CELLULOSE CHEMISTRY AND TECHNOLOGY

MOLECULAR DYNAMICS STUDY ON THE EFFECT OF MOISTURE CONTENT ON THE MECHANICAL PROPERTIES OF AMORPHOUS CELLULOSE

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The alteration of mechanical properties because of moisture is an inevitable problem in the practical use of cellulosic materials, as well as green and high-performance materials synthesized based on cellulose. Although researchers have analyzed and reported this issue from various aspects, it is necessary to report the variation of mechanical properties of the cellulose system and its causes in detail from the molecular level as well. Herein, the effect of moisture content on the mechanical properties of cellulose is methodically examined by molecular dynamics methods. The main reasons for the structural changes caused by the stiffness and activity space of the cellulose chains and the number of hydrogen bonds in the system are explained and discussed. The obtained results reveal that, in the simulated range of moisture content, low moisture (0 to 4%) exhibits a positive effect on the mechanical properties of the amorphous cellulose region, whereas the effect of high moisture content (4 to 8%) is negative. The mobility of cellulose chains first reduces and then intensifies as the number of water molecules increases, while the rigidity of the corresponding system first increases and then decreases. Additionally, the free volume of the system increases first and then decreases as the number of water molecules rises. The mechanical properties of the amorphous region of cellulose are proportionally correlated with the number of hydrogen bonds in the system. Based on these results, a moisture content of 2% can enhance the properties, increasing the H-bond density in the cellulose network.

Keywords: mechanical properties, amorphous cellulose, hydrogen bond, molecular dynamics

INTRODUCTION

With the widespread use of non-degradable plastic products in industrial production and daily life, "white pollution" caused by plastic residues and microplastic particles in the ecosystem has attracted widespread concerns. In the face of the serious pollution produced by plastic waste and the ever-increasing depletion of traditional fossil resources, such as oil and coal, renewable, green and high-performance composite materials are attracting great attention worldwide. Cellulose is an abundant and renewable natural resource, and is the best alternative to petroleum products due to its renewability, low cost, environmental friendliness, and biocompatibility.[1,2] Additionally, cellulose can be mixed with other materials to arrive at more advanced composite materials, which have been the focus of scientists' attention.

Existing investigations have demonstrated the effectiveness of cellulose as a reinforcing base in the development of high-performance materials.[3,4] Unfortunately, in the process of application of cellulose materials and high-performance composite materials developed on the basis of cellulose, degradation of material stability and performance caused by moisture is unavoidable,[5] which remarkably restricts the application of cellulose-based composite materials. The insolubility, small size, and curly morphology of cellulose make the extraction of cellulose from vegetation a very problematic task for physical experimental research.[6]

Molecular dynamics (MD) simulation, however, has been proved to be a powerful tool for investigating the nature of cellulose. Bregado *et al.*

investigated the thermophysical properties of amorphous/paracrystalline celluloses by molecular dynamics.[7,8] Yan *et al.* simulated the dry friction of amorphous and crystalline cellulose with chromium (Cr).[9,10] Fan *et al.* studied the friction of amorphous and crystalline cellulose with Cr using water as a lubricant.[11,12] The existing research is devoted to examination of the degradation of cellulose performance in humid and hot environments based on theoretical simulations. Kulasinski *et al.*[13] adopted molecular dynamics methods to simulate and calculate the intrinsic physicochemical properties of amorphous cellulose at moisture content in the range of 0 and 50%. The achieved results revealed that the interactions between water and cellulose structure lead to a reduction of its mechanical properties and the cellulose exhibits a rubber-like behavior in high moisture content. In that study, the results indicated that the decrease in the system performance is essentially attributed to the decrease in the number of hydrogen bonds. Besides, the disruption of the hydrogen bond network not only affects its mechanical response, but also controls the evolution of porosity and volumetric strain of the system in the presence of various water contents. Wang *et al.*[14] employed molecular dynamics approaches to calculate the thermal stability of cellulose and cellulose containing water. The obtained results revealed that the glass transition temperatures of amorphous cellulose and cellulose containing water were 448 K and 418 K, respectively. It was displayed that the disruption of the original hydrogen bonding network between the cellulose chains by water molecules leads to a substantial lessening of the glass transition temperature of cellulose containing water, which affects the thermal stability of cellulose. Jiang *et al.*[15] pointed out that the moisture-induced decrease in the properties of cellulose is chiefly related to the lessening of the glass transition temperature of the cellulose system, as well as various forms of water molecules in the system. Dan *et al.*[16] reported water diffusion behavior in cellulosic systems and its effect on its virgin structure, mechanical strength and chemical stability at the molecular level. The results indicate that the diffusion coefficient of water in amorphous cellulose is 10 times that of crystalline cellulose, which shows that amorphous cellulose possesses a strong water absorption capacity. At high moisture contents (25% water), the mechanical strength of amorphous cellulose exhibited a substantial descending trend, where the elastic modulus (G) and shear modulus (E) reduce by 3.5 GPa and 1.1 GPa, respectively, compared to dry cellulose. Although investigators have conducted relevant research on the performance of water-induced cellulose systems from behavior to mechanism, it is still necessary to report in detail the movement of the cellulose chain, variations of free volume and the destruction and reconstruction of hydrogen bond networks in the water-containing cellulose system, arriving at a more systematic and in-depth understanding of the degradation behavior of cellulose in the presence of water.

