Reinforcing cement with pristine and functionalized carbon nanotubes: experimental and simulation studies

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ABSTRACT
In recent years, the addition of carbon nanotubes to construction materials has attracted considerable interest, due to the improvement of mechanical, electrical, and thermal properties of cement. The incorporation of carbon nanotubes into a cement matrix causes an increase of several mechanical properties of up to 170% even with low carbon nanotubes concentrations. The objective of this study is to analyze the influence of the type of functionalization and number of walls of carbon nanotubes on the interaction between these nanostructures and a cement surface and thus, on the improvement of their mechanical properties. Thus, single-walled and double-walled carbon nanotubes were used to investigate the influence of the number of walls. The effect of carbon nanotube functionalization was studied using carbon nanotubes functionalized with carboxyl and carboxylate groups. The experimental results demonstrate that the incorporation of carbon nanotubes into the cement matrix improves the mechanical properties of the resulting material. Functionalized carbon nanotubes perform better than pristine carbon nanotubes. Electrostatic attractions play a central role in establishing strong interactions between the carbon nanotubes and the cement surface. The presence of neutral polar groups on the carbon nanotube surface also improves this interaction. The number of walls seems to be less important.
1. Introduction

During the last few years, there have been an increasing number of research studies on composites made of cement and CNTs [1–4]. The latter are long cylindrical molecules made only of carbon atoms and discovered by Iijima in 1991 [5]. They can be described as rolled-up graphene layers and are classified as single-walled carbon nanotubes (SWCNTs) [6] or multi-walled carbon nanotubes (MWCNTs) depending on the number of graphene layers. Their exceptional electronic, chemical, and mechanical properties [7,8,9] make them ideal candidates for diverse applications such as composite materials, microelectronics, or energy storage among others [10,11]. CNTs have a high Young modulus of 1000 GPa and tensile strength of approximately 100 GPa [12]. Due to these characteristics, they hold great promise as reinforcing materials in cement composites. Indeed, the influence of CNTs on the mechanical properties of cement has already been investigated by numerous authors. Diverse studies show that concentration, type of CNT, and functionalization of their surface, among other factors, play a crucial role in the improvement of the properties of the composites [13–16]. Various studies have shown that the incorporation of CNTs into a cement matrix causes an increase of several mechanical properties of up to 170% in some cases, even with low CNTs concentrations [3,17,18]. Porosity [19], electrical resistance, and piezoresistivity [21] are other properties that benefit from the use of CNTs in cement composites.

Despite the widespread interest in the use of CNTs as reinforcing agents, the problems related to their homogenous dispersion in the cement matrix constitute a major obstacle to achieving new materials with improved properties. CNTs present a strong tendency to agglomerate and form bundles due to Van der Waals forces and a large surface area to volume ratio. This makes their dispersion into cement very difficult and does not promote strong adhesion to it [14,15]. This, in turn, affects the improvement of the aforementioned properties.

To circumvent this problem, several methods to improve the distribution and mixing of CNTs inside a cement matrix have been tested. They usually consist of ultrasonication in combination with some kind of functionalization agent, which modifies the CNT surface and makes it more suitable for dispersion [18]. The functionalization processes can be classified into two broad groups, depending on the nature of the interaction established between the CNTs and the molecules linked to them [22]. On the one hand, covalent functionalization implies the formation of strong chemical bonds, which can modify the electronic structure and properties of CNTs [23,24]. On the other hand, CNTs solubility and dispersion can be increased by noncovalent functionalization. In this case, CNTs integrity and properties are preserved as the interaction established between the CNTs surfaces and the adsorbates is purely physical [25]. Different approaches have been used to functionalize CNTs in a noncovalent way, including π-π stacking [26] and hydrophobic interactions [27]. In order to disperse CNTs in water, it is worth noting the use of surfactants, both ionic [28], nonionic [29], or even mixtures of different surfactants to achieve a synergistic effect [30,31]. The hydrophobic part of these molecules adsorbs on the CNT surface while the hydrophilic part produces a hydrated layer that expands away from the CNT surface, improving CNTs solubility and dispersion in aqueous solvents. CNTs for cement composites are typically functionalized with carboxyl groups produced by strong acids treatment [32], a large variety of surfactants
such as sodium dodecyl sulfate [21] or superplasticizers commonly used in the cement industry [33,34]. Moreover, the modification of the CNT surface allows the creation of chemical bonds between the CNTs and the cementitious matrix, enhancing the adhesion between both components [19,35].

