

Effect of Vacuum and Heat Treatment on a Single Chain of Cellulose: Molecular Dynamics Simulation

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Molecular dynamics simulation was used to better understand a single, non-crystalline cellulose molecular chain and its response to high-temperature treatment. The system temperature was varied from 430 K to 510 K, and the temperature interval was 20 K. Under the polymer consistent force field (PCFF), the dynamics simulation of each temperature was completed under the constant pressure/constant temperature dynamics (NPT). The experimental results showed that the mechanical properties of cellulose heat-treated at high temperature in a vacuum environment initially increased and then decreased with the increase of temperature. When the temperature was at 450 K, the mechanical properties reached an optimal state. Moreover, its mechanical properties were noticeably related to the connection of hydrogen bonds in the cellulose molecular chain and the thermal motion of the molecular chain.

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INTRODUCTION

High temperature heat treatment of wood is a method of wood modification. It usually refers to the heat treatment of wood at a temperature in the range of 160 to 230 °C. After the wood has been treated with steam, nitrogen, water, or heat transfer oil as the heating medium for several hours, the wood chemical components are changed. Physical and chemical changes, as well as purely physical wood modification to alleviate the internal growth and drying stresses of the wood, can be achieved. Depending on the heating medium, the most successful heat treatment processes so far mainly include Thermowood process (Ferreira *et al.* 2014), Plato-Wood process (Esteves *et al.* 2005), Rectification process, and Oil Heat-treatment (OHT) process (Andreas *et al.* 1983). These four heat treatment processes are considered the most classic and mature heat treatment processes, and the various heat treatment processes that have emerged since then have been adjusted and evolved on the basis of these processes.

The main components of wood are cellulose, hemicellulose, and lignin. Among them, cellulose plays the role of skeleton in the wood cell wall, and its chemical properties and supramolecular structure have an important influence on the strength of wood. The basic ring of cellulose is a macromolecular polysaccharide composed of β -1,4-glycosidic bonds of D-glucose. The ordered lattice structure in natural cellulose is called the crystalline region, and the irregularly arranged structure is called the amorphous region. The amorphous region directly affects the mechanical, thermal, and adsorption properties

of fibers. Moreover, the pure region of amorphous cellulose actually exists in wood, which has an important effect on the structure and properties of wood. Nishiyama *et al.* (2003) showed that the amorphous regions in ramie cellulose microfibrils are arranged periodically and that ramie is one of the few plants in which cellulose microfibrils are arranged almost entirely along plant fibers. Therefore, in order to present a more understandable representation for future readers, this paper was combined with the Tassal microbeam model proposed by Bryant. The blue line represents the crystalline region of cellulose, and the red curve represents the amorphous region of cellulose to describe the wood cellulose model, as shown in Fig 1.

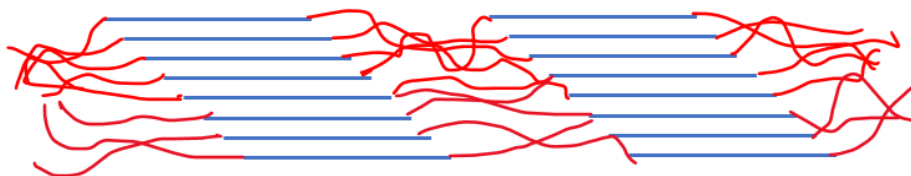


Fig. 1. Schematic diagram of the crystalline and amorphous regions of the cellulose chain