Most investigations have been devoted to the degradation of cellulose properties due to the presence of water, which is mainly caused by changes in the microscopic structure of the amorphous cellulose system. The main reason behind this is that, although cellulose has a two-phase structure, the molecular chains in the crystalline structure are closely packed and the interactional forces' magnitudes are high. Water molecules are not able to influence the internal structure through the crystal surface, since it has little or almost no effect on the properties of the cellulose crystal.[17] There exist gaps and cavities in the molecular chain in the amorphous region of cellulose, and water molecules could readily enter the system and be absorbed into the cellulose chain to destroy the internal molecular structure of cellulose and thereby lead to changes in the performance of the system.

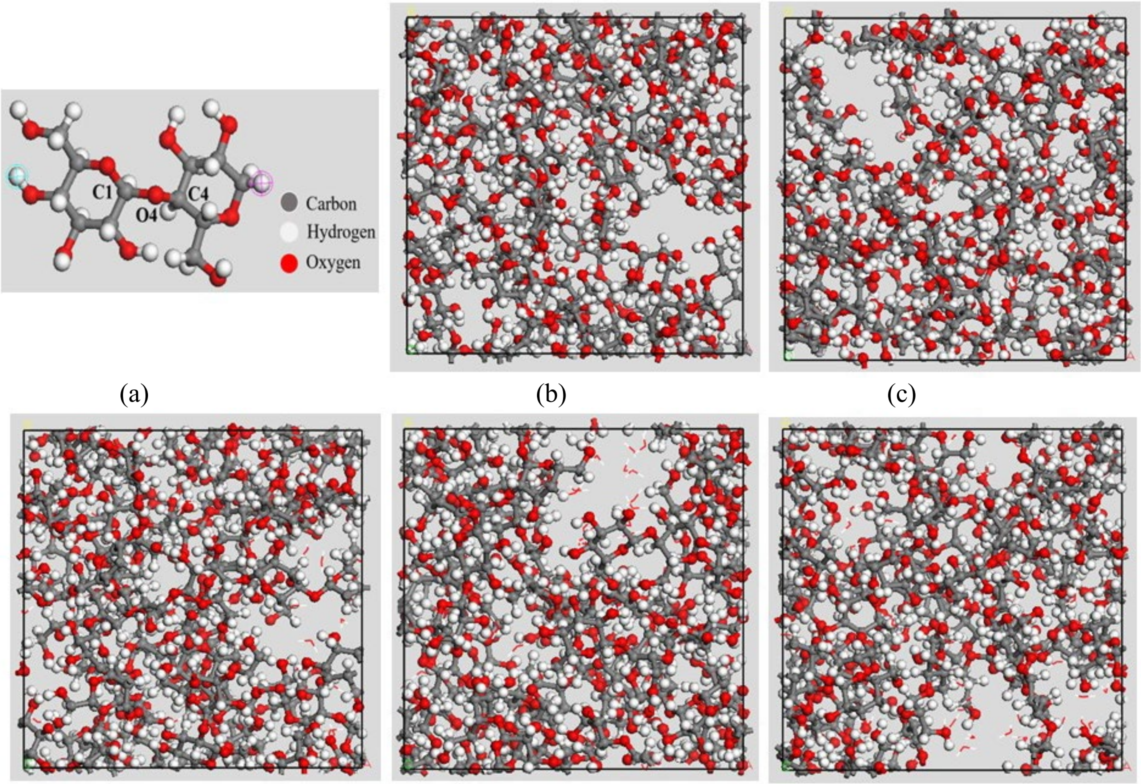
In the present work, amorphous cellulose models are methodically established for five different moisture contents (0, 2, 4, 6 and 8%), and the molecular dynamics approach is appropriately utilized to examine the influence of moisture content on the properties of amorphous cellulose. The changes in the stiffness of the cellulose chains, the free volume, and the number of hydrogen bonds in the system are analyzed. Materials Studio (MS) simulation software (7.0) of Accelrys is implemented to model cellulose containing water, as well as the overall molecular dynamics.

