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Molecular modeling study of the structure and stability of polymer/carbon nanotube interfaces

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ABSTRACT

A molecular modeling strategy is proposed to characterize the morphological and energetic properties polymer chains and carbon nanotubes interfaces and is applied to polyethylene/carbon nanotubes (PE/CNT) interfaces. The influence on the polymer chain adsorption and stability of a number of parameters (polymer molecular weight, nanotube structure and diameter, nanotube functionalization) is examined. The polymer chains are found to form regular lamellar-type structures on the CNT surface, which may act as template for the organization of the polymer around the nanotubes. Also, the nanotube diameter and the presence of hydroxyl groups clearly affect the PE chain adsorption: the interface stability decreases with the curvature of the carbon surface, while the chemical groups present on the tube wall sterically hinder the formation of the lamellar structures. Finally, the behavior of a cluster of PE chains (representing a polymer melt) interacting with the nanotube is compared to that of a single chain.

1. Introduction

Since their discovery in 1991 by Iijima [1], carbon nanotubes, CNTs, have been widely investigated in particular because of their electrical and mechanical properties. Of great interest is the possibility to improve the electrical and mechanical properties of polymer materials by dispersing CNTs into the material bulk [2–6]. As with other nanocharges, the improvement of those properties critically depends on the quality of the nanotube dispersion in the polymer matrix. Reaching a fine dispersion is by no means a trivial issue, since CNTs naturally tend to form aggregates in which the nanotubes strongly interact, driven by favorable van der Waals interactions between the CNTs external walls. It is therefore of prime importance to understand in detail the nature of the interactions taking place at the polymer/nanotube interfaces, in order to design strategies to favor the dispersion of the CNTs in the matrices and generate stable nanocomposites with optimal microscopic morphology. Modeling has recently been used to investigate the interactions between polymer chains and nanotubes, both at the quantum-chemical [7] and force field [6,8–10] levels. Due to the inherent complexity of quantum-chemical calculations, the characteristics of the polymer/nanotube interfaces are often extrapolated from the description of small polymer fragments, i.e., typically a couple of monomer units, interacting with a small portion of nanotube wall. While the interaction energy can in principle be calculated with a high level of precision, those models yield molecular conformations that might not be accessible to real macromolecules, due to constraints or steric hindrance associated with the rest of the chain. This aspect can be taken into account with force field calculations, which are less computationally demanding and allow for the description of the interaction between nanotubes and an entire polymer chain. Force field-based models for the interactions between polymer and nanotubes have been already reported in literature, with different degrees of approximation. Some of those studies still consider the interaction of short oligomers rather than polymer chains [11–13], while others have been primarily focused on the characterization of the adsorption of a single polymer chain on a carbon nanotube in vacuum [14–16], while very few information have been reported in terms of characterization of stable, i.e., fully equilibrated, polymer/nanotube interfaces: those force field simulations are long enough to allow the polymer chain to enter in contact with the nanotube; however they do not fully account for the full equilibration of the polymer chains on the nanotube, which occurs on a longer time scale and which is essential to understand the properties of the actual nanocomposites. In this work we intend to improve the theoretical description of the polymer/nanotube interfaces by presenting a comprehensive molecular modeling strategy suitable for the full characterization of polymer/nanotube interfaces, both from the energetic and morphological points of view. In particular, we are interested in the detailed analysis of the energetics and

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morphology of different polymer/nanotube interfaces, where single or multiple polymer chains are interacting with pristine or chemically functionalized nanotubes in different environments. In this paper, we describe the modeling methodology and we apply it to a prototypical system: the polyethylene (PE)/carbon nanotube interface. Polyethylene is among the most important plastic materials; the dispersion of CNTs in PE matrices is of prime interest but it remains a major challenge in the field of carbon-based nanocomposite materials [17,18]. Understanding the details of the PE/CNT interface interactions can therefore contribute to new strategies for efficient dispersion. The influence on the interface properties of the polymer molecular weight, the nanotube structure, diameter and functionalization, as well as the influence of the environment (vacuum vs. polymer melt) has been studied by comparing different model systems.

2. Methodology

All the simulations presented in this work were performed using the GROMACS 4.0.7 [19] molecular modeling package and its implemented version of the OPLS-AA force field [20,21]. The OPLS-AA force field was chosen for its accuracy [22] in describing the so-called CH-π interactions [23], which are expected to take place between the nanotube and polymer chains, in particular polyethylene. The accuracy of the OPLS-AA force field in describing the energetics and the morphology of the polymer/nanotube interface was validated by comparing the adsorption energy and equilibrium geometry of a short PE chain made of 4 monomer units adsorbed on graphite obtained with the force field and at the Density Functional Theory (DFT) level. Periodic DFT calculations have been performed using the VASP package [24–26] with the PBE functional [27,28] accompanied by a semi-empirical vdW correction [29]. The results obtained are in very good agreement with those from molecular mechanics calculations using the OPLS-AA force field: the adsorption equilibrium distance is found to be 3.5 Å with both methods and the OPLS-AA-calculated adsorption energy (-67.4 kJ mol^{-1}) is remarkably close to the DFT value (-64.7 kJ mol^{-1}).