High temperature heat treatment of wood can improve dimensional stability and reduce its equilibrium moisture content (Minkah *et al.* 2021). The change of cell wall microstructure under high temperature may be the main reason for this phenomenon (Chu *et al.* 2019). After high temperature treatment, the hydrophilic hydroxyl groups in the wood components are eliminated, and other hydrophobic groups are generated at the same time (Tjeerdsma and Militz 2005) to improve the dimensional stability, decay resistance, and durability of wood. Compared with the untreated wood, the mechanical properties of the wood after heat treatment have different degrees of change, among which different treatment medium, treatment methods, treatment time, and other factors have a greater impact on the final mechanical properties (Wang and Cooper 2005). Bal (2018) studied the thermal modification of wood in vacuum, nitrogen, and air. Through measuring the mechanical properties, such as elastic modulus and fracture modulus, of wood before and after heat treatment, the vacuum environment had the smallest effect on the mechanical properties of wood (Bal 2018). Candelier *et al.* (2013) investigated a comparison of the chemical composition and decay resistance of heat-treated wood under nitrogen and vacuum as inert atmospheres and showed that vacuum-treated wood had lower degradation (Candelier *et al.* 2013). There are only few studies available on wood heat treatment in vacuum environment, especially the research part on the modification of vacuum heat-treated wood from the microscopic level. Therefore, the aim of this study was to determine the microscopic effect of a new generation of processing under vacuum conditions on the changes in mechanical properties that occur during processing. This preliminary work focuses on a single cellulose molecular chain in isolation. Because cellulose in nature is always highly bonded to other cellulose molecules, as well as other wood components, and because natural cellulose is highly crystalline, further studies will be needed to achieve a fuller description (Wang *et al.* 2018).

EXPERIMENTAL

The essence of molecular dynamics is to simulate the motion of a large number of atoms, relying on computer technology to build a basic model, analyze its microstructure and dynamic trajectory, and play a huge role in the microstructure of biological macromolecules. Therefore, in this study, the molecular dynamics method was used to simulate the vacuum environment and the heat treatment of wood cellulose to study the change of mechanical properties. Natural cellulose is repeatedly linked together by D-glucose residues, and the crystallinity of the cellulose material is typically 70% to 80%, so the chain length contained in the amorphous region is limited. In studying the properties of the amorphous region of cellulose chains, models of the amorphous region were constructed using cellulose chains of different lengths, *i.e.*, different degrees of polymerization (Mazeau and Heux 2003). The results were similar to the experimental results when studying the amorphous region of cellulose with cellulose chains with a degree of polymerization of 20 (Chen *et al.* 2004). Based on the above considerations, the degree of polymerization of cellulose chains used was assumed to be 20 in amorphous regions.

Calculation Details

Modeling and simulation experiments were carried out with Materials Studio software (Materials Studio 20.1, BIOVIA, San Diego, CA, USA), and the Forcite module was used to complete the molecular dynamics simulation. Because it increased the calculation parameters of the polymer, all calculations were based on the PCFF force field. The amorphous cell module enables the construction of three-dimensional periodic structures of amorphous polymers and other materials for the construction of cellulose chain in amorphous regions. Because the amorphous region of the cellulose chain is short and the degree of polymerization has little effect on the experimental results, a cellulose chain with a degree of polymerization of 20 was selected. In the energy calculation, the Ewald method and the atom-based method were used for electrostatic interaction and Van der Waals interaction, respectively (Wang *et al.* 2020).

It is known from the *Polymer Handbook* that the density of the amorphous part of cellulose is between 1.482 and 1.489 g/cm³, so the target density was set to 1.5 g/cm³ (Onyon 1972). Five groups of cellulose models under vacuum environment were established. To describe the effect of temperature on the pure region of amorphous cellulose under vacuum condition, this is shown in Fig. 2. The temperature corresponding to different cellulose models is shown in Table 1. The size of the model box used is 19.6 × 19.6 × 19.6 (Å³).