MODELLING AND SIMULATION APPROACH

Model construction

Natural cellulose is a polymer of linear unbranched glucose molecules whose repeating unit is the cellobiose (*i.e.*, $(C_6H_{10}O_5)n$). The cellulose chain is a disorderly arrangement of crystalline and amorphous regions. It should be mentioned in the introduction that the interaction of water and cellulose is more concentrated in the amorphous cellulose region, so we chose amorphous cellulose as the study model here. The size of the simulated system determines the duration of the simulation and the accuracy of the simulation results. Mazeau and Heux[18] simulated and calculated the properties of cellulose models made of cellulose chains with various degrees of polymerization (DP) of 10, 20, and 40, and found no substantial discrepancies. However, Wang *et al.*[19] showed that the simulated cellulose chains with a DP above 10 are capable of exhibiting physicochemical properties closest to those of natural cellulose. Considering the results of existing investigations and the time required for simulations, cellulose chains are made with DP 20, and then three cellulose chains are appropriately filled using the amorphous cell (AC) module in a cubic box with periodic boundary conditions using the AC module in MS software. Amorphous Cell allows for the possibility of establishing representative models for complex amorphous systems and predicting the main properties.

This model was established based on the method for making amorphous polymer presented by Theodorou and Suter,[20] with a target initial density of 1.2 g/cm^3, which is much lower than the actual density of cellulose. The density of pure cellulose (*i.e.*, 0% moisture content) after kinetic optimization was 1.477 g/cm^3, which is close to the actual density value of 1.5 g/cm^3 reported in the literature,[22] and the deviation obtained is of only 1.5%. This is mainly ascribed to the difference in the molecular weights of the simulated cellulose and the natural cellulose. The reasonableness of the model structure is suitably verified by comparison with the actual density of cellulose of 1.5 g/cm^3.[21] The optimized structural models are illustrated in Figure 1. In addition, the density structures of five models with various moisture content are displayed in Figure 2. The details of the model are also presented in Table 1. Five amorphous cellulose models were constructed for five moisture contents (*i.e.*, 0, 2, 4, 6, and 8%) to achieve the goal of changing the moisture content of the system by adjusting the number of water molecules. Cotton is a natural raw material with the highest amount of cellulose and is also essential for the textile industry and daily activities. In previous works, the range of moisture content was determined based on the metric moisture return of cotton under atmospheric conditions of less than 8.5%.[21]



(a) (b) (c)

(d) (e) (f)

Figure 1: (a) Repeating units (hydrogen atoms marked by blue circles are head atoms, hydrogen atoms marked by red circles are tail atoms, and C1-O4-C4 are connecting bonds of cellulose), (b-f) cellulose models with moisture content of 0, 2, 4, 6, and 8%, respectively

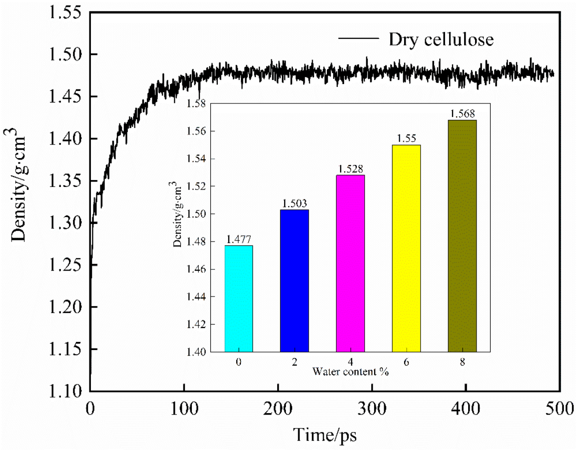


Figure 2: Density of different moisture content models after dynamic equilibrium

Table 1
Details on different moisture content models

Water content	0%	2%	4%	6%	8%
Number of water molecules	0	11	23	34	47
Total number of atoms	1266	1299	1335	1368	1407
Volume, Å^3	23.8^3	24^3	24.1^3	24.3^3	24.5^3

EXPERIMENTAL

Simulation process

The COMPASS force field is employed for the dynamic simulation process, and the mechanical properties of the cellulose system are described by this force field in the existing research.[23,24] The energy expression of the COMPASS force field is as follows:

$$U_{total} = E_b + E_\theta + E_\emptyset + E_\chi + E_{cross} + E_{vdw} + E_{elec}$$

$$= \sum_b [k_2(b-b_0)^2 + k_3(b-b_0)^3 + k_2(b-b_0)^4]$$

$$+ \sum_\theta [k_2(\theta-\theta_0)^2 + k_3(\theta-\theta_0)^3 + k_2(\theta-\theta_0)^4]$$

$$+ \sum_\emptyset [k_1(1-cos\emptyset) + k_2(1-cos2\emptyset) + k_3(1-cos3\emptyset)]$$

$$+ \sum_\chi k_2\chi^2 + \sum_b \sum_{b'} k(b-b_o)(b'-b_o') + \sum_b \sum_\theta k(b-b_o)(\theta-\theta_o')$$

$$+ \sum_b \sum_\phi k(b-b_o)(k_1cos\phi + k_2cos2\phi + k_3cos3\phi)$$

$$+ \sum_\theta \sum_\phi (\theta-\theta_o)(k_1cos\phi + k_2cos2\phi + k_3cos3\phi) + \sum_{\theta'} \sum_\theta k(b-b_o)(\theta-\theta_o'$$

