of that, an effective dispersion process is crucial. Studies involving CNTs dispersion in cement particles in presence of a non-aqueous media of isopropanol resulted in improvements in mechanical properties suggesting a good dispersion and strong bond between CNTs and cement particles. Considering that, the present paper analysed a cement paste reinforced with 0%, 0.05% and 0.10% of CNTs dispersed in a non-aqueous media of isopropanol through three-point bending tests in notched specimens and direct tensile tests. The influence of CNTs on the material fracture energy, flexural strength, and tensile strength was addressed. The results pointed out an improvement of 90% of fracture energy in composites with 0.05% of CNTs. The results of direct tensile tests indicate an improvement of about 20% tensile strength in cement paste with 0.05% of CNTs and images by scanning electron microscopy indicate a better dispersion by this proportion. These results suggest not only an effective dispersion of CNTs in cement matrix by the used dispersion methodology at a dosage of 0.05% of CNTs, but also that the cement composites properties may be improved by the presence of them.

1. INTRODUCTION

Cement pastes usually present low fracture energy and low tensile strength, leading them to early cracking and making the cement matrix susceptible to penetration of deleterious agents. This behaviour implies that the durability of cement-based materials is a concern; however, they can be improved by the presence of other materials forming composites with better mechanical properties.

Carbon nanotubes (CNTs) have been studied as reinforcement in ordinary Portland cement (OPC) due to their extraordinary mechanical properties [1]. CNTs dispersion, however, appears as the greatest challenge to the incorporation of them in cement composites. They are hydrophobic and tend to agglomerate in the presence of water, which can reduce the cement pastes mechanical performance [2]. Researches, however, by the proper dispersion process recorded improvements in mechanical properties of cement-based composites prepared with CNTs [1-6].

Wang and Liu (2013) [3] prepared cement pastes with the incorporation of up to 0.15% of multi-walled carbon nanotubes (MWCNTs) modified by anionic gum and dispersed by a surfactant-ultrasonic method. The results showed an increase of 57.5% in flexural strength and 501% in fracture energy in the presence of 0.08% MWCNTs when compared with the reference paste (0%). In general, research involving dispersion of carbon nanotubes in surfactants use rates ranging from 0.045% [4] to 0.50% [5].

The cement pastes prepared by ZOU et al. (2015) [1] had additions of 0.038% to 0.075% of MWCNTS that were previously functionalized in COOH and dispersed using a polycarboxylate plasticizer and ultrasonication energy in aqueous solution. The results pointed out an increase of 31.5% in Young’s modulus, 49.9% in flexural strength and 62.6% in fracture energy with a paste incorporating 0.075% of CNTs.

HU et al. (2014) [6] dispersed MWCNTs in concentrations of 0.05% and 0.10% in COOH and SDS surfactant and ultrasonic frequency, separately. An improvement in the presence of 0.10% of CNTs was achieved, recording 26.9% of gain in fracture energy dispersed in SDS surfactant and 42.9% dispersed in COOH; 19.2% dispersed in COOH and 11.4% dispersed in SDS surfactant as results of fractural toughness. These results suggest that CNTs can be used as a reinforcement material by both dispersion processes researched by HU et al. (2014) [6] at a proportion of 0.10% of CNTs.

CNTs dispersed in cement particles in the presence of a non-aqueous media of isopropanol resulted in evidences of bond between the CNTs and cement matrix [7], CNTs acting as crack propagation controllers [7], densification of C-S-H [8] and compressive and splitting tensile strengths gains of approximately 50% [2]. The results obtained by Rocha and Ludvig (2017) [2] suggest that the optimum range for incorporation of MWCNTs by dispersion on cement particles in an aqueous media of isopropanol is close to the 0.05% ratio.

According to those results, the present work investigates the fracture energy under flexural loading and direct tensile behaviour of cement paste reinforced with MWCNTs at proportions of 0%, 0.05% and 0.10% (by cement weight) dispersed on the cement particles in a non-aqueous isopropanol media by sonication, and tested after 28 days of curing.

2. MATERIALS

The materials used are: (i) Brazilian Type CP-V Portland cement, due to its low percentage of mineral additions; (ii) multi-walled carbon nanotubes (MWCNTs), with estimated tube lengths between 5µm and 30µm, 99% of external diameter between 10nm and 50nm, and purity greater than 93%, produced in the Nanomaterials Laboratory of the Physics Department of the Federal University of Minas Gerais (UFMG); and (iii) isopropanol absolute grade.

