MOLECULAR MODELING OF MECHANICAL PROPERTIES OF THE CHITOSAN BASED GRAPHENE COMPOSITES

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Molecular mechanics and dynamic simulations at atomistic scale were used to investigate the mechanical behavior of the graphene based chitosan (CS) composite with different reinforcing agent content. The improvement of the Young's moduli depends on dispersion mode and interface interaction between the graphene sheets and the polymer matrix. The elastic moduli of the composite increased with increasing of graphene amount in the computational bulk systems and the values range from 8.55 GPa in the case of neat CS to 11.55 GPa for graphene/CS composite with 14.28 wt.% graphene.

Keywords: molecular modeling, graphene, Young's moduli

1. Introduction

One of the purposes of the tissue engineering research is to obtain biocompatible scaffold which replaces regenerates or repairs the damaged tissues and mimics the structure of the extracellular matrix [1]. Natural polymers including collagen, chitosan (CS), alginate and so on are ideal materials for the synthesis of biological scaffold materials because they present good biocompatibility, biodegradability, non-toxicity and low cost [2, 3]. Among the several biopolymers, chitosan is one of the most widely investigated in biomedical field and posses most of the properties in achieving a convenient scaffold for the patient.

Up to date, CS based materials were obtained in different forms, such as films, hydrogels, fibers, beads and mico/nanoparticles for applications in the biomedical field [4, 5]. Despite the above mentioned advantages CS exhibits some major drawbacks such as low mechanical strength and hard procesability [6].

In recent years, graphene, a 2D sheet of sp^2 hybridized carbon atoms, have attracted a great deal of attention especially for tissue engineering due to their unique structure, lack of cytotoxicity and remarkable properties [7]. Graphene – polymer nanocomposites showed a significant increase in elastic modulus, tensile strength, thermal stability and electrical conductivity even at low loading of

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graphene filler [8]. The main challenge in manufacture such composite is archiving a homogeneous dispersion of graphene nanosheets in polymer hosts. On the other hand, controlling the uniformity of dispersion and the degree of alignment of graphene sheets is difficult by experimental means, but computational modelling can ensure some essential vision**.** However, performing such simulation is not a trivial task due to the complex nature of composite system (polymer and nanofiller).

Furthermore, to the best of our knowledge there are very few works reporting the computational characterization of polymer-graphene composites [9, 10]. The aim of this study is to use molecular modeling at atomistic scale in order to predict the mechanical properties of the CS-graphene biomaterial by varying the graphene composition.

2. Materials and method

2.1. Simulation methodology

Atomistic simulations using Material Studio 5.5 (Accelrys, Inc) software were performed in order to construct and equilibrate the bulk models of the CS and CS-graphene composite. The force field applied in the simulation for both polymer and the composites was COMPASS [11]. Material Studio 5.5 software provides a versatile sketching tool „Build Polymers/Homopolymer", which allows constructing the monomer of chitosan manually. The CS chain models were constructed by linking randomly 100 structural repeat units. In order to obtain a stable starting structure the energy of polymer chain was minimized. A polymer conformation was achieved by packing the polymer chain models into a cubic cell using Amorphous Cell tool. The density of computational cubic cell was decrease by two/three orders of magnitude (0.01/0.001 g/cm^3) in order to avoid the ring catenation phenomenon [11]. The number of the atoms within the computational bulk model of CS biopolymer and CS-graphene composites was chosen according to Hofmann and co-workers suggestions [12]: the cell has to be sufficiently large so that the interaction between the atoms is avoided; the number of the polymeric chain allows random orientation; the computational costs are low.

The graphene sheet was manually constructed, further charge groups were assigned and energy was minimized in order to obtain a stable starting structure. The CS and graphene atomic model has been well equilibrated and reaches an energy derivative of 7.94×10^{-4} and 9.3×10^{-4} respectively.

Computational bulk model of graphene/CS with various amount of graphene (4, 7.67, 14.28 wt. %) were constructed using Amorphous Cell module. Computational models were implemented with different contents of graphene in order to determine the influence of graphene amount on the mechanical behavior of the composite systems. Each bulk model includes about 9000 atoms.

2.2. Equilibration of the bulk model

All the models were subject to a complex equilibration protocol. First, molecular dynamics simulation (MD) was performed. The simulations were carried out with constant number of atoms, volume and temperature (NVT) ensemble at a temperature of 300 K for 10 ps by using a time step of 1 fs. The temperature was controlled during simulations by using the Anderson thermostat. Table 1 describes main features of the models.

Table 1

The characteristics of the CS and the CS-graphene computational models

Model name	No of graphene sheets	No of atoms in the model	No of graphene atoms	No of polymer atoms	Model density
CS	0	8808	0	8808	0.76
GRAPHENE/CS	1	9031	223	8808	0.81
GRAPHENE/CS	2	9254	446	8808	0.87
GRAPHENE/CS	4	9700	892	8808	0.94

*Graphene density was considered to be 2.2 g/cm^3 [13].

Each MD simulation was followed by molecular mechanic calculations (MM) of about 300.000 steps. The energy minimization was achieved using Conjugate Gradient- Fletcher Reeves algorithm [11].

