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The effect of rippled graphene sheet roughness on the adhesive characteristics of a collagen–graphene system

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ABSTRACT

A great amount of effort has been made in order to reach a more precise understanding of the adhesion phenomenon that happens as a vital component of several biological systems. Therefore, a firm understanding of the important factors that influence this phenomenon is of special importance in triggering the adhesive characteristics of different biological, bio-inspired and synthetic materials in fields such as tissue engineering.

In this study the adhesive characteristics of a multi-material system consisting of the frequently used synthetic material, graphene, in the form of armchair-configuration sheets, and an important biological filament which is type 1 Collagen consisting of 3 alpha helices, has been studied in detail. The main emphasis of this study is placed on understanding the effects of the roughness characteristics of the inorganic elements which are the graphene sheets on the overall adhesive features of the system which are quantified within the framework of two main criteria: adhesion energy and peeling force. At first, the methodology used in order to obtain graphene sheets with various roughness values is described in detail. The abovementioned criteria are then evaluated through Molecular Dynamics (MD) modeling of the system in the NAMD simulation software environment and various simulation scenarios are studied.

1. Introduction

The topic of adhesion has attracted a great amount of attention in the recent years. Several studies have aimed at unfolding the underlying physics of this complex phenomenon in order to understand how it influences many important biological mechanisms that happen in intricate Micro- and Nano-scale biological systems. We can see the critical influence of adhesion on destructive and unpleasant mechanisms such as the growth of bacteria disease or the migration phenotypes that happen as a result of cell adhesion with the Extracellular Matrix (ECM), and also in rather useful and pleasant ones such as wound closure, sealing mechanisms and blood clotting which are the topics of several bioengineering studies such as [1] that specifically focuses on such applications of a collagen–graphene composite system. The triggering of such mechanisms can also be of vital importance when dealing with vascular problems such as bypass grafting where the patients need synthetic blood vessels to replace their own unhealthy and therefore non-harvestable blood vessels. Thus, adhesion that happens naturally in biological organisms has always been a unique pattern in bio-mimetics where sometimes we find adhesive characteristics of synthetic building blocks extremely essential to the functionality of that element in a biological environment. Furthermore, in these cases we have to functionalize the materials not only for good stiffness, elasticity and strength but also for perfect biocompatibility, therefore we find bioinspired adhesives and their adhesion mechanisms very attractive for study [2]. In most of the situations that happen in bioengineering applications, the adhesion of an organic material to an inorganic one is the subject of interest, therefore this study is also focused on a similar practical problem which is the adhesion of collagen and graphene.

One of the most important areas in tissue engineering and stem cell research is the production of scaffolds possessing not only suitable mechanical and biological properties but also good biocompatibility. Collagen biopolymer is one of the most outstanding natural polymers which is a suitable matrix in tissue engineering and many other biomedical applications [3]. This is due to its excellent porosity and biocompatibility advantages. However, its poor mechanical properties and difficult processing make it an unsuitable scaffold for cell culture purposes. Therefore there has been an increasing interest in studies that concentrate on the enhancement and perfection of this unique material with the use of composite material methods. In this regard, reinforcing nanoparticles, nanotubes and flakes of several different materials are of desirable characteristics [4]. Nano-fillers such as silica and carbon

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have been studied and resulted in a dramatic improvement in mechanical properties. In the last decade, carbon nanostructures have been applied as one of the best Nano-fillers because of their outstanding mechanical properties [5]. With the growing attention towards unveiling the excellent properties of flatland, graphene has proved to be one of the excellent candidates.

Regis et al. have carried out a research in [6], studying the adsorption of Fn-III to 3 different types of functionalized Polycaprolactones (PCLs) that included aminated, hydrolyzed and controlled PCL. The study aimed at a thorough investigation of the effects of functionalization on the adsorption of these two substances for scaffolding purposes in tissue regeneration applications. The research was based on MD methods and the adhesion energy parameter was the quantitative measure of the amount of adhesion.

The adhesion of biological polymers, such as collagen, on graphene, polycaprolactone, and titanium oxide has been the research focus for a number of computational studies in the recent years. It is shown that the proteins conduct more contact points with these surfaces with the increase of contact area per molecule, and hence the adhesion energy of collagen on surface rises. Ebrahimi and Raffi-Tabar [7] investigated the effect of surface roughness on the adhesion energy of collagen on titanium. Their results showed that with an increase in the roughness of a ceramic surface, the adhesion energy experiences a significant increase in its value.