$$+ \sum_{\theta'} \sum_\theta \sum_\phi k(\theta-\theta_o)(\theta'-\theta_o')cos\phi$$

$$+ \sum_i \sum_j \frac{q_iq_j}{r_{ij}} + \sum_i \sum_j \varepsilon_{ij}\left[2\left(\frac{r_{ij}^0}{r_{ij}}\right)^9 - 3\left(\frac{r_{ij}^0}{r_{ij}}\right)^6\right] \quad (1)$$

where E_{total} is the total energy of the system, E_b is the bond stretching energy, E_θ represents the bond angle bending energy, $E_\emptyset$ denotes the bond torsion energy, E_χ signifies the bending energy of the bond angle plane, E_{cross} is the mutual coupling energy between the four, E_{vdw} represents the van der Waals energy, and E_{elec} denotes the Coulomb force energy.

The details of the performed simulations are presented in Figure 3. The initially constructed amorphous cellulose model cannot be directly simulated by molecular dynamics because of its high internal energy. The first step in the simulation is to minimize the energy of the model. In the energy minimization process, the energy convergence accuracy is taken as 0.001 kcal/mol, and the number of iterations is set as 5000. After that, in order to further balance the model, the system is subjected to ten consecutive annealing equilibrations under the NVT ensemble at 300-800 K, each in 10 ps. After the annealing cycle, the configuration of the simulated system is gradually stabilized and the lowest energy configuration is considered the initial dynamic equilibrium configuration. In general, the dynamic equilibrium can be divided into two steps: the first step was to run 500 ps kinetic equilibrium, under the NVT ensemble and the second step was to run 500 ps molecular dynamic equilibrium under the NPT ensemble. The simulated temperature was set as 300 K for both stages. The time step of the entire kinetic simulation is 1 fs, and the atomic velocity and coordinate information are saved once every 1 ps for subsequent calculations and analyses. Andersen's method is employed for temperature control and Berendsen's method is used for pressure control. The pressure for the simulation process was set as 101.3 kPa. The Verlet method is utilized to solve the equations of motion. The atom-based method is utilized to evaluate the van der Waals force of the simulated system. Additionally, the Ewald method to calculate the electrostatic potential of the simulated system, and the initial velocity of each atom is appropriately evaluated according to the Boltzmann distribution. The densities of five model structures with various moisture content were calculated. In continuing, the effect of water content on the mechanical properties of cellulose is examined through the change of elastic modulus, mean square displacement (MSD) of cellulose chain, change of free volume, and number of hydrogen bonds.

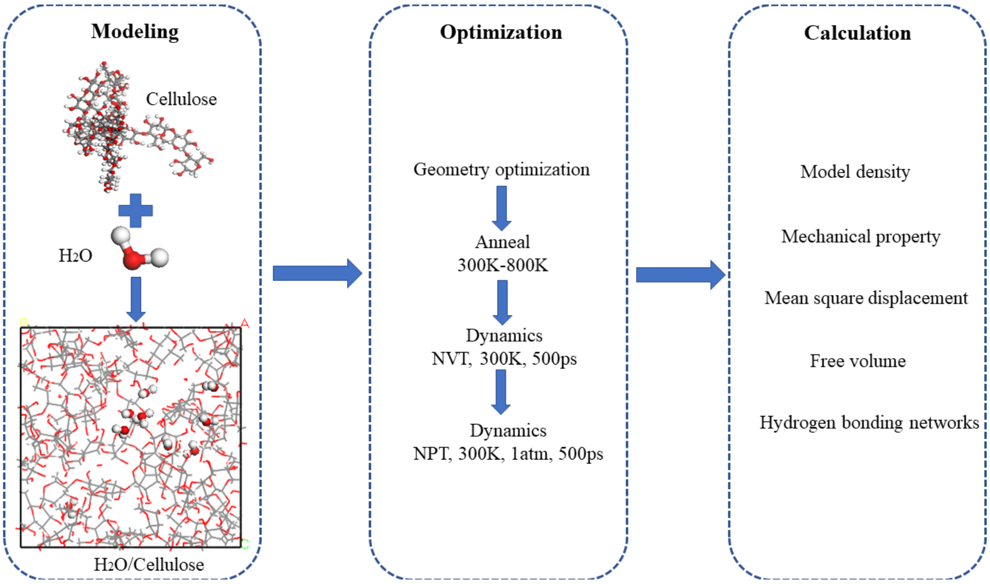


Figure 3: Simulation details

RESULTS AND DISCUSSION

Mechanical properties

The parameters elastic modulus (*E*) and shear modulus (*G*) were used to evaluate the influence of water on the mechanical properties of cellulose. Based on the elastic stiffness matrix (C_{ij}) and Equations (2)-(5), the parameters *E* and *G* are calculated. The elastic stiffness coefficient matrix (C_{ij}) was evaluated via the Mechanical Property module in MS software. The obtained results are illustrated in Figure 4.

