Full Length Article

A molecular dynamics study on the buckling behavior of cross-linked functionalized carbon nanotubes under physical adsorption of polymer chains

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ABSTRACT

The buckling behavior of cross-linked functionalized carbon nanotubes (CNTs) with polyethylene (PE) chains under physical adsorption of polymers (cfCNTs/polymer) is studied by classical molecular dynamics (MD) simulations, and the results are compared with those for the pure CNTs under the physical adsorption of polymers. Considering non-covalent functionalization, the effect of type of functional group, i.e. aramid and PE chains, on the interactions between polymers and cfCNTs is investigated. Based on the results, the gyration radius of cfCNTs/polymer increases by raising the weight percentage of non-covalent polymer chains. Also, the simulation results for most cases demonstrate that the gyration radius of cfCNTs/polymer is larger than that of pure CNTs/polymer for the similar weight percentage of non-covalent polymer chains. Moreover, the critical buckling force and the critical buckling strain of the cfCNTs/polymer are lower than those of pure CNT/polymer for the similar weight percentage of non-covalent polymer chains, although some exceptions can be observed. Besides, by raising the weight percentage of non-covalent polymer chains, the critical buckling force cfCNTs/polymer increases for a specific weight percentage of cross-linked PE chains.

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1. Introduction

Carbon nanotubes (CNTs) due to their unique structure with sp^2 hybridization demonstrate various potential applications in nanocomposites, nanoelectronics, nanosensors, and nanofilms [1–5]. Despite superior electrical, mechanical, and thermal properties of CNTs, the poor interfacial interaction with matrices, the strong van der Waals (vdW) interaction among their walls, insolubility and agglomeration considerably limit their potential applications [6–11]. In order to eliminate those drawbacks and use CNTs in applications such as polymer matrix reinforcement, several methods have been developed [12,13]. Commonly, the methods can be categorized into two types, which are covalent (chemical) and non-covalent (physical) functionalization [14–18]. In the chemical functionalization approach, the natural physio-chemical properties of CNTs is noticeably altered by changing the hybridization of host structure from sp^2 to sp^3. Addition-

ally, it is observed that the chemical functionalization leads to enhancement of load transfer under various mechanical loading conditions [19–21]. In this regard, polyethylene (PE) as one of the important functional groups in CNT-based nanocomposites is used for the cross-linked functionalization [22,23]. PE is a very simple polymer with the chemical formula of $(C_2H_4)_n$ in which four hydrogen atoms are connected to a single bond between two carbon atoms, i.e. ($-C-C-$) [24]. Numerous researchers have investigated the modification of the properties of the CNTs based on the chemical functionalization approach [17,19–21] through different experimental and theoretical methods [25–28]. In the second category, the physical functionalization approach, van der Waals (vdW) force as well as π–π stacking interactions are the most essential factors in controlling the mechanical properties of the CNT-based nanocomposites. Also, the non-covalent functionalization which contains wrapping of polymer chains, surfactants, and biomacromolecules leads to better dispersion of CNTs in various solvents [29–32]. In the case of non-covalent functionalization, two well-known polymer structures, namely aramid and PE chains are selected [33–35]. Aramid with the structural formula of $(-CO-C_6H_4-CO-NH-C_6H_4-NH-)_n$ is known as one

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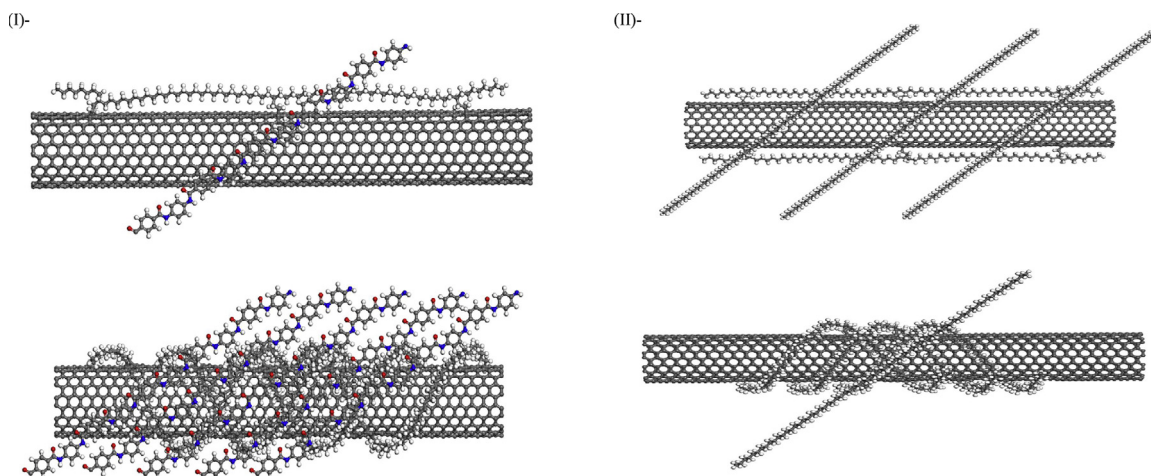 *E-mail address:* r_ansari@guilan.ac.ir (R. Ansari).

