Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations

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Abstract

The goal of the study is to improve the mechanical properties of cellulosic-based composites by gaining a deeper fundamental understanding of the mechanical behaviour of the cellulose structure in wood microfibre. A three-dimensional periodic simulation cell was utilized to create and alter the amorphous cellulose structure using molecular static and molecular dynamics simulations. In order to mimic the atomic interactions and complicated bonding of cellulose, the 14-β-D-glucose structure and a reactive force field, ReaxFF, were selected. The projected geometric, energy, and elastic properties of materials were compared with published modelling results and actual data after mechanical properties were computed for these models. The study is important because it lays the groundwork for next predictive micromechanical models of polymer-cellulose. The interfacial compatibility between the polymer and cellulose, as well as the effects of deposited nanoparticles and nanophases on cellulose surfaces, can be clarified using these prediction models.

Keywords: amorphous cellulose, molecular dynamics simulation, mechanical properties, ReaxFF, polymer-cellulose compatibility, nanophases, stress-strain behaviour.

Introduction

Nanocellulose research is a popular field right now. Many people are particularly interested in adding nanophases to polymer composites since they can greatly enhance the material's mechanical properties. Nonetheless, the literature is lacking in details regarding how nanophases applied to the surface of cellulose fibre enhance the fibre-polymer interfacial compatibility. Simulations of molecular dynamics may help clarify this matter and offer a basic comprehension of the effectiveness and functions of nanoparticles in cellulosic fibres to improve the properties of composites.

Whether in its original or regenerated form, cellulose is one of the most often utilized polysaccharides in industry as a reinforcing material. It is the most prevalent renewable organic material in the world. The proportion of crystalline to amorphous phases influences cellulose's mechanical characteristics. Numerous crystalline forms have been discovered since its discovery 160 years ago. Nevertheless, a great deal of research remains focused on the structure and morphology of the amorphous phase. Amorphous cellulose's complicated structure and different bonding types make it particularly difficult to understand its mechanical behaviour at the atomic level.

In addition to being time-consuming, experimental methods are frequently constrained by the ability

Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations



to prepare specimens, carry out experiments, and analyse the change in structure during deformation. Conversely, computer modelling is a potent instrument for studying atomistic phenomena. Iteratively solving Newton's equations of motion using empirical or semi-empirical interatomic potentials in order to describe the forces between atoms is one of the many computational approaches that can be used to determine the physical and mechanical properties of materials at the nanoscale. Molecular dynamics simulations are one such method. In some circumstances, nanoscale simulations can offer extra information (such as atomic locations, velocities, and forces) that is difficult to gather from experiments, and they can also supplement experimental efforts.

Carbon nanotubes, graphite/epoxy nanocomposites, and other polymers' mechanical characteristics have been the subject of a number of molecular dynamics simulations in recent years. Furthermore, to assess cellulose's behaviour, atomistic simulation has also been run. The characteristics of cellulose's ordered (crystalline) and disordered (amorphous) molecular regions can be used to describe its mechanical qualities. While the crystalline cellulose portions contribute to the materials' elasticity, the amorphous cellulose sections allow the bulk microfibril to be flexible and pliable. Thermal responsiveness, glass transition temperature, and chain modulus of elasticity are among the parameters of two native crystalline phase celluloses (I α and I β) that have been evaluated in order to study the latter component. To examine the cellulose chains in the material, molecular modeling is a useful tool. One way to forecast the relative stability of the various cellulosic allomorphs is to use modelling techniques that use "minicrystals," which are simple minimizations of finite-sized systems (without periodic boundary constraints). However, in such calculations, large uncontrolled edge effects are anticipated. Computations using NVT and NPT group molecular dynamics have been used to resolve this problem and provide structural and energy information on various crystalline forms. We are able to obtain a true overall image of the crystal structures thanks to these investigations. There are relatively few research that examine how the structure changes during deformation in the amorphous phase, in contrast to the efforts to characterize the crystal structures of cellulose.