$$\lambda = \frac{1}{6}C_{12} + C_{13} + C_{21} + C_{23} + C_{31} + C_{32} \approx \frac{1}{3}(C_{12} + C_{23} + C_{13}) \quad (2)$$

$$\mu = \frac{1}{3}(C_{44} + C_{55} + C_{66}) \quad (3)$$

where λ and μ represent the Lamé constants. These constants are related to the above-mentioned moduli as follows:

$$E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} \quad (4)$$

$$G = \mu \quad (5)$$

According to Figure 4, the elastic modulus and the shear modulus of pure amorphous cellulose are obtained as 10.58 GPa and 6.23 GPa. These results are almost consistent with the data calculated in the study by Chen *et al.*,[25] indicating that the force field selected for the simulation and the size of the constructed model is reasonable. Before proceeding with the calculation, it can be predicted that the formation of a certain number of micropores due to the presence of water molecules could induce cracks and voids in the cellulose chain, which affects the internal structure and properties of cellulose.[16] Figure 4 displays that the elastic modulus and shear modulus of the amorphous cellulose system first rise and then reduce with the increase in the number of water molecules. The mechanical properties of the amorphous cellulose system with moisture contents of 2% and 4% are somewhat increased. Especially for the amorphous cellulose system with 2% water content, the elastic modulus and shear modulus enlarged by 26.8% and 25.3%, respectively, compared to pure cellulose. As the number of water molecules in the system increased, the mechanical properties of the system began to deteriorate. At 8% moisture content, the elastic and shear moduli of the cellulose system in order are predicted to be 7.9 and 3.85 GPa, which are 33.9% and 38.2% lower than those of pure cellulose (*i.e.*, 10.58 and 6.23 GPa). Compared to the superlative mechanical properties of cellulose system with 2% moisture content (13.42 and 7.81 GPa), it decreased by 41.1% and 50.7%, respectively.

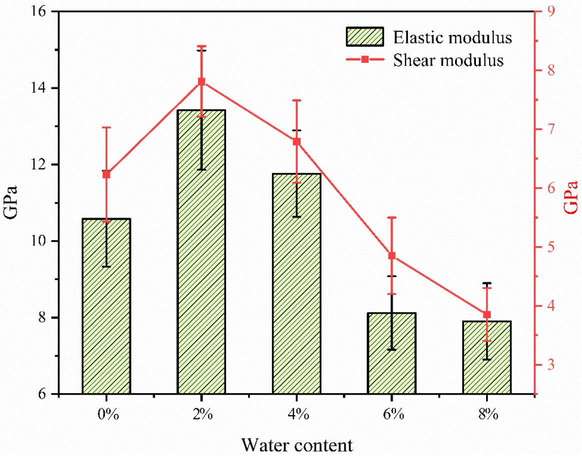


Figure 4: Mechanical property parameters of amorphous cellulose systems with different moisture contents

Stiffness of cellulose chains

The stiffness of cellulose chains has a direct impact on the mechanical performance of cellulose systems. The MSD and diffusion coefficient of the cellulose chain are able to reflect the stiffness of the cellulose chain to some extent, and the calculation formulas for these parameters are as follows:

$$\mathrm{MSD} = R(t) = \langle |r(t) - r(0)|^2 \rangle \tag{6}$$

$$D = \lim_{t\to\infty} \langle \frac{|r(t)-r(0)|^2}{6t} \rangle \tag{7}$$

where *r(0)* represents the initial positions of the particles, *r(t)* signifies the final positions of the particles, and the bracket < > indicates the average of all particles in the system.

The obtained results are presented in Figure 5 and Table 2. During the process of increasing the moisture content from 0% to 4%, the MSD value of the simulated cellulose chain decreases, the diffusion coefficient decreases, the rigidity of the cellulose chain increases, and the corresponding mechanical properties of the system are generally enhanced. The diffusion coefficient of cellulose chains in systems with 2% and 4% moisture content reduced by 33.3% and 29.8%, respectively, compared to 0% moisture content. However, it was observed that there would exist only a correlation between the increase in mechanical properties and the decrease in diffusion coefficient, without a precise corresponding ratio. As can be seen from Table 2, the diffusion coefficient of the cellulose chain in the 6% moisture content system is greater than that of the dry cellulose system, which reveals that the stiffness of the cellulose chain in the system is high. However, it can be seen from Figure 3 that the mechanical properties of the system with 6% moisture content are somewhat reduced compared to dry cellulose, indicating that the mechanical properties of cellulose are not only affected by the stiffness of the cellulose chains, but also related to the voids and cracks formed by micropores due to the presence of water molecules.