In this study, the interaction between the collagen biopolymer and Graphene Nano-ribbons (GNRs) at the molecular level has been modeled. For this purpose, we explore the effect of ripples on the graphene surface on the interfacial properties of the collagen–graphene system in different settings.

2. Materials and methods

The major factors that influence the adhesive characteristics of a multi-molecular system are considered to be Van der Waals (VDW) intermolecular interactions, osmotic forces, protein bindings and the entanglement which happens in complex polymeric networks. In the dimensional scale of the present study which we have binding radii scales of less than 10 nm, the significance of the VDW interactions is the most important criteria and shows a domination over the other abovementioned factors. Molecular Dynamics (MD) based simulation methods have been proved to have an accurate prediction of the VDW energies of such complex biological systems because they use the interatomic potential field forces to predict the behavior of a molecular system. The dominance of this class of interactions in the present scale of study has also been taken account of in several previous studies.

In Ref. [8], the adsorption geometry of 1,3,5-tris(4-mercaptophenyl) benzene (TMB) on Cu(III) was determined with a high precision using two independent methods. These two methods included an experimental investigation using quantitative low energy electron diffraction and theoretically with the use of corrected VDW. Structural refinement using both methods consistently resulted in similar adsorption sites and geometries. Ref. [9] investigated the adsorption of the four DNA nucleobases on graphene sheets, using VDW energy-corrected DFT calculations, considering the contributions of VDW interactions to the binding energy as the dominant term, and, for comparison, LDA were carried out as well as generalized gradient approximation (GGA) calculations.

2.1. Inter-atomic potentials

The Lennard-Jones potential has been described as the energetics of the non-bonding interactions between all pairs of collagen and graphene atoms:

$$\cup(r_{ij}) = \begin{cases} 0, & r_{ij} \geq r_{cut} \\ 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right], & r_{ij} < r_{cut} \end{cases} \quad (1)$$

where r_{ij} is the separation distance, ε_{ij} is the equilibrium energy, σ_{ij} is the equilibrium distance between atoms i and j, and r_{cut} is the cut-off distance.

The Brenner potentials have been used for carbon atoms in the graphene layers which is shown in Eq. (2):

$$E_b = \sum_i \sum_{j(>i)} \left[V^R_{(rij)} - b_{ij} V^A_{(rij)}\right] \quad (2)$$

The collagen inter-atomic potentials are modeled with following equations:

$$U(r_l) = \frac{1}{2} k_r (r_L - r_{l0})^2 \quad (3)$$

$$U(\theta_{ijk}) = \frac{1}{2} k_\theta (\theta_{ijk} - \theta_{ijk0})^2 \quad (4)$$

where r_L is the length of bond L. r_{l0} is the equilibrium length of bond L. θ_{ijk} is the angle between atoms i, j and k, θ_{ijk0} is the equilibrium angle. k_r and k_θ are the equilibrium energy parameters of bond-stretch and bond-bending, respectively.

The dihedral potential is of the form:

$$U(\varnothing_{ijkl}) = A_1(1+\cos\ \varnothing_{ijkl}) + A_2(1+\cos\ 2\varnothing_{ijkl}) + A_3(1+\cos\ 3\varnothing_{ijkl}) \quad (5)$$

where $\varnothing_{ijkl}$ is the angle formed by i, j, k and l bonds and A_i are the constant parameters. All the bond-stretch, bond-bending and dihedral potential parameters were obtained from the parameter file of CHARMM which is widely used in the NAMD software platform for biological molecules. Table 1 shows the parameters of the non-bonding potentials and the rest of the parameters described in this section are included in the abovementioned package for every atom and bond.

2.2. Simulation parameters

In this section, MD simulation parameters that were considered for running all of the simulations will be discussed. The molecular structure of the collagen is shown in Fig. 1(a). The structure of the collagen used in this study was a typical structure including a triple-helix collagen molecule of length 116 Å and diameter 17.0 Å which was obtained from the Protein Data Bank. Three-layers of armchair graphene sheets were made in 120 Å by 30 Å dimensions using the VMD software which is shown in Fig. 1(b).

The temperature was set to $T=310$ K which is the normal temperature of biological systems such as the human body and the time step was set to 2 ps. The cutoff distance for the interatomic potentials was set to 12 Å and Langevin dynamics was also included in the simulations with a damping coefficient of 1 ps^{-1}.

Table 1
Parameters of the non-bonding potentials.

Atoms	*e* (kCal/mol)	*r* (Å)
C	0.110000	3.563595
H	0.120000	3.029056
O	0.022000	2.351973
N	0.200000	3.296325