3. METHODS

3.1. CNTs dispersion

The dispersion methodology adopted was based on process described by Rocha and Ludvig (2017) [2]: 10% of the total amount of cement was mixed with CNTs, stirred and sonicated in a solution of isopropanol for one hour at 42Hz. The CNTs were previously sonicated in isopropanol for 30 minutes. The isopropanol was later left to evaporate resulting in a dry powder of cement particles incorporated with CNTs. Rocha and Ludvig (2017) [2] suggest an effective dispersion at those proportions due to the gains in mechanical resistance achieved.

After the dispersion process, a small sample of cement with dispersed CNTs was analyzed by scanning electron microscopy. The images were obtained in a FEG - Quanta 200 FEI (Center of Microscopy, UFMG). A five nanometers carbon coating was used to ensure the sample conductivity.

3.2. Preparation of cement paste specimens

The obtained dry dispersion was mixed with the remaining quantity of cement. Water was added and three types of cement pastes were prepared in a mortar blender: (i) ISO-REF: without CNTs, (ii) ISO-0.05: with 0.05% of CNTs and (ii) ISO-0.10: with 0.10% of CNTs. The procedures to prepare and cure the cement pastes were the same as described by Rocha and Ludvig (2017) [2]. Figure 1 illustrates the dispersion process and cement paste preparation.

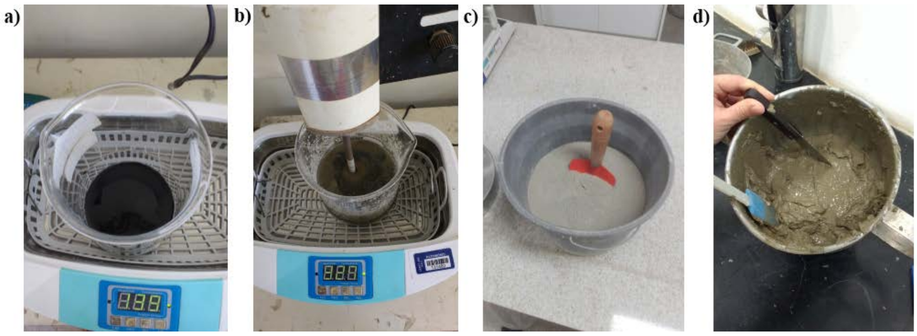


Figure 1: (a) Carbon nanotubes and isopropanol by sonication; (b) Carbon nanotubes, cement and isopropanol mixture being mechanically stirred and sonicated; (c) dry powder cement particles incorporated with CNTs mixed with the remaining quantity of cement; (d) cement paste with carbon nanotubes.

Nine specimens were prepared for each type of cement paste. Three of them were prismatic with 160 mm of length, 40 mm of width and 40 mm of height, used to three-point bending tests. Three of them were cylindrical with 5 cm of diameter and 10 cm height for splitting tensile tests. Tthe other three were used for direct tensile tests. The specimen geometry plan view is illustrated in Figure 2. The specimens had 40 mm of both height and width. The geometry adopted was defined according to the specimen specifications of Mechtcherine et al. (2011) [9] used to run direct tensile tests in cement based composites incorporated with short PVA fibers.

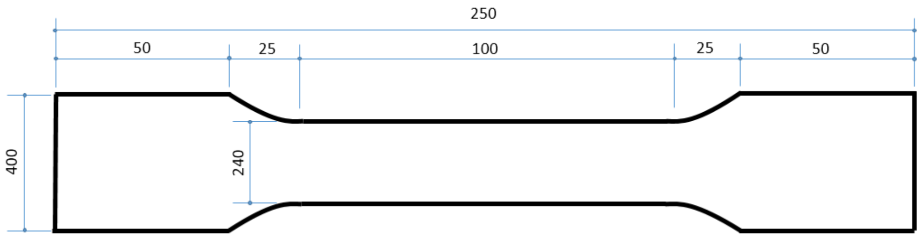


Figure 2: Specimen geometry used for tensile tests.

Three-point bending, splitting tensile test and direct tensile tests were performed after 28 days curing in a tank of lime-saturated water.