Afterwards, the computational bulk models were subject of a short MD-NPT simulation (constant number of atoms, pressure and temperature) at p = 0.5 GPa and 300 K for about 5000 steps. The aim of this cycle was to compress the models in order to reach a density closer to that of the real material. The pressure control during simulation was done using Anderson barostat.

After the compression stage the simulated packing models were further equilibrated. For the equilibration of the computational bulk models a complex approach which combined various steps of MM and MS calculations with scaling factors (SF) was used [11]. A sequence of 7 MM and MD simulations in which both bond interaction and non-bond interaction were scaled down using SF from 0.001 to 1 were performed. In more details our equilibration routine is describe in table 2.

Table 2

Step of equilibration protocol

Nr. crt.	Calculation method	No of steps , [ps]
1	MM	2.000
2	MD-NVT	200.000
	MD-NPT	5.000

Scaling factors	1	MM	0.001 (B); 0.001 (NB)	300.000
		MD	0.001 (B); 0.001 (NB)	200.000
	2	MM	0.01 (B); 0.001 (NB)	300.000
		MD	0.01 (B); 0.001 (NB)	200.000
	3	MM	0.01 (B); 0.01 (NB)	300.000
		MD	0.01 (B); 0.01 (NB)	200.000
	4	MM	0.1 (B); 0.01(NB)	300.000
		MD	0.1 (B); 0.01(NB)	200.000
	5	MM	0.1 (B); 0.1 (NB)	300.000
		MD	0.1 (B); 0.1 (NB)	200.000
	6	MM	1 (B); 0.1 (NB)	300.000
		MD	1 (B); 0.1 (NB)	200.000
	7	MM	1 (B); 1(NB)	300.000
		MD	1 (B); 1(NB)	200.000

3. Results and discussion

After the equilibration precedure the density of the CS and graphene/CS composite systems was in accordance with that of the real material. Moreover, the computational systems were energetically stable and present an uniform and random distribution (Fig. 1 A) of polymer chain and graphene sheets.

For the composite systems containing 14.28 wt. % graphene sheets (Fig. 1 B) an agglomeration of the inorganic filler within the polymer matrix was observed.

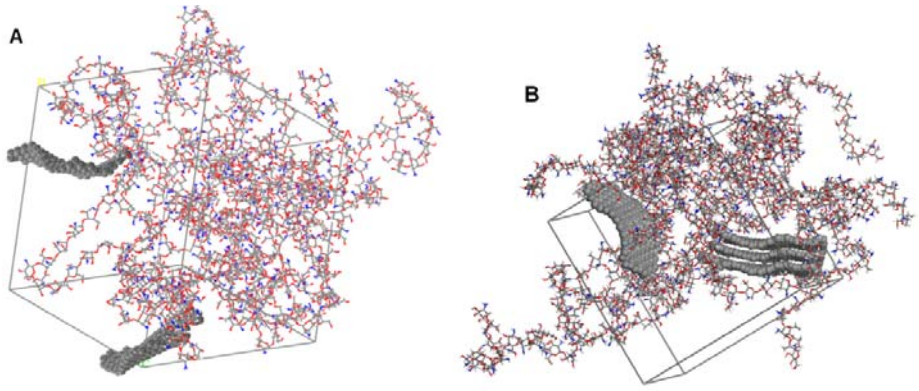

Fig.1. The computational bulk model of A) graphene/CS (7.67 wt. % graphene) and B) graphene/CS (14.28 wt. % graphene) after equilibration process

Nevertheless, several configurations have been generated after the equilibration proceedure, graphene nanosheets agglomeration was observed in all the cases. The total potential energy of the composite systems after equilibration varies between $2.92x10^{-4}$ for CS and $5.84x10^{-4}$ in the case of 14.28 wt. % graphene contents.

Further, mechanical behavior of the composite systems was evaluated. In order to test the mechanical properties we used the Elastic Properties Analysis tool implemented in the MS software. A procedure described elsewhere was applied for the calculation of the Young's moduli [14] and the results are summarized in table 3.

Table 3

Elastic moduli for the CS and CS-graphene computational bulk models

Material	Young's modulus [GPa]
CS	8.55
GRAPHENE/CS (4 wt. % graphene)	9.17
GRAPHENE/CS (7.67 wt. % graphene)	11.14
GRAPHENE/CS (14.28 wt. % graphene)	11.55

The Young's moduli outcame from the MD simulations at 300 K increase from 8.55 GPa in the case of pure CS to 11.55 GPa in the case of graphene/CS with 14.28 wt. % graphene. It was noticed that by adding 4 wt. % or 7.67 wt. % of the graphene to the CS matrix an increase of about 6.76 % and 23.25 % respectively was obtained. By future increasing the graphene content to 14.28 wt. % just a marginal effect was observed. This lower increase of the Young's moduli displayed by the computational system with highest amount of graphene might be due to the graphene agglomeration. The improvement of the mechanical properties of CS is attributed to electrostatic interaction between the inorganic reinforcing agent and the polymer matrices.

4. Conclusions

The elastic moduli constants for the pure CS and graphene/CS composite systems have been calculated by using molecular modeling at atomistic scale. A reinforcement of CS was observed with the addition of the graphene. The largest increase (~ 23%) was observed in the case of the composite with 7.67 wt. % graphene in their structure, by further increasing the graphene amount this tends to agglomerate and produced just a marginal effect.

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