Free volume

To further investigate the reasons for changes in the mobility of cellulose chains in the system, the hard ball probe methodology was utilized to evaluate the free volume of cellulose systems in the presence of various moisture contents.[26] Water molecules are adopted as a probe with a van der Waals radius of 1.45 Å. Using the Atom Volume and Surface Module in MS software, the lattice radius is chosen as 1.45 Å, and the free volume diagram has been illustrated in Figure 6. To make the results of calculations more intuitive, the process of changes of both occupied volume and free volume in the system subjected to different moisture contents is presented in Figure 7.

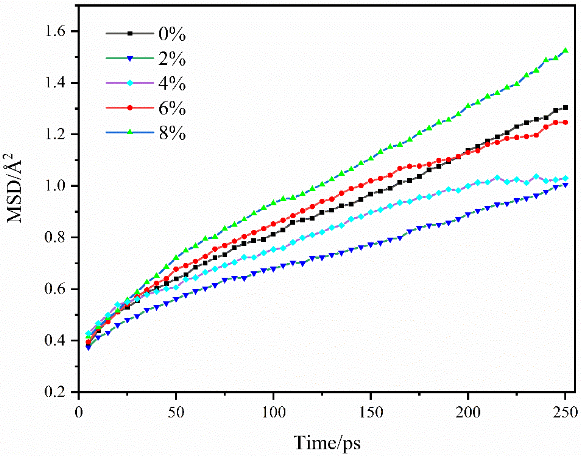


Figure 5: MSD of cellulose chains in models with different moisture contents

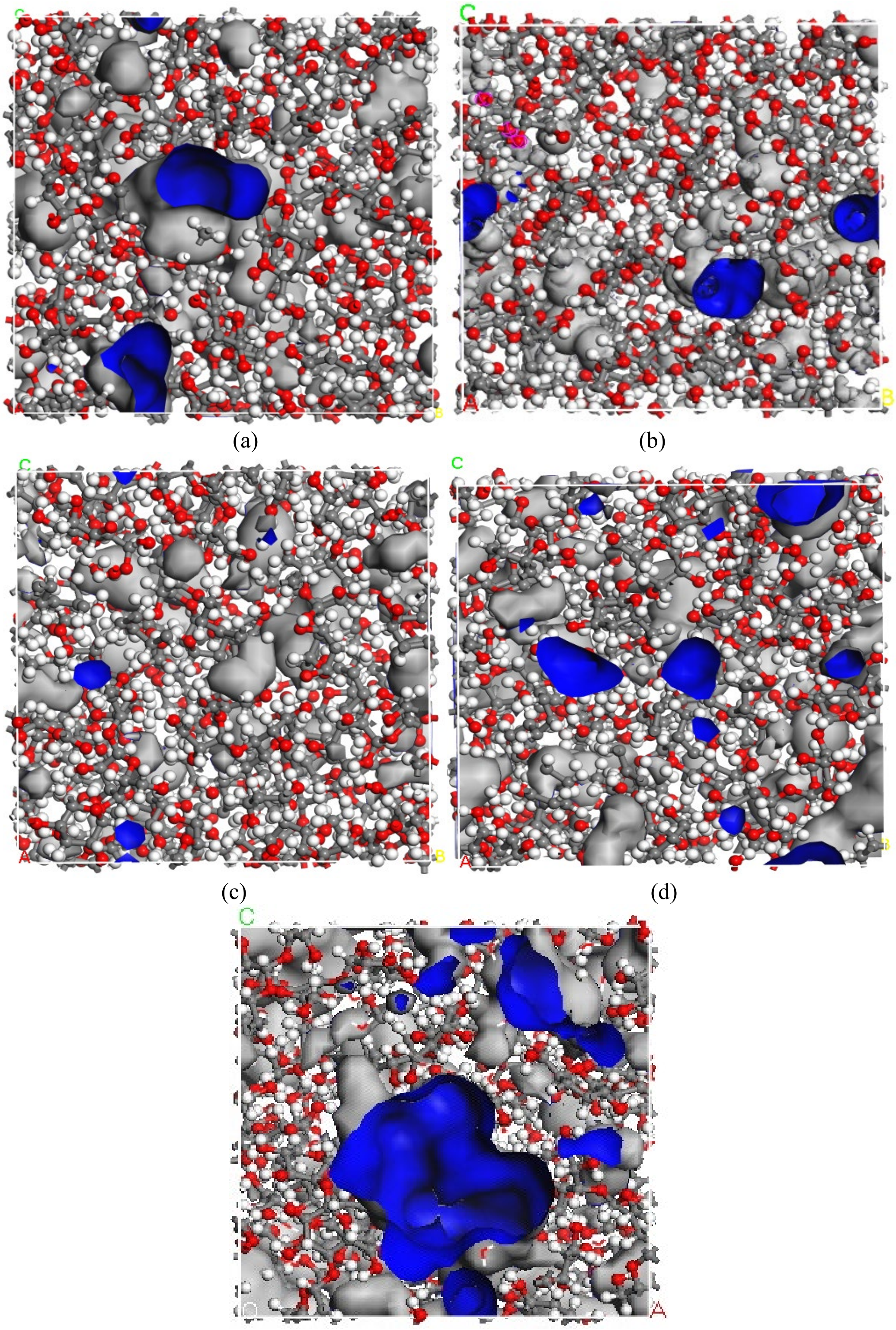
Table 2
Diffusion coefficients of cellulose chains in models with different moisture contents