Table 1. Temperature Corresponding to Different Cellulose Models

Model	a	b	c	d	e
Temperature (K)	430	450	470	490	510

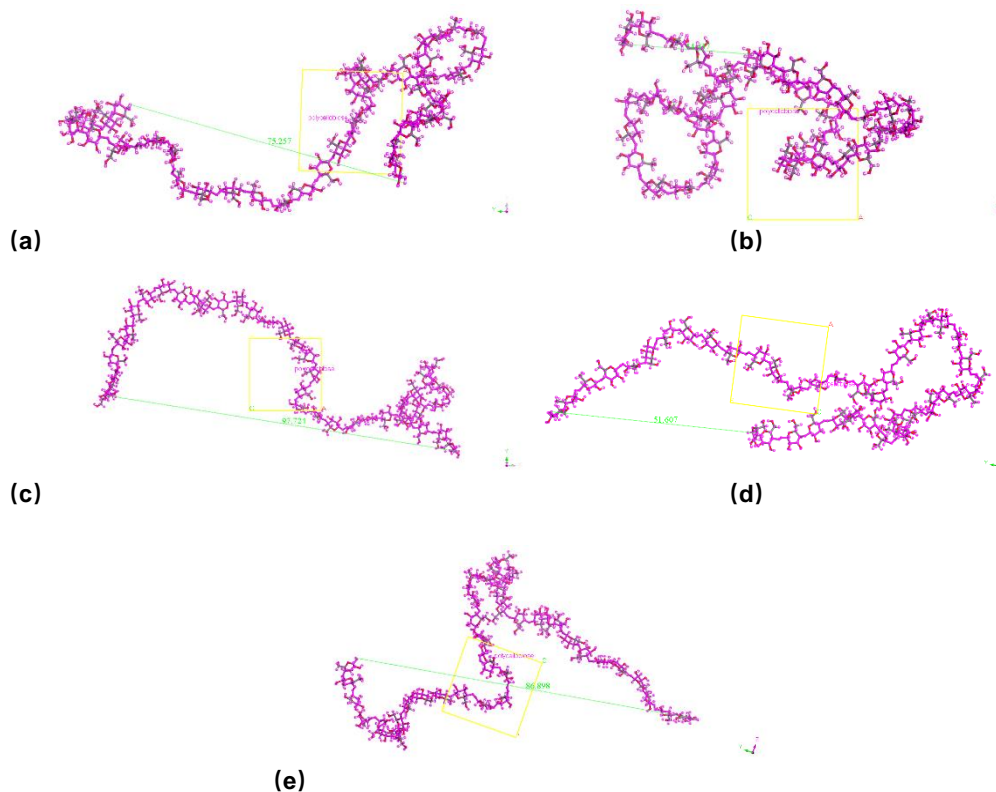


Fig. 2. Cellulose models used in vacuum environment: a through e: see Table 1

Dynamic Simulation

After the model was established, the authors used the PCFF force field for simulation experiments at each stage. Geometric optimization was completed to optimize the energy, and then a molecular dynamics simulation of 1,000,000 steps was completed in an isothermal isobaric (NPT) ensemble at five temperature groups of 430, 450, 470, 490, and 510 K at random initial velocity. The pressure used was 2×10^{-5} GPa with a step size of 1.0 fs. A total simulation time of 1000 ps was used, and one frame has output of every 5000 steps. Temperature and pressure were controlled by the Andersen (Andrea *et al.* 1983) and Berendsen methods (Berendsen *et al.* 1984), respectively. The Van der Waals interaction force was calculated using the Atom-based method, and the electrostatic interaction force was calculated using the Ewald method (Ewald 1921).

RESULTS AND DISCUSSION

System Balance

Through analyzing the simulation results of temperature and energy, it can be judged whether the system reached an equilibrium state. As shown in Figs. 3 and 4, the change of energy can be used to determine whether the whole system reached the equilibrium state. Figure 3 denotes the dynamic energy diagram of Forcite module when the temperature was 450 K and the simulation time was 1000 ps. It can be seen from Fig. 3 that in the last 200 ps of the simulation, the total energy (Total) value of the system fluctuated up and down from its average value, indicating that the system reached an

equilibrium state. The energy-time curves at other temperatures of the system were similar, so all systems were in equilibrium.