In this work, the strain-stress behaviour of amorphous cellulose under uniaxial tensile deformation was calculated using molecular dynamics simulations. Initially, 14-β-D-glucose chains were simulated in three dimensions (3D) using a periodic cell that had the same density as the experiments. Here, the atomic interactions were described by a reactive force field (ReaxFF), which, in contrast to earlier molecular simulations in the literature, permits dynamic bond scission and bond creation. The results of the simulation demonstrate the comparison between the calculated geometric, energy, and elastic material parameters with published modelling and experimental data.

2. Modelling and simulation approach

2.1 Model building

The model cubic simulation cell was constructed following the Amorphous Cell Protocol, which was first put out by Theodorou and Suter (1985). The system's initial configuration was created using Accelrys' commercial Materials Studio software. A predetermined quantity of 14-2-D-glucose chains

Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations



had to be inserted into the periodic simulation cell in order to create amorphous cellulose models. Cellobiose is the repeat unit for cellulose, and its chemical structure is depicted in Figure 1. To explore the possible impact of the simulation cell size, two chain lengths—20 and 50 repeat units per chain—were used. With periodic boundary conditions, the unit cell of 50 monomers in a single chain is depicted in Figure 2. The system has a starting density of 0.8 g/cm3. But as the simulation cell relaxed to zero pressure at 298 K, the density changed from 1.28 g/cm3 to 1.44 g/cm3. All three directions were subject to periodic boundary conditions.

For all future molecular dynamics' simulations, the LAMMPS simulation tool was utilized (Plimpton, 1995). In order to simulate additional atoms, the unit models of cells were duplicated by $3 \times 3 \times 3$, as seen in Figure 3. To reduce the energy of every component and effectively relax the structure, standard energy minimization techniques were applied to the built cell. Additionally, an isothermal/isobaric (NPT) ensemble was used to equilibrate the system at the selected temperature with a modest time step ($\Delta t = 0.5$ fs) for a 250 ps equilibration duration. Then, using the NPT ensemble, the amorphous cell's equilibrium density was reached at the selected temperature and fixed pressure in the atmosphere (P = 0.0001 GPa). The deformation simulations were then carried out using the equilibrated systems under a uniaxial tensile strain imposed at a constant strain rate. According to van Duin et al. (2001) and Chenoweth et al. (2008), the atomic interactions for dynamic connection scission and bond creation can be described by the ReaxFF utilized here. 108 s-1, 109 s-1, and 1,010 s-1 were the three strain rates that were applied to the simulation cell for varying chain lengths and numbers of chains. Deformation of the amorphous cellulose structures occurred around 298 K, which is significantly lower than the glass transition temperatures. Instead of replicating the real thermodynamic state (P, V, and T) of the amorphous cellulose structure, the temperature and pressure employed in our simulation are practical computational parameters to relax the structure.



Figure 1: Cellobiose's chemical structure, atom names, and torsion angles (colors are shown in the online version)

 $\Phi = H1-C1-O4'-C4'$ $\Psi = C1-O4'-C4'-H4'$ $\omega = O5-C5-C6-O6$

Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations





Figure 2: Amorphous cellulose structures modeled by simulation cells (colors are shown in the online version)



Figure 3: Three-range unit cell model supercell (colors are shown in the online version)

Every computation was carried out at Mississippi State University's Center for Advanced Vehicular Systems (CAVS).

2.2 The ReaxFF technique

In this study, we simulated the bonding between the different glucose components using the ReaxFF. A generic bond-order-dependent force field called ReaxFF accurately describes how bonds are formed and broken in dynamic simulations. Bond orders derived from interatomic distances that are updated with each MD step determine the connection in ReaxFF, which is the primary distinction between it and the conventional unreactive force fields. This enables relationships to form and break throughout the simulation. The ReaxFF splits the system energy Esystem into contributions from different partial energy terms, much like the empirical non-ReaxFFs do. This can be shown in the following way:

 $E_{\text{system}} = E_{\text{bond}} + E_{\text{under}} + E_{\text{over}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdwaals}} + E_{\text{coulomb}}$ (1)