Moisture content	0%	2%	4%	6%	8%
Diffusion coefficient, 10^{-11}m^2/s	0.57	0.38	0.4	0.53	0.7

According to the Free Volume Theory presented by Flory and Fox,[27] the volume of a liquid or solid material consists of two parts, one is the volume occupied by its own molecules, which is called the occupied volume, and the other is the unoccupied volume, which is called the free volume. The free volume is scattered as "holes" formed in the entire material. The free volume can be regarded as the active space of the molecular chain, the larger the free volume, the greater the possibility of molecular chain movement. When the free volume in the system is gradually reduced to a certain extent, the motion of the chain is frozen. In Figure 6, the gray part represents the surface of the free volume, and the interior of the surface is the free volume. Considering that the simulation box is a periodic boundary, the gray part is not necessarily closed and the open part is blue. It can be seen from Figure 7 that, with the increase of water molecules, the total number of atoms in the system continues to increase, and as a result, the occupied volume of the system increases, but the free volume does not exhibit a continuous upward or downward trend. Within the studied moisture content range, the minimum free volume of the system is 697.79 Å^3 at 2% moisture content, which is 52.76% less than the 1476.97 Å^3 at 0% moisture content. As explained in the Free Volume Theory, with the reduction of free volume, the active space of the molecular chain segments decreases, the possibility of molecular chain movement decreases, the diffusion coefficient of the cellulose chain decreases, and the relative stiffness increases. The system exhibits excellent mechanical properties.

Hydrogen bond

Hydrogen bonds are generally understood as a weak Coulomb interaction between a highly electronegative atom and another hydrogen atom that has formed a covalent bond with a highly electronegative atom. Although hydrogen bonds are a weak interaction, they play a crucial role in expressing the mechanical properties of cellulosic materials.[28] In this simulation, the geometric definition of the hydrogen bond is: the distance r_{AH} between the hydrogen atom and the acceptor (A) is small 2 Å; the angle (θ) formed by the donor (B), the hydrogen atom and the acceptor is greater than 110° (Fig. 8). This hydrogen bond parameter is the same as the setting condition of hydrogen bonds in cellulose, which was determined by Nishiyama's experiment.[29] The secondary hydroxyl group exposed to the cellulose chain exhibits a strong attraction to water, and water molecules could easily configure hydrogen bonds with it.[5] Therefore, the original hydrogen bond network of the cellulose chain is destroyed, which leads to the degradation of the performance of cellulose materials during use.



(a) (b) (c) (d) (e)

Figure 6: Schematic diagram of free volume at different moisture contents: (a) 0%, (b) 2%, (c) 4%, (d) 6%, and (e) 8%

The number of hydrogen bonds was counted in various moisture content systems, and the achieved results are provided in Table 2. At 0% moisture content, the number of hydrogen bonds in the cellulose system is approximately 209. With the growth of water molecules, the number of hydrogen bonds in cellulose first increases and then decreases. Especially in the amorphous cellulose system with 8% moisture content, the number of hydrogen bonds is only 186, which is 11% less than the dry cellulose model. The water molecules adsorbed on the cellulose chain destroyed the initial hydrogen bond network structure of the cellulose chain through the action of hydrogen bonding, and the number of hydrogen bonds decreased, and thereby, the mechanical properties of the system deteriorated.

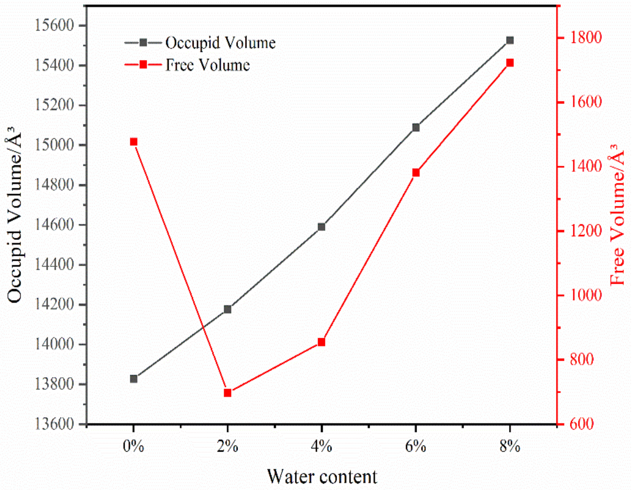


Figure 7: Occupied volume and free volume of cellulose amorphous systems with different moisture content

