

Understanding of Interface Interactions between Cellulose I β and Graphite Oxide (GO) through Molecular Dynamics (MD) Simulations

(Qian Mao)

(Department of Mechanical Engineering)
(Clemson University)
qianm@clemson.edu

(Huijuan Zhao, Assistant Professor)

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Biography

My name is Qian Mao, and I am now a PhD student in Dr. Huijuan Zhao's research group. I got my bachelor degree at Wuhan Institute of Technology in China, mainly working on thermofluids problems in HVAC systems and high-power LED chips. I had been using FEA software solving heat transfer problems and optimizing the design for microchannel heat exchangers in high-power LED chips throughout all my senior year and another half year after undergraduate study. Since then I have developed a great interest in multiscale modeling and simulations, at the thought of unravelling the mechanisms behind the engineering problems.



Overview:

Cellulose, the most abundant and accessible biopolymer on earth, can be utilized as the fundamental matrix material reinforced by carbon nanotubes (CNTs) and graphite as well as their functionalized ramifications for cellulose-based nanopaper and membrane. Cellulose-based nanocomposites are of great importance for energy saving, environmentally friendly manufacturing and engineering due to their appealing chemical and mechanical properties. To date, there is no definitive rationale at atomic level for explaining how the cellulose matrix and the reinforcements interact and function, as a vast range of experimental research reveal the enhancement of such composites in hydrophilicity or sometimes hydrophobicity in need[1][2][3], or both strength and toughness in advanced material design[4][5]. In this work, reactive force field (ReaxFF) was applied and the atomic interaction between cellulose I β and GO within interlayers was examined using molecular dynamics (MD) simulations. Infinite large cellulose I β configurations with either (2 0 0) or (1 1 0) plane (hydrophobic or hydrophilic plane) exposed to the highly oxidized -COOH or -OH single graphene sheet were modeled, and the conformational and dynamic behaviors taken place within the interlayer were then analyzed. It was found that the existence of GO altered the hydrogen bonding pattern that used to appear in origin-center layers of pristine cellulose I β . Further, such a variation caused conformational change in omega, omega', phi and psi dihedral angles, conversion between hydrophilic and hydrophobic groups, as well as tilting in anhydroglucose rings. To our knowledge, this is the first comprehensive molecular dynamics study that addresses interlayer interactions and conformational behaviors in cellulose-based nanocomposites.

Motivation

Deformation tests were performed in different types of cellulose-based nanopaper and membrane, obtaining an improvement in strength and toughness compared with the pristine material, but the

mechanism of strengthened interfaces in transverse direction still remains unclear. Further X-ray diffraction (XRD) study found that the (2 0 0) peak intensity weakened or even diminished as the highly oxidized GO sheet was reinforced to cellulose I β membrane. This might be the indicator as the hydrophilic and hydrophobic groups are reversed with each other, which on the other hand provides a new approach to selectively designing a composite material that either easily dissolves in solution or produces superhydrophobic surfaces for the specific need by simply adding highly oxidized nanosheet. However so far there is no relevant study reported validating such a hypothesis. From experimental perspective, it entails complicated material preparation process and lacks clarity in observation of microstructural variations and transitions. Reactive force field such as ReaxFF in MD has the ability to capture the bond forming and breaking yet it is quite time consuming. Commonly used non-reactive force fields are more computationally effective but the bonding state cannot be monitored during the simulation resulting in the incapability of performing hydrogen bonding and conformational analysis. Moreover, even with sufficient computational resource and time provided, thermal and mechanical behaviors can be of huge discrepancy if the parametrization and post-processing procedures are not carefully carried out [7].

State of the Art

Due to the space limitation, the current state of tackling this problem can be summarized below.

Experimental approaches: wide-angle X-ray scattering (WAXS), solid-state ^{13}C NMR, FTIR, Raman scattering etc. [9][etc].

Computational approaches: DFT, MD including AMBER, LAMMPS, GroMacs, NAMD etc. [6][7][8].

Intellectual Merit

Research questions: (1) how does GO affect the conformation and morphology of the near interlayer cellulose? (2) Do $-\text{COOH}$ and $-\text{OH}$ terminal groups function differently as the GO flips the hydrophilic with hydrophobic groups? (3) Does the (1 1 0) plane (hydrophilic plane) react with GO oppositely as the (2 0 0) plane (hydrophobic plane) does as we expect? (4) Does the existence of GO indeed weaken or shift the peak intensity of the composites based on simulations?

Hypotheses: (1) The cellulose matrix in the composite is infinite large, so the surface effects may not be captured. (2) The composites at 100K and atmosphere pressure remain their microcrystal structures. (3) The representative volume element (RVE) with periodic boundary condition (PBC) has sufficient precision for simulations and post-processing procedure.

Reasons to pay attention to this work: please see "Overview" and "Motivation" sections.

Broader Impact

Researchers will have better understanding of interfacial reaction mechanisms when designing the surface materials with great freedom of switching between hydrophilic and hydrophobic materials at will. Moreover it opens up abundant opportunities to use a new class of functional materials that are both strong and tough.

Research Approach

Materials Studio + MatLab->generate data files of pristine and composite models

LAMMPS->compute and output the trajectory of atoms and other useful information such as energy terms, lattice parameters, etc.

MatLab->post-process trajectory files for analysis

Findings to Date

- (1) GO alters the conformation and morphology of the near interlayer cellulose and even subsequent layers.
- (2) Center chain layer of cellulose is more susceptible to the presence of GO as opposed to the origin chain layer.
- (3) With the same mole number of Oxygen, GO-COOH cellulose composite has higher possibility to flip hydrophilic groups from interior to exterior surface near interlayer.
- (4) The existence of GO does weaken the peak intensity and shift its position due to the change in lattice spacing.

Conclusions

- (1) GO has the ability to reverse most of hydrophilic groups from interior to exterior surface near interlayer, as the (2 0 0) plane of cellulose exposed to GO.
- (2) With the same mole number of Oxygen, GO-COOH cellulose composite has higher possibility to flip hydrophilic groups from interior to exterior surface near interlayer.

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