3.3. Three-point bending tests

The prismatic specimens were prepared with a notch in order to conduct the crack during the loading application. The cutting was performed using a specific apparatus developed for this purpose in order to ensure the alignment of the cut in the prismatic bars, and was executed in a depth of approximately 10 mm.

Close to the notch, two metal plates were attached, as indicated in Figure 3a. An MTS 632.02B-20 model extensometer was attached on the plates to measure crack mouth opening displacement, as showed in Figure 3b.

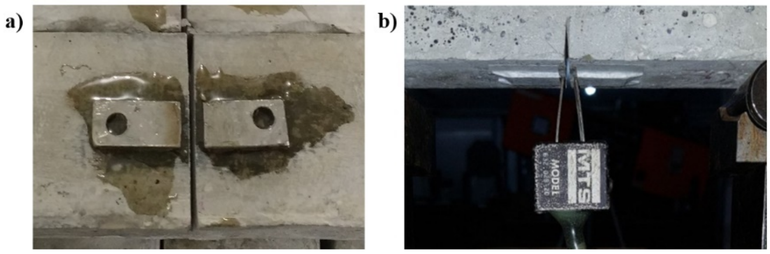


Figure 3: (a) Metal plates glued on the prismatic specimens; (b) extensometer placed on the prismatic specimens for three-point bending tests.

The three-point bending tests were carried on using a servo-hydraulic MTS testing system with closed loop control and a load cell of 2.5 kN. All specimens were tested at a constant crack mouth opening displacement (CMOD) rate of 0.008 mm/min, in order to keep the crack growth stable.

The maximum load applied divided by the effective cross section area was used to calculate the flexural strength. The area below the Stress x CMOD (Crack mouth opening displacement) graph, limited to 0.04 mm of displacement, was used to calculate the fracture energy. The results of flexural strength and the fracture energy were the mean values of the three results of each type of paste.

3.4. Splitting tensile tests

The splitting tensile strength tests were performed using an apparatus specially developed for this test, as showed in Figure 4. The tests were carried on using an EMIC brand test equipment with load cell of 20kN. The load increment used was equal to 1.0 mm/min.

Figure 4: Splitting tensile strength test

3.5. Direct tensile tests

At the age of 28 days, the specimens for tensile tests were placed between rubber papers, sandpapers and metal claws as showed in Figure 5a. The rubber paper and the sandpaper were used to create a friction between the specimen and the metal claws, and a torque of 5 N.m was applied at the screws. The metal claws were attached to the equipment, and a Linear Variable

Differential Transformer (LVDT) was placed to record the linear displacement, as showed in Figure 5b.

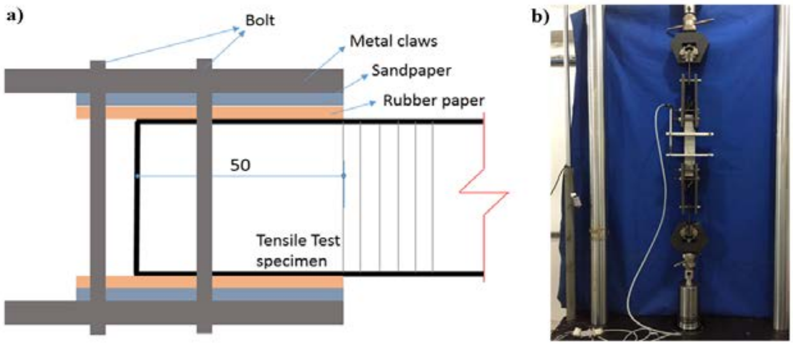


Figure 5: (a) Sketch showing the assembly and preparation of the specimens for tensile tests; (b) Specimens properly positioned in the equipment before testing

The tensile tests were carried on using a servo hydraulic MTS 810 load frame with closed loop control and a load cell of 250 kN. All specimens were tested under a displacement rate of 0.06 mm/min. The maximum load applied divided by the cross-section area (240 mm x 400 mm) was used to calculate the tensile stress.

4. RESULTS AND ANALYSIS

4.1. Three-point bending tests

The results obtained in the three-point tests are showed in Tables 1 and 2. The Figure 6 shows the graphs corresponding to the stress x CMOD behaviour of the specimens during the loading of the ISO-REF, ISO-0.05 and ISO-0.10.