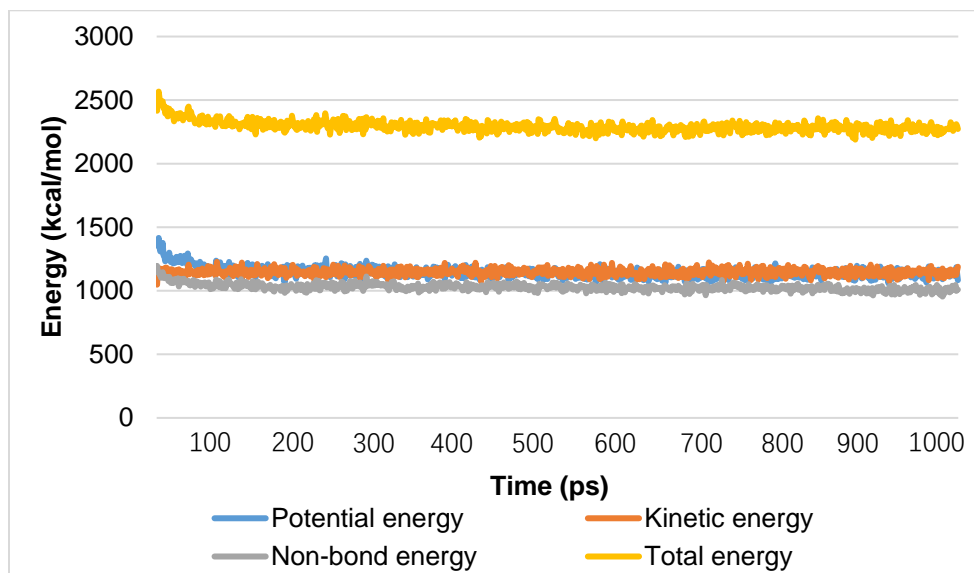


Fig. 3. Energy versus time curve

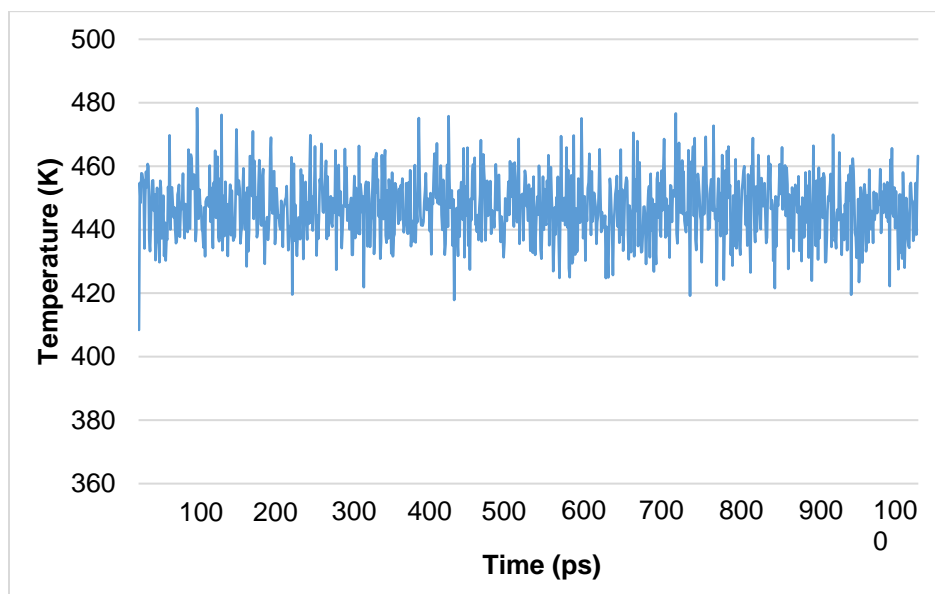


Fig. 4. Temperature curve with time

Figure 4 shows the temperature-time changes at 450 K. The temperature changed slightly with time, but the overall temperature was controlled within the range of ± 25 K, which indicates that the system reached an equilibrium during relaxation. The temperature-time change diagram at other temperatures of the system were similar to this; therefore all systems were considered to be in equilibrium.

