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Influence of single-walled carbon nantotubes structure and density on the ductility of cement paste

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HIGHLIGHTS

- Different atomic models with various CNT's types were created.
- The 11 Å-tobermorite with Ca/Si ratio of 1 was selected as prototype of C-S-H gel.
- We provide the information about brittle/ductile behaviors of the composite.
- The best concentration of CNT allows increase bulk, shear and Young's.

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ABSTRACT

The main objective of the present work is to investigate the possibility of using new reinforcing material, such as carbon nanotubes (CNTs), into the cement matrix. To this end different atomic models with various CNT's types were created. The 11 Å-tobermorite with Ca/Si ratio of 1 was selected here as prototype of the calcium silicate hydrate (C-S-H) gel, which keeps the concrete components together. Molecular dynamics simulation method was employed to evaluate the different mechanical and physical quantities by considering the best type of carbon nanotube in 11 Å-tobermorite. Besides, results provide the information about brittle/ductile behaviors of the composite, modified by CNTs and give clear explanation about the anisotropy of these systems. In addition, various models representing the concrete modified by CNTs were constructed to study the density effect of carbon nanotubes in the cementitious composites. Optimal concentration of CNT was fixed and the best concentration allowing increase bulk, shear and Young's moduli is 5.2% of weight of tobermorite.

1. Introduction

Carbon nanotubes possess an exceptional interest from fundamental and practical points of view [1–5]. CNT are chemically stable, mechanically very strong and electrically conductive supramolecules with a diameter smaller than 100 nm, and reaching to the micron-sized length. Consequently, they open up new opportunities for practical application in electronic and photonic devices [6–9], in composites materials [10–12] for different field of the industry.

Ideal single-walled carbon nanotube (SWCNT) can be represented as a result of the rolling up of 2-dimensional carbon atoms layer that are bonded together in a hexagonal lattice, called "graphene", to cylindrical form (Fig. 1a).

Depending on the rolling up direction of 2-dimensional layer of carbon atoms, SWCNT have different conformation, which is determined by chiral angle θ and chiral vector C_h.

The rolling up of the graphene sheet is performed in such a way that the two points connected by the chiral vector coincide with each other. The number of possible chiral vectors determined by a combination of the integers m and n. These integers determine the chirality of CNT, obtained by folding the graphene sheet along the appropriate vector. "Zigzag" ($m \neq 0$, $n = 0$) and "Armchair" ($m = n \neq 0$) are two common types of nanotubes based on the manner the graphene sheet can be folded to form CNT shown in Fig. 1b.

Carbon nanotubes are used to modify various construction materials in order to improve their performance and impart new properties for obtained composites. In the field of civil engineering, concrete is the most widely used material. From way back, the improving of cement material's characteristics on micro and macro levels was a priority goal of many researches. Since the advent of

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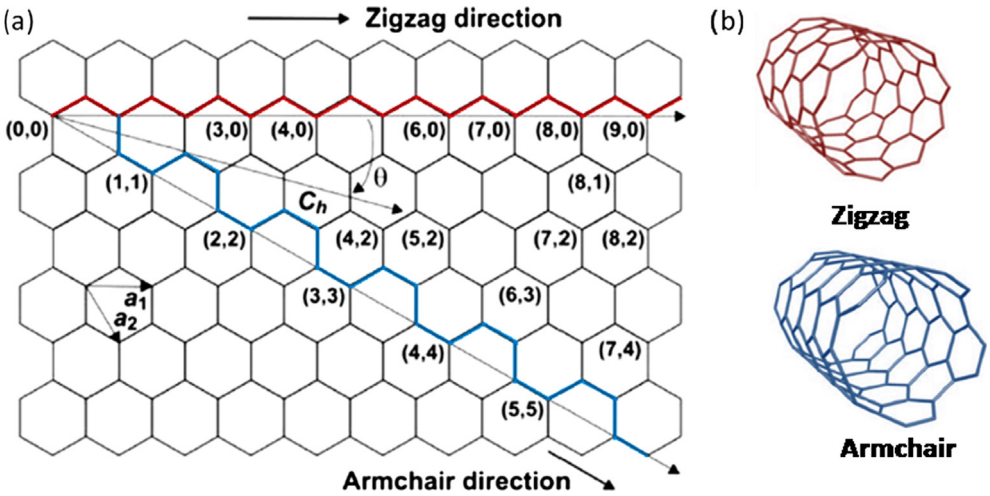

Fig. 1. Structure of the 2-dimensional lattice of graphene and its main geometrical characteristics: (a) Zigzag and armchair nanotube's forms (b).

carbon nanotubes, modification of concretes went over to nano level.