The theoretical study of the properties and structure of cement can be carried out using molecular simulation techniques [36–39]. There are different simulation methods, but those that describe the interactions between the atoms that make up the system through a set of equations and parameters, the so-called force-field methods, are the most appropriate for the study of this material, since they allow handling a greater number of atoms in reasonable computational calculation times [40]. Specifically, the use of the molecular dynamics (MD) method [41] allows analyzing the temporal evolution of a system by applying Newton’s equations of motion, and gives access to the calculation of a wide variety of properties such as structure, mechanical behavior, or interaction energies between different components, among others [42–44]. Thus, Sánchez et al. [45] studied the influence of functionalization on the interaction between graphite surfaces and the 9 Å tobermorite structure by MD. The effect of CNT chirality and diameter on the mechanical properties of 11 Å tobermorite was analyzed by Lushnikova et al. [46,47]. Fan et al. studied the interfacial stress transfer in graphene oxide cementitious composites. The mechanical properties of pure cement and CNT cement composites were calculated by Hajilar et al. [48] and Lushnikova et al. [49], respectively. In the present work, experimental characterization and MD simulations were carried out to study the properties of cement reinforced with different kinds of CNTs.

The main objective of this study is to analyze, through experimental and simulations studies, the influence of the type of functionalization and number of walls of CNTs on the interaction between these nanostructures and a cement surface and thus, on the improvement of their mechanical properties. We hope that the results of this study will help to understand the key parameters allowing reinforcement of this interaction and improvement of the mechanical properties of these materials. Thus, both single-walled CNTs and double-walled CNTs were used to investigate the influence of the number of walls. The effect of CNT functionalization was studied using pristine CNTs or CNTs functionalized with different concentrations of carboxyl and carboxylate groups.

2. Materials and methods

2.1. Experimental procedure

2.1.1. Materials

Portland cement II/B-L 32,5R grade was used in this study. The characteristics of the CNTs incorporated in the cement paste are shown in Table 1.

2.1.2. Methods

Cement paste was prepared in a cement-water weight ratio of 2:1. The CNTs were dispersed previously in water, and then added in an amount of 0.02% by weight to the cement powder.
Table 1. Characteristics of the CNTs used in the experimental study.

| Carbon nanotubes                     | Average Diameter (nm) | Average Length (µm) |
|--------------------------------------|-----------------------|---------------------|
| COOH functionalized multi-walled     | 9.5                   | 1.5                 |
| Single-walled                        | 0.78                  | 1                   |

To prepare and characterize the test specimens, the following steps were taken:

1. Dispersion of the CNTs in water: the CNTs were mixed with water, and the mixture was ultrasonicated in a horn sonicator (Sonoplus HD 2070, Bandelin) for 1 h.
2. Mixture and specimen preparation: the CNTs-water dispersion was mixed with the cement powder at a high-speed mixing (maximum speed of 18,000 rpm). To measure the mechanical properties, cylindrical specimens of 2 cm high and 1 cm diameter were molded with the freshly prepared cement paste.
3. Mechanical properties measurement: the indirect tensile strength of test pieces after 28 days aging was measured with a universal testing machine at 24 N/s speed.

2.2. Calculation method and model systems

The calculations were done with the Forcite module of the Materials Studio 7.0 software [50] in the NVT ensemble (number of particles N, volume V and temperature T, constants) and maximum simulation times of 2.5 ns using a time step of 1fs. The maximum simulation time was dependent on each particular system and was determined after thermodynamic equilibrium had been reached (constant total potential energy). The temperature was controlled by a Nose-Hoover thermostat and kept constant at 298 K [51]. The forcefield used to calculate the interaction between the cement and the CNT was the condensed-phase optimized molecular potential for atomistic simulation studies forcefield (COMPASSII) [52], a forcefield based on ab initio calculations that allows describing the structure and properties of molecules and condensed phase systems, in a wide range of temperature and pressure values. COMPASSII has been successfully applied in the simulation of systems containing CNTs and different materials derived from cement [53–57]. To calculate coulomb interactions, the Ewald summation method was used and an atom-based cutoff method was applied for van der Waal interactions [58]. The cutoff distance for both interactions was taken to be 12.5 Å. Before the MD simulation runs, the energies of the initial configurations were minimized using the smart minimizer algorithm and the system was considered to be converged when an energy gradient of 0.001 kcal/mole was reached.