Bond energy E_{bond} , atom under-/overcoordination E_{under} , E_{over} , valence angle E_{val} , penalty energy E_{pen} , and torsion angle are some examples of these partial energies. Conjugation energy E_{conj} words to appropriately manage the van der Waals $E_{vdwaals}$ and Coulomb $E_{coulomb}$ interactions, as well as phrases to handle the nature of preferred configurations of atomic and consequent molecular orbitals. These latter non-bonded interactions are insulated to prevent excessive repulsion at close ranges and are computed between each pair of atoms, regardless of connection. ReaxFF's transferability is significantly increased by its ability to represent covalent, ionic, and intermediate materials due to its

Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations



treatment of non-bonded interactions. The study by van Duin et al. (2001) goes into additional detail about the potential energy functions connected to each of these partial energy contributions.

3 Findings and discussions

3.1 The conditions of the simulation

ReaxFF allows for charge and bond order changes at each time step, an appropriate time step is necessary. Simulating for as long as feasible while using the least amount of computer work is the ultimate goal. Therefore, the selection of time step is a trade-off between a small number that enables faster calculation of each time step and a high value that will require fewer molecular dynamics MD steps for known simulated interval. Dynamics must accurately conserve the system's total energy if the time step is small enough.

The 1 fs time step scenario in Figure 4 exhibits a larger temperature fluctuation from the initial value, but the 0.5 fs time step computes the temperature more steadily.

When the simulated cell is equilibrated, a significant temperature increase is observed for the 1 fs timestep example. Figure 5 displays the energy (total, kinetic, and potential) for the identical setups as a function of simulation time. In order to achieve equilibrium without discernible drift, the system operates more quickly with a time step of 0.5 fs. All of these numbers start to oscillate if the initial velocities are assigned during the NVE molecular dynamics model with a 1 fs time step, according to a breakdown of the total energy into its potential and kinetic energy. When atoms approach too closely, they may be ejected from the simulated cell, which is another indication of instability with the 1 fs. Consequently, a time step of less than 0.5 fs must be used in subsequent simulations.



Figure 4 Temperature evolution as a function of simulation time for 0.5 fs (a) and 1 fs (b) using a molecular dynamics simulation with constant volume and energy (NVE) (colors are shown in the online version).

Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations



3.2 Mechanical and physical characteristics

The final model's mechanical and physical characteristics, including density, Young's modulus, shear modulus, and Poisson's ratio, were selected to assess the model parameters in order to replicate the mechanical characteristics of actual amorphous cellulose. During molecular dynamics simulations, the density can change since the cell parameters are permitted to change. One important metric for assessing the simulated microstructures' realism is density. Table 1 displays the computed properties. When the equilibrium amorphous cellulose model using ReaxFF was compared to experimental and literature values (Chen et al., 2004), its characteristics were strikingly similar to those reported in the literature. The predicted MD results and the experimentally measured parameters often agree, which is sufficient validation for additional research. Particularly given that the molecular dynamics results presented here employ a semi-empirical potential with an idealized amorphous structure, experimental structures may contain heterogeneities, such as regions of crystallized and amorphous structure, chain length distributions, and impurities/moisture, which can produce properties that differ from those of the idealized structure.



Figure 5 Using a constant volume and energy (NVE) molecular dynamics simulation, the energy (Et Ep and Ek) changes as a function of simulation duration for 0.5 fs (a) and 1 fs (b) (for colors, view the online version).

Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations Dr. Gajendra Gupta



Properties	ReaxFF	Literature value
Density (g/cm ³)	1.347	1.385
Young's modulus (GPa)	9.37	10.42 ± 1.08
Shear modulus (GPa)	3.94	5.955 ± 0.673
Poisson's ratio	0.189	0.232 ± 0.0313

Table 1: Amorphous cellulose models' mechanical characteristics at 298 K (28,404 atoms)



Figure 6 shows the potential energy histogram of the three atoms in the initial deformation structure (28,404 atoms, C for 8,100, H for 13,554, and O for 6,750; colors are shown in the online version).



Figure 7 shows the potential energy histogram of three atoms following deformation (28,404 atoms, C for 8,100, H for 13,554, and O for 6,750; colors are shown in the online version).

Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations



3.3 Potential energy

The aim of structural equilibration is to match the potential energy's energy minimum. Internal compression or tension should not exist in the construction. In order to make sure the amorphous cellulose structure was suitable for deformation simulations; the potential energy of each atom was determined and their evolutions were monitored after the structure had been adjusted. In the initial deformation structure, Figure 6 illustrates the possible energy distributions of 28,404 atoms (8,100 carbon atoms, 13,554 hydrogen atoms, and 6,750 oxygen atoms). The potential energy changed as illustrated in Figure 7 during tensile stress at a strain rate of 1,010 s-1. Carbon atoms have a more stable potential energy than the others. Notably, modelling the H-bonding—a crucial structural element—was linked to the hydrogen atom's potential energy. The most significant component is the massive, negative coulomb term, which is obtained by separating the total potential energy into its bound and non-bonded (van der Waals and Coulomb) components. It seems that amorphous cellulose is not much affected by the weak and positive inappropriate van der Waals interaction.

3.4 Behaviour related to stress

Using tensile loading in the x-direction and zero pressure on the directions orthogonal to the loading direction (i.e., uniaxial tension), the strain-stress behaviour of the amorphous cellulose was determined. The unit cell characteristics and amorphous cellulose structure are displayed in Figure 8 both after equilibration (up) and after 100% true strain (down).

At a strain rate of 1,010 s-1, the stress-strain behaviour of a simulated cell made of 28,404 atoms of amorphous cellulose is displayed in Figure 9. This dispersion may be typical of polymer deformation in molecular dynamics. All stress values are depicted as a function of strain (loading direction is red, lateral directions are blue and green), with the averaged response represented by the black line. Elastic, yield, and hardening are the three different regimes of the strain-stress curve. Following an initial elastic regime, strain hardening is found after yield. In the directions lateral to the loading direction, the stresses are cantered about 0 GPa, as required by the boundary requirements for uniaxial tension. Both actual results and earlier calculations in the literature are comparable to this stress-strain curve. Future research will investigate the mechanics underlying these various regimes at the nanoscale.



Figure 8 shows the model system in equilibrium at 100 K and following uniaxial deformation; colors are shown in the online version.

Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations Dr. Gajendra Gupta





Note: The colors C, H, and O stand for the various sorts of atoms.

Figure 9: A typical stress-strain curve for amorphous cellulose (28,404 atoms, temperature of 100 K, strain rate of 1,010 s-1) (colors are shown in the online version)

Notes: The average stress response in the tensile direction is shown by the black line. The distribution of the instantaneous stresses in the loading direction and two lateral directions is represented by red, green, and blue dots, respectively.

4. Conclusions and upcoming projects

The strain-stress behaviour of amorphous cellulose under uniaxial tensile loading was investigated using molecular dynamics simulations. ReaxFF was successfully used to create the amorphous cellulose models. For amorphous cellulose, preliminary molecular dynamical simulations have been provided. We discovered that future simulations using ReaxFF should employ a reasonable timestep of 0.5 fs.

The strain-stress behaviour of amorphous cellulose under uniaxial tensile loading was investigated using molecular dynamics simulations. ReaxFF was successfully used to create the amorphous cellulose models. For amorphous cellulose, preliminary molecular simulations that are dynamic have been provided. We discovered that future simulations using ReaxFF should employ a reasonable timestep of 0.5 fs. The mechanical characteristics and computed energy of cellulose were similar to those found in earlier experimental investigations and molecular dynamics simulations. Similar qualitative and quantitative patterns were seen in the simulated stress-strain behaviour utilizing molecular dynamics as compared to the experimental testing for amorphous cellulose. At low strain, which is equivalent to elastic deformation, a linear relationship between stress and strain was noted. The amorphous cellulose vielded and showed strain hardening at higher stresses. The interfacial compatibility between cellulose and polymer, as well as the effects of deposited nanoparticles and

Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations



nanophases on cellulose surfaces, can be clarified using these prediction models.

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Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations



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Mechanical Properties of Amorphous Cellulose Explored Through Molecular Simulations Dr. Gajendra Gupta