Concrete is a multi-phase nanostructured composite material. It consists of an amorphous phase, crystals with the size from nano to micrometer and held water. The calcium silicate hydrate (C-S-H) is the amorphous phase, the gel that holds the concrete components. The C-S-H gel in itself is a nanomaterial [13]. Transcription "C-S-H gel" means that the composition of hydration products include various calcium silicate hydrates, which have predominantly the amorphous structure and have uncertain composition of basicity (the ratio CaO/SiO_2) and water content. We notice here that computational methods were widely used for C-S-H gel [14–17].

Our own review of literature shows that most of the work on the modification of cement concrete with the carbon nanotubes was carried out experimentally [18–22]. However, computer simulation plays a decisive role in order to predict the properties of the resulting composite and save the time and costs of experimentation.

It is the goal of the present study to investigate in details the influence of various carbon nanotube on the mechanical and physical properties of C-S-H. The work is conducted from classical molecular dynamics approach.

2. Materials and methods

2.1. Molecular models for the system Tobermorite/CNT

For this study two types of carbon nanotubes were chosen: "Armchair" and "Zigzag". We prepared five CNTs of the length ~17 Å with different diameters CNT (3, 0) with d = 2.351 Å; CNT (4, 0) with d = 3.135 Å; CNT (5, 0) with d = 3.919 Å; CNT (2, 2) with d = 2.715 Å; and CNT (3, 3) with d = 4.073 Å.

The C-S-H gel structure revealed the poorly crystallized regions having a resemblance to the structures such as Tobermorite and Jennite. The most used model to present the structure of C-S-H gel is 11 Å-tobermorite [23–25]. One of the most important factors in presenting a realistic molecular model of Tobermorite is Ca/Si ratio. The best known Ca/Si ratios for 11 Å-tobermorite are 0.66; 0.83 and 1[26]. This variation depends on the age of cement pastes and the water/cement ratio. In the present study we used the Hamid's model of 11 Å-tobermorite [27] with Ca/Si ratio of 1, which is presented in Fig. 2. In this model the silicate chains repeats at intervals of three tetrahedra forming a Drierketten type of structure where, on the one side, the silica tetrahedra connected to only one silica tetrahedra Q^1 and, the other side, with two other silica tetrahedral Q^2.

The 11 Å-tobermorite is a monoclinic structure classified under P_{21} space group. The unit cell has the following dimensions: a = 7.39 Å, b = 22.779 Å, c = 6.69 Å and $\alpha = 90°$, $\beta = 123.49°$, $\gamma = 90°$. We used 30 and 105 crystallographic units to create a $5 \times 2 \times 3$ and $5 \times 3 \times 7$ supercells respectively for two main sized model of different study's purposes.

In order to create the system Tobermorite/CNT we inserted the carbon nanotube into the structure of the 11 Å-tobermorite (Fig. 3). The hole in the structure of Tobermorite was created keeping the neutral charge of the system.

2.2. Energy minimization method and force field

The energy minimization process determinates the most stable configuration of molecules, which corresponds to a local minimum energy. When a molecule is built, the initial geometry does not necessarily correspond to one of the stable structural phase. Therefore, energy minimization is usually implemented to find a stable phase in which the atomic configuration is closes to the initial atomic coordinates. There are numerous methods for actually varying the geometry to find the minimum. We used here the New ton-Raphson/Broyden-Fletcher-Goldfarb-Shanno method [28].

Since we are dealing with a model, which is represented such as an ionic crystal, a polarization effect could occur. We used the "core shell" approach that would be better to take into account this effect. Interatomic potential energy was described by the parameters of Buckingham, Morse, three body, and spring potentials [24]. To describe the interaction between the carbon atoms in the CNT's structure the Tersoff potential [29] was used. The potentials parameters from the Ref. [24,30,31] were used to calculate the interaction between atoms of CNT and 11 Å-tobermorite employing the Lorentz-Berthelot mixing rule [30].

3. Results and discussions

3.1. Inter-structural interaction energy

In the first instance, it is important to know which type of CNT will be the best to modify 11 Å-tobermorite with the ratio Ca/Si = 1. At the same time it is necessary to understand the distance needed for vacuum between these examined structures.