Fig. 1. Samples of prepared models with the mapped and wrapped configurations, respectively, (I) cfCNTs/aramid (II) cfCNTs/PE.

of the most common polymer structures employed in aerospace and military applications and ballistic composites [36]. Its high potential applications makes aramid an ideal candidate for the modification the properties of nanotubes. Similar to the chemical functionalization, various experimental studies and MD simulations are performed on the physical adsorption of polymers around the wall of the CNTs [37–40].

By reviewing the previous studies on the properties of functionalized CNTs under physical adsorption of polymers especially in nanocomposites [41–43], the lack of a comprehensive investigation on the buckling of covalently functionalized CNTs under physical adsorption of polymer chains can be detected [44]. Hence, MD simulations are employed in the present article to comprehensively study the buckling of cfCNTs subjected to physical adsorption of polymers. The effects of different distribution patterns of covalently attached cross-linked PE chains (cPE), i.e. mapped and wrapped as well as various weight percentages, and types of polymers on the buckling behavior of cfCNTs/polymer are explored. First of all, the physical adsorption of polymers on the cfCNTs is considered. Then, the critical buckling force and the critical buckling strain of cfCNTs/polymer are calculated and the samples of buckling mode shapes are shown. Accordingly, the novelty of this investigation is the exploration of the effect of simultaneous covalent and non-covalent functionalization on the buckling behavior of CNTs which can be considered as the benchmark for further analysis on the mechanical behavior of functionalized CNT based nanocomposites.

2. Methodology and models

2.1. Methodology

The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package is employed for MD simulations technique [45]. In order to evaluate interactions of atoms, the classical equations of motion is solved by using the Velocity-Verlet scheme. Also, the AMBER force field is selected to model the physical system [46,47]. This force field computes interatomic interactions in molecules consist of H, C, N, O, S, P, and halogens [48]. During the whole simulations, the NVT canonical ensemble (constant number of molecules, constant volume, and constant temperature) is applied. To this end, the Nose-Hoover thermostat algorithm with the fixed time step of 1 fs is selected to maintain the temperature of system at 300 K. It should be noted that using the Nose–Hoover thermostat together with the chosen time step guarantees the good long-time stability and reduction of the temperature fluctuation in the system [49–51]. Firstly, the simulation system relaxes for 300 ps

to reach the equilibrated phase with the minimum state of energy at the room temperature. After the relaxation process, the axial compressive displacement of 0.01 Å is imposed to the boundaries of the cfCNTs at each step then it relaxes for 5 ps. Finally, the force, strain and strain energy of cfCNTs/polymer are stored at the end of each step [41].

2.2. Simulation models and polymer chains

(10, 10) armchair single-walled carbon nanotubes (SWCNTs) with the length of ∼100 Å and radius of 6.78 Å are chosen with fully clamped boundary conditions. Initially, in the cross-linked functionalization, each PE chain consists of 245 atoms, i.e. 82 carbon atoms and 163 hydrogen atoms, are covalently attached to the walls of SWCNTs by two methylene groups with the structural formula of $(H2C :)_2$. To have a comprehensive study, the cross-linked PE chains with two kinds of distribution patterns and four different weight percentages ranging from 6% to 24% are taken into consideration. In the mapped distribution pattern, PE chains are connected to the SWCNTs in three points parallel to the CNT axis, whereas in the wrapped distribution pattern, PE chains are attached to the SWCNTs in the helical shape around the wall of CNTs. In the case of non-covalent functionalization, aramid and PE chains with different weight percentages are placed around the cfCNTs. To generate comparable results, the weight percentage of aramid chains is chosen approximately the same as that of PE chains. For both non-covalent polymer chains, the number of chains is considered 1, 3, 5 and 7. Further, the aramid chains are placed around the wall of cfCNTs with four different weight percentages varying from ∼6% to 42%. Each aramid chain includes 70 carbon atoms, 10 hydrogen atoms, 10 nitrogen atoms and 10 oxygen atoms. Similarly, the non-covalent PE chains are selected in four different weight percentages ranging from 5.1% to 35.7%. For this purpose, each non-covalent PE chain corresponds to 70 carbon atoms, 142 hydrogen atoms. The initial schematics of cfCNTs/polymer with different configurations (mapped and wrapped distribution patterns) are revealed in Fig. 1.

3. Results and discussion

3.1. Physical adsorption and wrapping process

The adsorption of polymers on the cfCNTs occurs due to the vdW interaction between the molecules, i.e. cfCNT and polymers. After the initial relaxation process, the polymers wrap around the surface of the cfCNTs. The samples of equilibration and wrapping process during relaxation time for physical adsorption of prepared models