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Review

A review on the chemical, mechanical and microstructural characterization of carbon nanotubes-cement based composites

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HIGHLIGHTS

- The mechanisms by which CNT's interact with cement are not fully understood.
- Characterization techniques must be adapted to better understand the composites.
- Specific testing standardization is needed to develop the CNT's-cement technology.

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ABSTRACT

It is known that carbon nanotubes (CNT's) modify the properties of cement based composites in fresh and hardened state; it is also known that these modifications are positive when appropriate dispersion of CNT's within the matrix is achieved. Traditional experimental approaches used for fiber reinforced composites have been widely applied to study CNT's-cement composites; nevertheless, high statistical dispersions and conflicting reports have been found to be a common issue due to the nanometric nature of CNT's. This review presents a critical analysis of the most commonly used techniques to test CNT's-cement composites, opening the discussion of the necessity of specific testing standardization for the development of the technology. Topics such as CNT's dispersion and measurement of mechanical performance, electromagnetic properties and durability of CNT's-cement composites are addressed.

It is concluded that the benefits of CNT's in cement composites have been fairly identified, but the mechanisms by which nanotubes maintain dispersion within the matrix, interact with hydrating cement, and modify properties of composites are not yet fully understood. Understanding these mechanisms is considered of most importance to identify the limitations of CNT's-cement composites and define which applications are achievable with the use of CNT's. Better characterization of the interaction between CNT's and hydration products at the nanoscale is required to develop more efficient composites, targeting the enhancement of multiple properties at the same time.

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1. Introduction

The development of more efficient characterization techniques has allowed a better understanding of the principles and mechanisms by which carbon nanotubes (CNT's) modify the properties of cement matrixes in multiple scales [1]. This better understanding led to the first steps in the development of the CNT's-cement based composites technology, finding some consensus within the literature regarding the most adequate methodologies to produce composites. Additionally, identification of the challenges inherent to the usage of CNT's has cleared the view regarding the expected impact of CNT's over the mechanical and electromagnetic properties of CNT's-cement composites. It is important to understand the potential and limitations of CNT's-cement composites to think the future applications accordingly. This will help to filter which applications can be obtained with micro and macro fibers, and which are only achievable with the use of CNT's.

Standardization of the properties of CNT's-cement composites is a necessary step towards mass production processes that guarantee reliable products. Existing technical regulations for Portland cement matrixes must be carefully adapted for this nanostructured composite; therefore, it is important to identify the key properties of the composite to be measured, and which techniques should be used to obtain repeatable results. In general, most of the current techniques used to measure mechanical properties and durability of cement matrixes can be adapted to CNT's-cement composites without substantial modifications, but an additional effort must be made to find the most adequate techniques to measure novel electromagnetic properties of the composites.

Production of CNT's-cement composites requires the application of a set of characterization techniques covering a range of scales from nano to macro. Aspects such as dispersion degree and integrity of CNT's must be evaluated at the nanoscale, while the performance of the composite is usually evaluated at the micro and macro scales. A combination of spectroscopic techniques, microscopy imaging, mechanical testing, electromagnetic measurements, and durability evaluations, among others, represent the minimum body knowledge required from a CNT's-cement composite to predict its performance. This review presents a state of the art of the CNT's-cement composites technology. First the characterization techniques used to measure the dispersion degree of CNT's are presented; then, the different methodologies used to produce such composites and test their mechanical and electromagnetic properties are reviewed. Finally, the potential of CNT's to improve the durability of cement composites is discussed. The goal of this review is to present and compare the range of characterization techniques available, giving an early insight on the need of specific testing standardization for nanotubes-cement composites.

2. Basic characterization of CNT's

A basic set of features must be known prior to the application of CNT's in a cement-based composite; these include diameter, length, multi wall or single wall character, degree of structural organization and surface functionalities. Diameter and length are used to calculate the aspect ratio of CNT's, which has been found to be a key parameter that controls the reinforcing efficiency [2] and strain sensing [3] capabilities of the composites. These values are usually obtained using transmission electron microscopy (TEM) [4] or scanning electron microscopy (SEM) [5]. Drawing conclusions from a single microscopy image can be misleading; image processing methods that identify variations in gray intensities to isolate individual CNT's must be applied to large groups of images to obtain a statistical analysis of length and diameter. This kind of analysis is time consuming, but allows a more reliable quantification of the dimensions of CNT's in terms of a size distribution, rather than in terms of a nominal value [6]. Particle size distribution techniques such as Dynamic Light Scattering (DLS) should not be used to characterize individual CNT's, since it has been demonstrated that the results obtained from these techniques are representative of agglomerations rather than individual nanotubes. Additionally, these results depend on the presence of a dispersing agent and the application of dispersion energy such as ultrasonic waves [7]. A similar issue occurs with the specific surface area measured by BET adsorption isotherms [5], bulk densities measured by traditional powder methods, and specific masses measured by pycnometer, are also dependent on the dispersion degree of CNT's agglomerations.

Structural characteristics of CNT's can be defined by their crystalline organization [8], chiral vector [9] and single wall or multi wall character [10]. The crystalline organization of CNT's can be characterized by the I_D/I_G ratio determined from RAMAN spectroscopy results. I_D/I_G represents the proportion between the organized and disorganized carbon structures in the CNT's, and uses the intensities of D (defective carbon) and G (graphitic carbon) bands located at high wave numbers in the RAMAN absorption spectrum [11]. I_D/I_G is a good quality indicator for CNT's, low I_D/I_G ratios are characteristic of highly graphitized structures [8]; with reports in the literature ranging from 0.65 for laboratory quality MWCNT's [12], to 2.04 for industrial grade MWCNT's [13].

The chiral vector of CNT's indicates the geometric organization of the hexagonal arrays of carbon atoms, and can be determined by electron diffraction [14]. The chiral vector is mostly relevant for single wall carbon nanotubes (SWCNT's), since it defines if they behave as metallic conductor or semi-conductors [9]. Electric and thermoelectric properties of individual CNT's can be measured using standard lithographic practices [15]. Multi walled or single walled character of the CNT's can also be determined using RAMAN spectroscopy by the radial breathing mode absorption bands, which are located at low wave numbers, and are characteristic of SWCNT's [16]. SWCNT's and MWCNT's differ in many properties such as Young's modulus [17–19], electrical conductivity, thermoelectric properties and optical properties [15]. Nevertheless, there are no reports in the literature indicating if the reinforcing efficiency or self-sensing capabilities of the cement-based composites are noticeably modified by differences in I_D/I_G, chiral vector, electric resistivity or single wall or multi wall character. A vast majority of the literature reports use MWCNT as reinforcement in CNT's-cement based composites [1]. Higher availability and lower cost seem to be the main criteria to select MWCNT's over SWCNT's.

Finally, the presence of functional groups on the surface of CNT's can be determined by Fourier Transform Infrared (FTIR) spectroscopy [20], through the vibrational modes of chemical bonds [21]. Physicochemical treatments are able to induce —OH or —COOH groups on the surface of the CNT's, these groups can be used to improve the interfacial bond between nanotubes and the cement matrix [22], or use this groups to graft different molecules on the surface of the nanotubes, which are capable of chemically interacting with the cement matrix [23]. The main goal of this treatment is to increase the load transmission efficiency, but some studies have shown negative effects due to agglomeration phenomena caused by the negatively charged surface of functionalized CNT's [24]. A summary of the techniques discussed in this section is presented in Table 1.