To represent the atomic structure of cement there are several models, although hydrated calcium silicate (CSH) is considered to be one of its main components and is the main responsible for the strength of concrete structures [59]. For molecular modeling purposes, one of the structures that can represent CSH structure is that of the crystalline mineral tobermorite [48,60,61] although it is well known that real systems present poor crystalline order with variable stoichiometry [37]. In this work, the crystalline structure of the tobermorite 11 Å (Figure 1(a)) was used as a model to represent the cement surface. This structure contains double silicon oxide chains interspersed with calcium oxide sheets and hydration water molecules. 11 Å indicates the basal spacing of the calcium oxide
The unit cell lattice parameters used in the present work are $a = 6.735 \text{ Å}$, $b = 7.385 \text{ Å}$, $c = 22.487 \text{ Å}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 123.25^\circ$.

To study the interaction between the CNTs and the tobermorite surface, the crystalline models shown in Figure 1(b) were constructed. These models consist of the (001) tobermorite surface and pristine or functionalized single-walled (CNT1) or double-walled (CNT2) (6, 6) CNTs placed above it at an initial distance of about 19 Å. The length of the CNTs is 20 Å and they were capped at both ends by H atoms. A $6 \times 5 \times 1$ supercell with dimensions of $40.5 \times 40.5 \times 82.5 \text{ Å}^3$ was built. The thickness of the corresponding surface is 22.5 Å and a vacuum layer of 60 Å was introduced to remove the interaction between periodic images of the structure along the z-axis. The surface area exposed to the interaction with the CNT corresponds to the calcium oxide sheet located between the silicate layers, which is usually the weakest part from a mechanical point of view [56,59]. It must be noted that this structure is a simplified model used to study the interaction between the CNTs and the tobermorite surface and does not take into account the whole complexity of real systems.

The CNTs were functionalized by the introduction of carboxyl (CNT-COOH) or carboxylate groups (CNT-COO\(^-\)) in two different concentrations (7 and 11 groups, which corresponds to percentages by weight of 11.92% and 17.54% for single-walled CNT and 4.49% for double-walled CNT).
and 6.88% for double-walled CNT). The total percentages by weight of CNT in the supercell are 4.8% and 12.71% for CNT1 and CNT2, respectively.

The binding energy ($E_B$) of the CNT to the tobermorite surface was calculated as

$$E_B = E_{CNT+Surface} - (E_{CNT} + E_{Surface})$$

where $E_{CNT+Surface}$ is the mean energy of the final equilibrium configurations of the CNT + surface systems and $E_{CNT}$ and $E_{Surface}$ are the final equilibrium energies of the pure, unmixed systems. It follows from this definition that negative $E_B$ values imply that final configurations are more stable than initial configurations and the adsorption process on the tobermorite surface is favorable from an energetic point of view.

3. Results

3.1. Experimental results

Figure 2 shows the indirect tensile strength results of samples reinforced with both pristine SWCNTs and MWCNTs functionalized with COOH. It can be seen that samples reinforced with functionalized MWCNTs exhibit a higher indirect tensile strength than samples reinforced with SWCNTs.

3.2. Molecular dynamics results

3.2.1. Binding energy

The $E_B$ values calculated from equation 1 are presented in Table 2. The minimum average distance between the CNT and the surface for each system is also shown in the right-hand column of this table. This distance is calculated as an average of the smallest distances.
from the last 25 snapshots of the trajectories, which corresponds to the final 120 ps of the simulation.

For the sake of clarity, these values are also shown in Figure 3. Positive \( E_B \) values are found for both pristine SWCNT and DWCNTs and the tobermorite surface. After CNT functionalization, the \( E_B \) values become negative, which indicates an attractive interaction between the CNTs and the tobermorite surface.

### 3.2.2. Hydrogen bonds (H-bonds)

The initial models used in the simulations consist of the tobermorite surface and a CNT placed above it at a distance of about 19 Å. Representative snapshots of the CNT2-11COO\(^-\) system at the beginning (\( t = 0 \) ps) and at the end of the simulation are shown in Figure 4. For the sake of clarity, only one of the systems is shown in the figure but they all behave in a similar way. After several thousand ps of simulation, the CNT has moved closer to the surface and a network of several different interactions has developed between its polar groups and the surface groups.