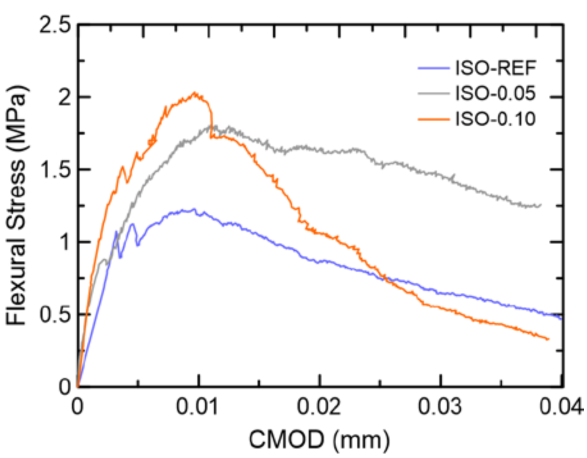
According to the information presented on Tables 1 and 2 and Figure 6, it is possible to affirm that the presence of CNTs contributes to enhance both fracture energy and flexural strength. The flexural strength was improved in the presence of CNTs, suggesting an effective dispersion by the used methodology and a strong bond between cement hydration products and CNTs. The flexural tests indicated a 31% of gain in flexural strength in the presence of 0.10% of CNTs while the cement paste with 0.05% indicated 26% of gain. This behaviour is showed at Figure 6 in which the cement pastes with 0.05% of CNTs were able to keep higher stresses even after the peak load. Differently, the ISO-REF and ISO-0.10 pastes show a more abrupt resistance drop after reaching the maximum load.

Table 1: Flexural Stress test results

	Flexural Stress (MPa)	Standard Deviation (MPa)
ISO-REF	1.21	0.18
ISO -0.05	1.63	0.12
ISO -0.10	1.76	0.07

Table 2: Fracture Energy test results

	Fracture Energy	Standard Deviation



	(N.mm)	(N.mm)
ISO-REF	6.72	0.48
ISO -0.05	12.76	2.71
ISO -0.10	8.99	0.92

Figure 6: Influence of carbon nanotubes on the flexural behaviour of cement pastes.

According to the information presented on Table 1, Table 2 and Figure 6, it is possible to affirm that the presence of CNTs contributes to enhance both fracture energy and flexural strength. The flexural strength was improved in the presence of CNTs, suggesting an effective dispersion by the used methodology and a strong bond between cement hydration products and CNTs. The flexural tests indicated a 31% of gain in flexural strength in the presence of 0.10% of CNTs while the cement paste with 0.05% indicated 26% of gain. This behaviour is showed at Figure 6 in which the cement pastes with 0.05% of CNTs were able to keep higher stresses even after the peak load. Differently, the ISO-REF and ISO-0.10 pastes show a more abrupt resistance drop after reaching the maximum load.

The difference pointed out by the fracture energy is more expressive in the presence of 0.05% of CNTs: 90%. In presence of 0.10% of CNTs the gain in fracture was 34%. These results suggest that the dispersion in isopropanol is effective and allows CNTs to act as crack propagation controllers as the ISO-0.05 cement paste absorbed more energy when the cracks propagated.

These results are related to the effective dispersion by the method adopted, and the more expressive gain in fracture energy of 0.05% CNT content when compared to ISO-0.10 paste may be related to the optimum range at this proportion using this methodology.

4.2. Splitting tensile tests

The results of splitting tensile tests are showed in Table 3 and Figure 7. The cement paste with 0.05% of CNTs recorded a resistance gain of 37% in comparison with the reference material, while the cement paste with 0.10% of CNTs recorded 28%.

Both splitting tensile strength and three-point bending tests showed better performances of pastes prepared with CNTs, suggesting that the proportions of 0.05% and 0.10% of CNTs dispersed in isopropanol may act as adequate reinforcements to the cement pastes.