Mean Square Displacement of Cellulose I β

Thus far, cellulose is divided into five categories due to different crystalline structures, namely natural cellulose (cellulose I), artificial cellulose II, III, IV, and cellulose X. Among them, cellulose I is the naturally occurring form of cellulose. Natural cellulose I also has two different crystal structures, namely cellulose I α and I β , which are bacterial cellulose and cellulose in the cell wall of higher plants, respectively. Wood cellulose belongs to natural cellulose and exists in the cell wall of wood plants, so wood cellulose belongs to cellulose I β .

The thermal stability mainly reflects the performance retention rate of the material in the thermal environment. A smaller performance loss resulted in better thermal stability. When the chain movement is more intense, the performance loss is greater and the thermal stability is worse. The chain motion can be characterized by the mean square displacement (MSD). The MSD value is a measure of the deviation of a particle's position over time relative to a reference position, and it is expressed in Eq. 1:

$$MSD = \langle |r_i(t) - r_i(0)|^2 \rangle \quad (1)$$

In Eq. 1, $r_i(0)$ and $r_i(t)$ represent the positions of the particle at time 0 and time t .

Figure 5 shows the MSD curves of cellulose molecular chains in different temperature models.

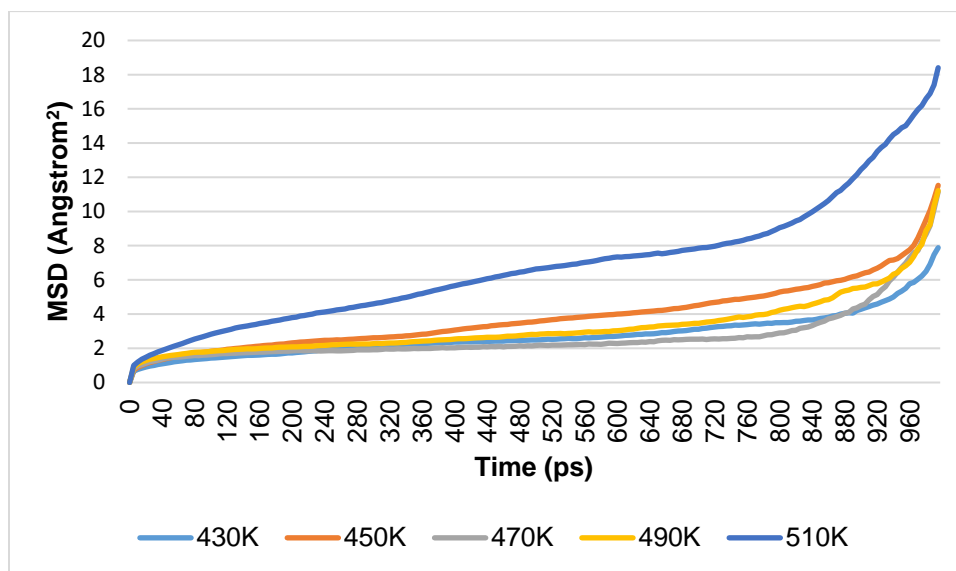


Fig. 5. MSD curves of cellulose chains at different temperatures

Figure 5 shows that the MSD value of cellulose I β chain was the lowest at 430 K temperature, and the MSD value of cellulose chain I β did not change noticeably from 450 to 490 K. When the temperature was increased to 510 K, the MSD value of cellulose chain I β also increased, reaching the maximum value among the five groups of temperatures, indicating that the stability of cellulose chain I β decreased with the increase of temperature. The order of the lines shown in Fig. 5 is not very regular in terms of temperature, but an overall trend is that the higher the temperature, the more intense the activity, especially at 510 K. At relatively low temperatures, the end result may happen to be stuck in a non-equilibrium state.

Hydrogen Bonding

The presence of a large number of hydrogen bonds and high degree of polymerization in cellulose could promote the mechanical properties of cellulose (Hinterstoisser *et al.* 2003). There are a large number of active hydroxyl groups (OH) distributed on cellulose chains. Among the hydroxyl (OH) groups, the O-atom tends to be slightly negatively charged and has a stronger electron-withdrawing ability, and H-atom tends to have a positive electron-donating ability. With the characteristic of positive and negative charges, the H-atom in the glucose of the cellulose chain will have a weak force to attract the O-atom of other glucose. A lot of hydrogen bonds are thus formed in the middle of the chain, and a force is generated by such interactions.