The CNTs functionalized with COOH and COO\(^-\) groups can establish H-bonds with the O atoms of the tobermorite surface. The number of H-bonds (\( N_h \)) formed between the

|            | \( E_B \) (J/m\(^2\)) | \( d \) (Å) |
|------------|------------------------|-------------|
| CNT1       | 0.12                   | 2.7         |
| CNT2       | 0.08                   | 2.6         |
| CNT1 + 7COOH | -0.16              | 1.3         |
| CNT2 + 7COOH | -0.11              | 1.3         |
| CNT1 + 11COOH | -0.24           | 1.3         |
| CNT2 + 11COOH | -0.01           | 1.3         |
| CNT1 + 7COO\(^-\) | -0.20          | 2.0         |
| CNT2 + 7COO\(^-\) | -0.26          | 2.0         |
| CNT1 + 11COO\(^-\) | -0.56          | 2.0         |
| CNT2 + 11COO\(^-\) | -0.24          | 2.0         |

Figure 3. Interaction energy (J/m\(^2\)) between pristine and functionalized CNTs and the tobermorite surface.
CNTs and the surface is shown in Table 3. The geometrical criteria for the existence of an H-bond are the following: the distance between the H of the donor group (D) and the O of the acceptor group (A) is less than 2.5 Å and the DH–A angle is greater than 90°.

As can be seen from the above table only the CNTs functionalized with carboxyl groups form H-bonds with the surface. In general, the more functional groups the CNTs have, the more bonds are formed. Some representative configurations showing the H-bonds as blue-dashed lines are shown in Figure 5. CNT2 gives similar results and are not depicted here. It will be shown below that carboxylate groups are preferably bonded to the Ca$^{2+}$ atoms of the surface and thus show no hydrogen-bonded atoms.

The radial distribution functions (RDFs) of the carboxyl H atoms-surface O atoms are shown in Figure 6. All the systems show intense and well-defined peaks at about 1.3 Å, which correlates well with the minimum average distances listed in Table 2.

### 3.2.3. Ca$^{2+}$-O bonds

The O atoms of the carboxyl groups, but more importantly, the deprotonated O atoms of the carboxylate groups can establish strong electrostatic interactions with the Ca$^{2+}$ ions of
the tobermorite surface. The number of \( \text{Ca}^{2+}-\text{O} \) bonds \( (N_{\text{Ca, O}}) \) formed between the CNTs and the surface is shown in Table 4. The average distance between the O atoms and the \( \text{Ca}^{2+} \) atoms is shown in the right-hand column of this table.

As can be seen, carboxylate groups are able to form a greater number of \( \text{Ca}^{2+}-\text{O} \) bonds than carboxyl groups, which would rather form H-bonds (see Table 3). In addition, the \( \text{Ca}^{2+}-\text{O} \) distance is smaller for carboxylate groups.

Figure 7 depicts some of the \( \text{Ca}^{2+}-\text{O} \) bonds formed between the O atoms of the CNTs and the \( \text{Ca}^{2+} \) of the surface. For the sake of simplicity, only some of the CNTs functionalized with carboxylate groups are shown. Similar results are obtained for carboxyl
groups, although bond lengths are longer. As can be seen, Ca$^{2+}$ cations coordinate to negatively charged O atoms of the carboxylate group and O atoms of the tobermorite surface.

The RDFs of the carboxyl (carboxylate) O-Ca$^{2+}$ atoms are shown in Figure 8. As can be seen, there are two sets of main peaks centered at about 2.1 and 2.4 Å, which correlates well with the distances shown in Table 4 for carboxylate and carboxyl groups, respectively.

The interaction between Ca$^{2+}$ and O atoms of the CNT suggests the diffusion of CNTs and Ca$^{2+}$ toward the interface in order to allow the formation of strong electrostatic Ca$^{2+}$-O bonds. Figure 9 shows the concentration profiles of Ca$^{2+}$ and O atoms along the z-axis, averaged over the last 25 frames of simulation, which corresponds to

### Table 4. Number of Ca$^{2+}$-O bonds formed between the O atoms of the polar groups of the CNTs and the Ca$^{2+}$-atoms of the tobermorite surface and minimum average distance between Ca$^{2+}$ and O.

|                | $N_{Ca,O}$ | d (Å) |
|----------------|------------|-------|
| CNT1 + 7COOH   | 1.6        | 2.4   |
| CNT2 + 7COOH   | 1.3        | 2.4   |
| CNT1 + 11COOH  | 1.8        | 2.5   |
| CNT2 + 11COOH  | 0.0        | -     |
| CNT1 + 7COO$^-$ | 8.1        | 2.1   |
| CNT2 + 7COO$^-$ | 7.9        | 2.1   |
| CNT1 + 11COO$^-$ | 13.1      | 2.1   |
| CNT2 + 11COO$^-$ | 6.0        | 2.1   |