Table 3: Splitting tensile strength test results

	Splitting Tensile Strength Test (MPa)	Standard Deviation (MPa)
ISO-REF	1.87	0.25
ISO-0.05	2.56	0.26
ISO-0.10	2.38	0.24

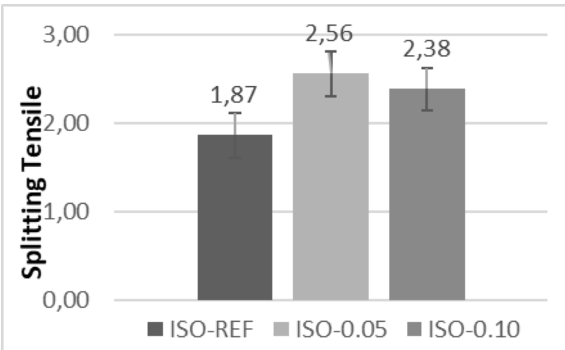


Figure 7: Splitting tensile test graph

4.3. Direct tensile tests

Three specimens of each type of cement paste were prepared. However, the fragility of the ceramic composites made it difficult to assembly the specimens to perform the direct tensile tests. During the test assembly, 67% of the specimens were lost due to the torque application or due to the eccentric positioning of the specimens in the equipment, which led to the realization of only one sample of each type of cement paste. It is noteworthy, however, that few results can be found in literature regarding direct tensile tests on CNT reinforced composites.

The obtained results in direct tensile tests are showed in Table 4. The Figure 8 shows the graphs corresponding to the stress x strain behaviour of the specimens during the loading of the ISO-REF, ISO-0.05 and ISO-0.10 pastes.

Despite the small number of specimens, the results of tensile tests are in accordance with the results presented by the splitting tensile and three-point bending tests, as they pointed out a better tensile performance of the cement paste with 0.05% of CNT. The ISO-0.05 achieved 19% of improvement in tensile.

The loss in tensile strength recorded for ISO-0.10 paste in comparison with ISO-0.05 may be attributed to the inefficiency of dispersion of CNTs at this proportion using this methodology. The maximum amount of CNTs that can be effectively dispersed on cement particles in isopropanol using sonication should be close to 0.05%. Only one sample was tested of each type of cement paste due to the difficulty of assembling and running the tensile tests, however these results are in accordance with the splitting tensile test results. Even though ISO-0.10 in both tensile and splitting tensile tests presents strength improvements in comparison to the reference material, ISO-0.05 recorded the higher tensile strength gain. It suggests that the effective dispersion limit of CNTs by this method has probably been achieved around 0.05% of CNTs, as affirmed by Rocha and Ludvig (2017) [2].

Table 4: Tensile tests results

	Tensile Strength (MPa)
ISO-REF	0.47
ISO -0.05	0.58
ISO -0.10	0.53

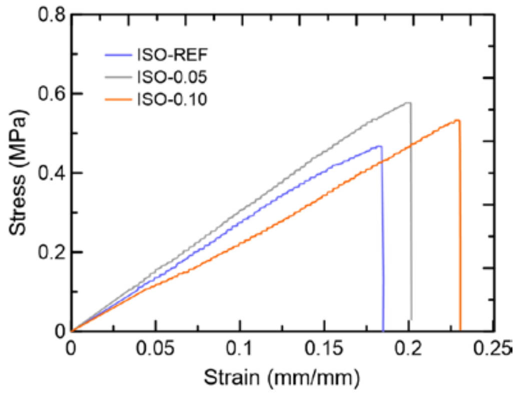


Figure 8: Influence of CNTs dosage on the tensile behavior of a cement paste

The values obtained by direct tensile tests were around 23% of the results of splitting tensile strength tests and around 35% of the results of splitting tensile strength tests. The difference recorded is natural due to the different specifications and methodologies used in each one of those tests. However, in all of them the presence of CNTs dispersed in isopropanol recorded an improvement in tensile strength of cement pastes, suggesting efficiency in the dispersion process carried out.

4.3. Scanning Electron Microscopy images

The scanning electron microscopy images of the cement anhydrous with the CNTs are seen in Figure 9 by enlargement of 50000x.

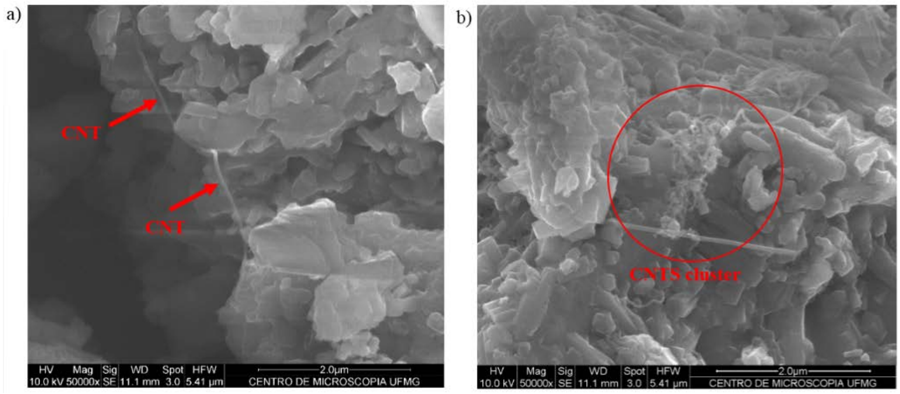


Figure 9: Scanning electron microscopy images of the anhydrous cement with (a) 0.05% of CNTs; (b) with 0.10% of CNTs