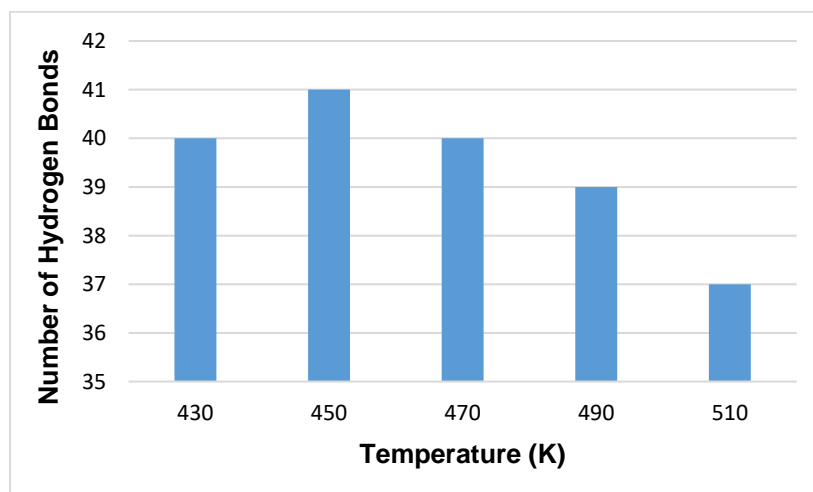


Fig. 6. The number of hydrogen bonds at different temperatures

Hydrogen bonds play an indispensable role in cellulose. Many long-chain celluloses are formed by weak hydrogen bonds. Therefore, the number of hydrogen bonds is directly related to the overall mechanical strength of cellulose chain. Since there is only one cellulose chain in the model construction in this paper, the hydrogen bond in this paper refers to the hydrogen bond within the cellulose chain. It can be seen from Fig. 6 that with the increase of temperature, the number of hydrogen bonds shows a trend of first increasing and then decreasing, and it reached a maximum value when the temperature was 450 K. This result indicates that at a lower temperature (450 K), the heat treatment in a vacuum environment can increase the number of hydrogen bonds in cellulose chain I β , and with the increasing temperature, the number of hydrogen bonds will continue to decrease. As the temperature increase from 450 K to 510 K, the number of hydrogen bonds were decreased from 41 to 37, and the number of hydrogen bonds in cellulose chain I β was decreased approximately 9.8%.

This may occur because at a lower temperature, with the increase of the heat treatment temperature, under the action of heat, the motion of the segments of the cellulose molecules is enhanced, and the distance between some of the molecules is reduced. Thus, the chance to form new hydrogen bonds increases and the number of bonds also increases. Further, as the temperature continues to increase, the movement of the cellulose molecular chain I β becomes more intense, and the intra-chain hydrogen bonds are partially broken due to the vigorous movement of the molecular chain, so the number of hydrogen bonds continues to decrease. The findings indicate that the increase of temperature will affect the

thermal stability of amorphous region of cellulose chain, thereby affecting its mechanical properties.

Mechanical Properties

Through molecular dynamics simulation, mechanical parameters can be obtained to characterize the mechanical properties of materials. For isotropic materials, there are only two independent elastic coefficients C_{11} and C_{12} as shown in Eqs. 2 and 3:

$$\lambda = C_{12} \quad (2)$$

$$\mu = \frac{C_{11} - C_{12}}{2} \quad (3)$$

There are two Lamé constants, the first order Lamé constant λ represents the compressibility of the material, and the second order Lamé constant μ represents the shear modulus of the material. The value of C_{ij} is given by Eq. 4:

$$[C_{ij}] = \begin{bmatrix} \lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{bmatrix} \quad (4)$$