*Figure 7. Ca$^{2+}$-O bonds in: a) CNT1-7COO$^-$ (top), CNT2-7COO$^-$ (bottom). Ca$^{2+}$ coordination numbers vary between 5 and 6.*
the final 120 ps of the simulation, for CNT2-11COOH (no Ca\textsuperscript{2+}-O bonds) and CNT1 + 11COO\textsuperscript{−} (13.1 O-Ca\textsuperscript{2+} bonds). The origin (z = 0) was defined as the plane where the surface Ca\textsuperscript{2+} atoms were located in the initial tobermorite structure. The peak corresponding to these atoms is also shown in this figure.

As can be seen, there are strong Ca\textsuperscript{2+} and O overlapping peaks at both sides of the interface for the (CNT1-11COO\textsuperscript{−}) system, which suggest the migration of these atoms to allow the formation of electrostatic bonds between them.

4. Discussion

Many experimental studies have shown improvement in several mechanical properties of construction materials through the incorporation of nanoparticles into cement matrixes. To shed some light on this issue, MD studies of different systems containing pristine and functionalized SWCNTS and MWCNTS interacting with a tobermorite surface were carried out. Our molecular modeling results showed that the

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**Figure 8.** RDF O (CNT)-Ca\textsuperscript{2+} atom. Peak maxima: CNT1-7COOH: 2.39, CNT2-7COOH: 2.41, CNT1-11COOH: 2.29, CNT1-7COO\textsuperscript{−}: 2.05, CNT2-7COO\textsuperscript{−}: 2.09, CNT1-11COO\textsuperscript{−}: 2.07, CNT2-11COO\textsuperscript{−}: 2.09.

**Figure 9.** Concentration profiles of Ca\textsuperscript{2+} (●) and O (▲) atoms along the z-axis for the systems with minimum (CNT2-11COOH) and maximum (CNT1-11COO\textsuperscript{−}) number of Ca\textsuperscript{2+}-O atoms bonds.
functionalized CNTs interact more strongly with the tobermorite surface. These results were supported by some experimental measurements. Indirect tensile strength results are better for carboxyl-functionalized CNTs than for pristine CNTs (see Figure 2). The functionalized CNTs increased the strength of the cement by approximately 20% compared to the plain cement. This increase in resistance is consistent with the results obtained by other authors, as reported by A. M. Rashad [62]. CNTs act as a pore filler, increasing the final density of the material. Additionally, the functional groups accelerate the hydration of cement. These phenomena lead to an enhancement of the strength when functionalized CNTs are used. Binding energy results show that surface functionalization of the CNT surface is a key step toward strengthening the interaction between the nanoparticles and the cement matrix. As can be seen in Figure 3 and Table 2, all the systems but those containing pristine CNTs, show negative binding energies, indicating that final configurations of the functionalized systems are more stable than initial configurations (no interaction between the CNTs and the tobermorite surface). The adsorption process seems to be favored from an energetic point of view in all these cases. On the contrary, both pristine SWCNTs and MWCNTs show slight positive energies, which could due to the chemical incompatibility between the highly hydrophobic CNTs and the hydrophilic tobermorite surface [63,64]. In addition, binding energies are more negative when the CNTs are functionalized with carboxylate groups, the only exception being the CNT1 + 11COOH system, whose energy is of the same order of magnitude as those calculated for the carboxylated CNTs. This could be due to the high number of H-bonds that this system is able to form, coupled with the fact that some of the last configurations of the trajectory show the existence of 1 or 2 Ca^{2+}-O carboxyl bonds (see discussion below).

Both carboxyl and carboxylate groups can potentially form H-bonds with the polar groups of the tobermorite surface (Si-O and Si-OH). The number of H-bonds listed in Table 3 demonstrates that only the carboxyl hydrogens interact with the tobermorite through H-bonding. In addition, the more functional groups the CNTs have, the more bonds are formed (6.6 (CNT1) and 5.1 (CNT2) for the CNTs functionalized with 11 carboxyl groups and 2.6 (CNT1) and 4 (CNT2) for the CNTs with 7 carboxyl groups). The number of walls does not appear to be important. We believe that the final orientation of the CNT toward the tobermorite surface is the key factor to achieve a strong interaction between them. The larger the number of carboxyl groups pointing toward the surface, the easier it will be to form H-bonds. The minimum average distance of 1.3 Å between the CNT and the surface for these carboxyl-containing systems (see the right-hand column of Table 2) corresponds to H-bonds as those shown in Figure 5 and correlates well with the main peak of the RDFs in Figure 6.