All force field molecular dynamics (MD) calculations were performed in the NVT ensemble (constant number of particles, volume and temperature) at 300 K, using the Nose-Hoover thermostat [30]. The strength of the coupling between the system and the thermostat was set to 0.5 ps^{-1}. Atomic charges for the polymer chains and hydroxyl groups are taken from the OPLS-AA force field (OPLS-AA charges are zero for the carbon atoms of the nanotube) and the Gromacs Coulomb cut-off-based algorithm is used to calculate electrostatic interactions (the complete set of charges used is reported in the ESI). The simulations box was orthorhombic and its size was constrained in the *Y*-direction by the length of the nanotube, so to be 10 × 20 × 10 nm. The LINCS algorithm [31] was used to constrain all the bonds in the polymer chain to the equilibrium lengths used in the force field. This allows for the use of a 2fs time step, which speeds up the simulations and thus allows to extend the MD runs to few hundreds of nanoseconds, to allow the polymer chain not only to adsorb onto the nanotube, but also to reach an equilibrated conformation on the nanotube wall. The cutoff for the non-bonded interactions, namely electrostatic and Van der Waals (vdW), was set to 1.5 nm.

2.1. Polymer chains

In this work, we considered two polyethylene chains with different molecular weight (Fig. 1a): a low molecular weight polymer chain of MW 2240 (80 monomer units), referred to as PE2K, and a higher molecular weight polymer chain of MW 5000 (178 monomer units), referred to as PE5K. An all-atomistic pseudo melt has also been modeled by considering five PE5K chains. The pseudo melt has been generated by running a simulation at high temperature (500 K) for 10 ns.

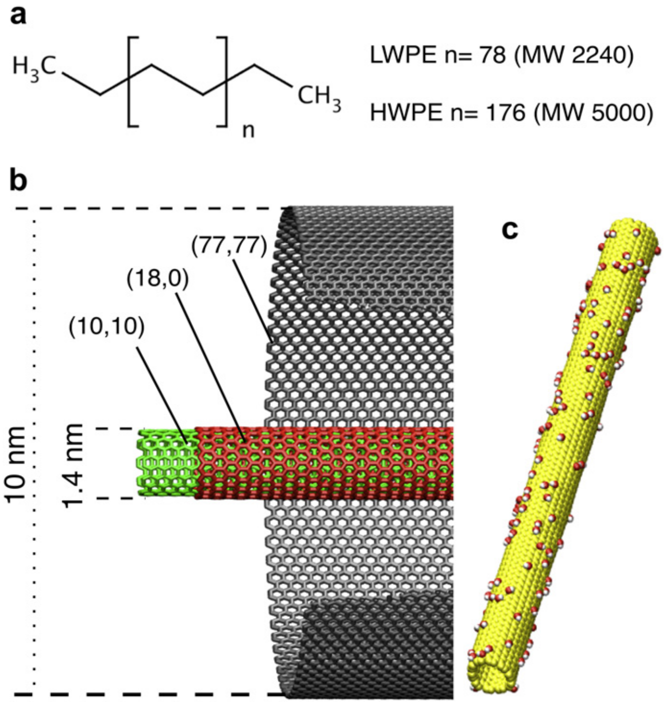

Fig. 1. (a) Structure of polyethylene, PE; two PE chains of MW 2240 (80 monomers) and 5000 (178 monomers) have been modeled. (b) The three pristine (10,10), (18,0) and (77,77) nanotubes are compared. (c) OH functionalized (10,10) SWNT (the oxygen and hydrogen atoms of the OH groups are shown in red and white respectively). The periodic box along the nanotube direction is 20 nm-long. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Nanotubes

We built different nanotubes in order to study the effect of the nanotube size, structure and functionalization on the polymer adsorption. A nanotube segment of 20 nm length is used as repeating unit and periodic boundary conditions are applied to simulate an infinite nanotube (hence removing edge effects). To reduce the computational effort, the nanotubes have been frozen to their equilibrium geometries, i.e., treated as a rigid body with fixed position in the simulation box. We have built single-wall armchair (10,10) and zig-zag (18,0) nanotubes, SWNTs, with diameters of 1.3 nm and 1.4 nm, respectively. The zig-zag and armchair notations refers to the way the graphene sheet is wrapped. This is represented by a pair of indices (n,m). The integers n and m denote the number of unit vectors along two directions in the honeycomb lattice of graphene. If $m = 0$, the nanotubes are called zig-zag nanotubes, and if $n = m$, the nanotubes are called armchair nanotubes. The values of the integers are linearly related to the nanotube diameter: higher numbers correspond to larger diameters. An armchair (77,77) SWNT with diameter of about 10 nm has also been built as a model for the external wall of a typical multi-walled nanotube, MWNT. As an isolated object, the (77,77) SWNT is rather flexible. However, the choice of keeping the structure of the (77,77) SWNT rigid here is justified, because it is used to represent the outer layer of MWCNTs, which are very rigid locally. Fig 1b shows a comparison between those nanotubes. Finally, we have generated an –OH functionalized