The various mechanical properties of the material can be calculated through the Lamé constant, and the formulas are shown in Eqs. 5 to 8:

$$E = \frac{\mu(3\lambda + 2\mu)}{\mu + \lambda} \quad (5)$$

$$G = \mu \quad (6)$$

$$K = \lambda + \frac{2}{3}\mu \quad (7)$$

$$\gamma = \frac{\lambda}{2(\lambda + \mu)} \quad (8)$$

Table 2 shows the mechanical properties of the amorphous region of cellulose at different temperatures. Bulk modulus (K) describes the elastic properties of isotropic materials, and it is a parameter that reflects the incompressibility of solid materials. Poisson's ratio (γ) is the ratio of transverse strain to longitudinal strain, also known as transverse deformation coefficient, which characterizes the magnitude of transverse deformation of the material. Young's modulus (E) is a measure of material stiffness and is defined as the ratio of stress to strain. Shear modulus (G) is the ratio of shear stress to shear strain.

Table 2. Mechanical Parameters of Cellulose at Different Temperatures

Temperature (K)	λ (Pa)	μ (Pa)	E (Pa)	G (Pa)	K (Pa)	γ	K/G
430	4.4697	6.6093	15.885	6.6093	4.5706	0.2017	0.691541
450	9.2549	6.9614	19.8958	6.9614	9.3507	0.2854	1.343221
470	7.7211	4.7151	12.3576	4.7151	7.8625	0.3104	1.667515
490	3.3782	3.6393	9.0305	3.6393	3.5614	0.2407	0.978595
510	6.0358	4.6662	11.964	4.6662	6.1787	0.2820	1.32414

The ratio of bulk modulus to shear modulus (K/G) characterizes the toughness of the material, and its performance is proportional to the value. Shear modulus, Young's modulus, and Poisson's ratio are the three parameters that represent the basic physical properties of materials.

Table 2 shows that with the increase of temperature, the mechanical parameters of cellulose I β showed a trend of first increasing and then decreasing as a whole. Among them, Young's modulus, shear modulus, and bulk modulus reach the maximum at the temperature of 450 K, and Poisson's ratio and the ratio of bulk modulus to shear modulus (K/G) reach the maximum at the temperature of 470 K. At the same time, the two moduli K and G are also at a better level at 450 K. When the temperature increased from 430 K to 450 K, the Young's modulus increased from 15.885 to 19.896 unit, and the macro mechanical strength of the wood increased 25.24%. As the temperature continued to rise from 450 K to 510 K, the Young's modulus decreased from 19.896 to 11.964, and the macro mechanical strength of the wood was decreased 39.87%.

Based on the above analysis, the mechanical strength of cellulose depends on the hydrogen bond connection, and the presence of more of these connections, translates to better mechanical properties. Because cellulose contains a large number of hydrogen bonds, at 450 K temperature, as the number of hydrogen bonds reaches the maximum, the molecular chain structure of cellulose is more close and is not easily destroyed, and the mechanical properties reach the optimal state. With high temperature heat treatment in vacuum environment, the mechanical properties first increased and then decreased with the increase of temperature. When the temperature was at 450 K, the comprehensive quality of mechanical properties of cellulose appeared the best.

CONCLUSIONS

In this molecular dynamics simulation experiment, the MSD value of cellulose chain I β and the change of the number of hydrogen bonds in the cellulose I β chain were analyzed, and the mechanical properties of wood cellulose under vacuum heat treatment at 430 to 510 K were also explored. The following conclusions are drawn:

1. The cellulose model was established by molecular dynamics simulation, and the effect of temperature on the properties of cellulose amorphous region in vacuum environment were considered. With the increase of temperature, when vacuum heat treatment was carried out at a lower temperature, the mechanical properties showed an upward trend. With the continuous increase of temperature, the mechanical properties began to decline. At 450 K, the mechanical properties reached the maximum state.
2. The number of hydrogen bonds in the cellulose chain and the movement of the cellulose molecular chain have a great influence on the mechanical properties of cellulose. As more hydrogen bonds are formed, the cellulose molecular chain structure becomes tighter, and its stability and mechanical properties are enhanced.

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