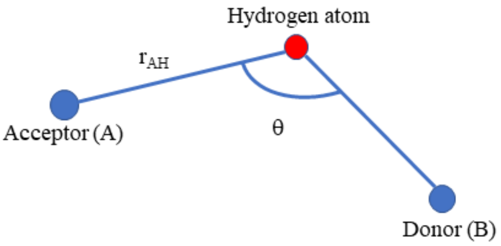


Figure 8: Adopted geometrical definition of hydrogen bond in the thesis

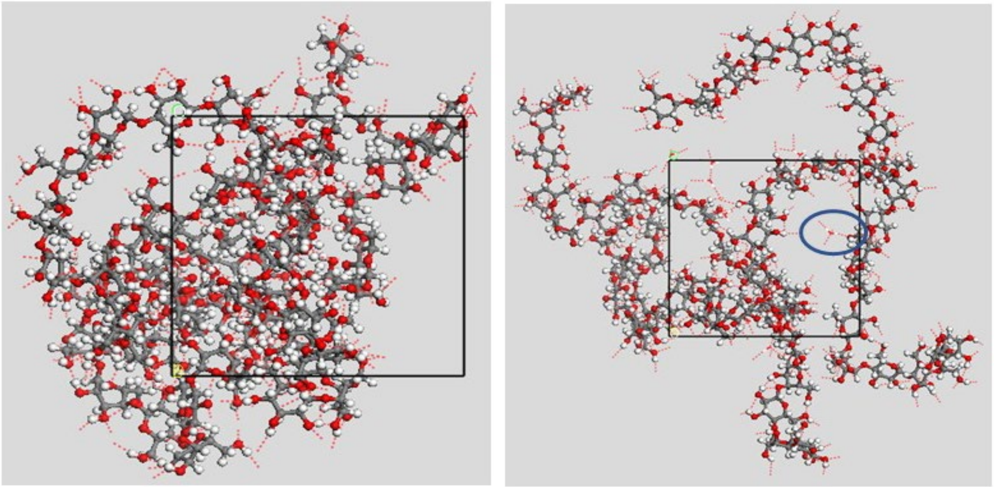


Figure 9: Hydrogen bond network in amorphous cellulose systems with different moisture content (the red dotted line indicates hydrogen bonding, and the hydrogen bond in the blue circle represents the hydrogen bond formed by water molecules and cellulose chain)

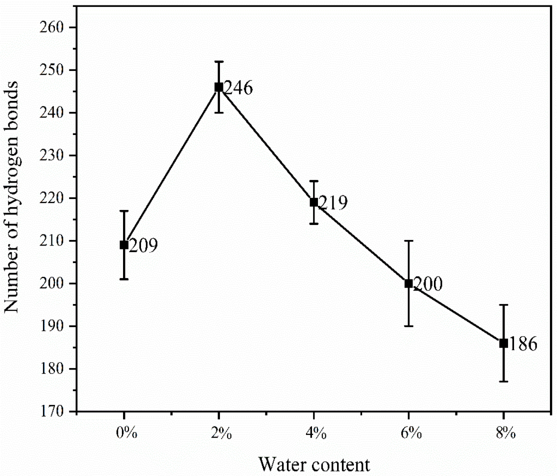


Figure 10: Number of hydrogen bonds in amorphous cellulose systems with different moisture contents

CONCLUSION

The molecular dynamics approach was effectively employed to investigate the effect of moisture content on the amorphous cellulose system. The mechanical properties of the system, the mobility of the cellulose chain, the free volume, and the number of hydrogen bonds were calculated. The results described below were obtained.

(1) The mechanical properties of amorphous cellulose systems in the presence of various moisture contents were calculated. When the moisture content was in the range of 0 and 4%, the presence of water exhibited a positive effect on the mechanical properties of cellulose. In the present investigation, the elastic modulus and shear modulus of the 2% moisture content system took their highest levels, which were 26.8% and 25.3% higher than those for dry cellulose. The mechanical properties were mostly influenced by the stiffness of cellulose chains and the coupling effect of cracks and voids caused by the presence of water molecules in the system.

(2) In the studied moisture content range, the free volume of the system first decreases and then increases with the growth of the number of water molecules. At 2% moisture content, the free volume of the system took its smallest value, which was 778.21 Å^3 less than the 1476.97 Å^3 of dry cellulose. The free volume represents the active space of the cellulose chain, and the reduction of the free volume partially enhanced the stiffness of the cellulose chain.

(3) The number of hydrogen bonds in the system subjected to various moisture contents was calculated during the simulation process. The achieved results revealed that in the amorphous cellulose system with 2% moisture content, there were not only the original hydrogen bonds, but also the hydrogen bonds formed by water molecules and hydroxyl groups on the cellulose chain. Increasing the number of hydrogen bonds led to the enhancement of the system's ability to withstand external loads, exhibiting exceptional mechanical properties.

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