Table 4 and Figure 7 demonstrate that carboxyl and carboxylate groups can establish strong electrostatic interactions with the Ca^{2+} atoms of the tobermorite surface. The number of Ca^{2+}-carboxyl O bonds is much smaller than the number of Ca^{2+}-carboxylate O bonds. This could be explained by the fact that carboxyl O is mainly involved in H-bonding (see Table 3). Indeed, the CNT2-11COOH system does not form Ca^{2+}-O bonds, which could influence on the small value of its binding energy. However, the deprotonated COO^- groups can develop strong electrostatic interactions with the Ca^{2+} atoms of the tobermorite surface and this is reflected in the high number of bonds listed in the
last four rows of Table 4. The interface of these materials is characterized by the coordination of Ca$^{2+}$ ions with the negatively charged O atoms of the carboxylate groups and the O atoms of the tobermorite surface, which results in Ca$^{2+}$ coordination numbers varying between 5 and 6 (see Figure 7). Prominent among these is the CNT1 + 11COO$^{-}$ system, which shows the highest number of electrostatic bonds (13.1) and the more negative binding energy. The distance between the O atoms of the functional groups and the Ca$^{2+}$ atoms is shown in the last column of Table 4. As can be seen, there are two sets of distances at about 2.1 and 2.4 Å. These two sets are also clearly visible in the RDFs shown in Figure 8. The larger distances correspond to the systems functionalized with carboxyl groups and reflect weaker electrostatic interactions and consequently, smaller binding energies.

The creation of Ca$^{2+}$-O bonds compels the atoms to diffuse across the interface so that they can become closer. In the CNT1-11COO$^{-}$ system, the tailing of the Ca$^{2+}$ and carboxylate O concentration profiles toward the interface suggests that both kind of atoms have migrated to form strong bonds. There is no such tailing in the CNT2-11COOH system, in which no Ca$^{2+}$-O bond formation is observed (Figure 9).

Previous experimental results have shown that MWCNTs are more widely used than SWCNTs because they are cheaper to produce, but there are no reports in the literature relating the reinforcing efficiency and the number of walls [1]. Campillo et al. [65] studied the enhancement effect of both MWCNTs and SWCNTs on the compressive strength of cement composites. They found that MWCNTS performed better but they attributed this behavior to the superior dispersion of MWCNTs because of their lower surface area. Our MD results indicate that the strength of the interaction between the CNTs and the tobermorite surface depends mostly on the number and type of functional groups and the relative orientation of the polar groups of the CNT with respect to the tobermorite surface. In no case, the effect of the number of walls of the CNT on the binding energy is clearly seen.

5. Conclusions

MD simulations were carried out to study the interaction between pristine and functionalized SWCNTs and MWCNTs and a tobermorite surface. The results obtained in the present work can be summarized as follows:

 Binding energy values and experimental results show that functionalized CNTs interact more strongly with the tobermorite surface than pristine CNTs do. Thus, surface functionalization is a key factor to strengthen the interaction between the nanoparticles and the cement surfaces.

 Carboxylate groups improve the binding capacity of the CNT, through the formation of strong electrostatic bonds between the negatively charged O atoms of the polar groups and the Ca$^{2+}$ ions of the tobermorite surface.

 CNT-functionaization with carboxyl groups results in the development of an H-bond network that contributes to bonding to the tobermorite surface. The more functional groups the CNTs have, the more bonds are formed.

 Carboxylate groups do not form H-bonds, as they are mainly involved in Ca$^{2+}$-carboxylate O bonds. On the contrary, both types of bonds are observed for carboxyl
groups, although the strength of Ca$^{2+}$-O bond is lower in this case, as reflected by larger bonding distances.

Diffusion of Ca$^{2+}$ atoms and CNTs across the interface allows the formation of reinforcing electrostatic bonds.

The number of walls do not seem to play a significant role in the binding capacity of the CNTs. The strength of the interaction depends mostly on the number and type of functional groups and the relative orientation of the polar groups of the CNT with respect to the tobermorite surface.

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