In presence of 0.05% of CNTs it was found a well dispersed CNTs filament among anhydrous cement particles and it was not possible to identify presence of CNTs clusters. In presence of 0.10%, however, the image suggests a small cluster, and the presence of clusters may be the cause of the lower tensile strength and fracture energy in comparison with ISO-0.05.

Those images are in agreement with the fracture energy and tensile strength results, in which the better mechanical behaviour of ISO-0.05 were due to an effective dispersion, also corroborating with Rocha and Ludvig (2017) [2] that the optimum range for incorporation of MWCNTs by dispersion on cement particles in an aqueous media of isopropanol is close to the 0.05% content.

5. CONCLUSIONS

According to the results, CNTs dispersed in isopropanol are effective and appropriate to prepare cement composites with enhanced mechanical properties. The flexural strength and fracture energy were improved in presence of CNTs, confirming that they can be used as a reinforcement material. The 90% of gain in fracture energy of composites with 0.05% of CNTs in comparison with 34% of gain achieved by the cement paste with 0.10% suggests a better dispersion of CNTs in the proportion of 0.05%. These findings corroborate with Rocha and Ludvig (2017) [2] results, in which the optimum CNT content using this dispersion methodology was 0.05%. The tensile strength was also higher in the presence of 0.05% of CNTs and the scanning electron microscopy images are in accordance with the mechanical behaviour, suggesting a better dispersion in a non-aqueous media of isopropanol methodology in presence of 0.05% of CNTs.

ACKNOWLEDGEMENTS

The authors would like to thank to CAPES, CEFET-MG, PUC-RIO, CTNANO, Center of Microscopy of UFMG, CNPq, FAPEMIG and UFMG for the financial and technical support provided for this work.

REFERENCES

[1] ZOU, B. et al. Effect of ultrasonication energy on engineering properties of carbon nanotube reinforced cement pastes. Carbon, v. 85, p. 212-220, 2015. ISSN 0008-6223.

[2] ROCHA V. V., LUDVIG P. Nanocomposites prepared by a dispersion of CNTs on cement particles. Architecture Civil Engineering Environment, 02/2018, p.71-75, 2018. ISSN 1899-0142.

[3] WANG, B.; HAN, Y.; LIU, S. Effect of highly dispersed carbon nanotubes on the flexural toughness of cement-based composites. Construction and Building Materials, v. 46, p. 8-12, 2013. ISSN 0950-0618.
[4] CWIRZEN, A.; HABERMEHL-CWIRZEN, K.; PENTTALA, V. Surface decoration of carbon nanotubes and mechanical properties of cement/carbon nanotube composites. Advances in cement research, v. 20, n. 2, p. 65-74, 2008.
[5] ROCHA V. V., LUDVIG P. Preparação e caracterização de nanocompósitos com nanotubos de carbono dispersos em surfactantes. The Journal of Engineering and Extract Sciences – JCEC, v. 3, p. 1097-1105, n. 8, 2017.
[6] HU, Y. et al. Fracture toughness enhancement of cement paste with multi-walled carbon nanotubes. Construction and Building Materials, v. 70, p. 332-338, 2014. ISSN 0950-0618.
[7] MAKAR, J.; MARGESON, J.; LUH, J. Carbon nanotube/cement composites-early results and potential applications. Conference on Construction Materials, 2005.
[8] MAKAR, J. M.; CHAN, G. W. Growth of Cement Hydration Products on Single-Walled Carbon Nanotubes. The American Ceramic Society, 2009.
[9] MECHTCHERINE, V. et al. Behaviour of strain-hardening cement-based composites under high strain rates. Journal of Advanced Concrete Technology, Vol. 9, No. 1, 51-62, 2011.