

Molecular Dynamics Study on the Structure Behavior of Cellulose II^{*}

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Abstract

The conformational changes of hydroxyl groups affect the structure behavior directly, it is important to study the structure properties of cellulose II. In order to explore them, the molecular structure was investigated by using the molecular dynamics simulation at different temperature. The results indicate that the initial model and the force field are reasonable. With the temperature raising, the standard deviations of the glycosidic torsion angle ϕ of center and origin chains increase 56.56% and 38.63% respectively. Likewise, the standard deviations of torsional angle ψ of the center chains and origin chains increase 32.89% and 34.91% respectively. The increase of standard deviations of these torsional angles promote the flexibility of the hydroxyl groups and further correspond to the reduction of the hydrogen bond probability. The distance and probability of intersheet hydrogen bond O2c-Hc...O6c' are the shortest and largest respectively at different temperature. This is related to only one peak of the dihedral angle τ_2 in the center chain, even if the peak decreases with temperature increasing. The large fluctuation of the intrachain hydrogen bond O3-H...O5 in probability and distance is directly related to the glycosidic torsion angle ϕ rather than the dihedral angle τ_3 . However, the intersheet hydrogen bond O6c-Hc...O6o' is very unstable and corresponds to the minimum steric hindrance for dihedral angle τ_6 . According to the probability, distance and angle of different hydrogen bond types, the intrasheet hydrogen bond of cellulose II crystal is more stable than that intersheet and intrachain hydrogen bonds at different temperature.

Keywords: Torsional Angle; Structure Behavior; Cellulose II; Hydrogen Bond; Molecular Dynamics Simulation

1 Introduction

Cellulose has been discovered and named by French botanist Anselme Payen [1]. It is an important renewable material. In 1891, It has been reported by Bevan and Beadle that cellulose II can be decomposed and precipitated by acid after alkali treatment. The chemical formula of cellulose

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I and II is the same, but the crystal structure of them is different [2]. The structure of cellulose II consists of two anti-parallel chains which are defined as origin and center. Nagarajan et al. suggested that cellulose II has a higher yield of fermentable sugar and ethanol than cellulose I. This is because of its lattice arrangement, porous volume and degree of polymerization [3]. The hydrogen bond (HB) plays an important role in thermal stability of cellulose II. Different kinds of HBs correspond to the conformational behavior of hydroxyl groups. This makes it necessary to study structural characteristics of cellulose II. Even though the hydrogen-bonding model of cellulose II has been obtained by neutron diffraction and x-ray analysis, the more detail structure of hydroxyl groups and related thermal properties at atom level are limited by conventional experiment methods [4, 5]. Molecular dynamics (MD) simulation has been identified as an effective technology to observe the microscopic detail of the crystal, such as hydroxyl groups behavior.

Yamane et al. has investigated the possibility of a folded structure with anti-parallel chains in the cellulose II polymorph [6]. The COMPASS force field (Accelrys Software Inc.) has been used in their work. They have compared the structure characters to study the boat and skew boat ring of glucose residues. They also showed that the main intra-chain HB was O3...O5 in cellulose II when the A-H distance of HB is less than 2.8 Å and the D-H-A angle is more than 110°. However, they did not analyze the relationship between the dihedral angles and intra-chain HB O3...O5 further. In this paper, the force field, the criteria of HB definition and the simulated time are different. We focus on the changes of structure behavior when the temperature rises. Miyamoto et al. have built two kinds of molecular sheet models for the cellulose II. These models have been performed molecular dynamics simulations by using the same method as Yamane's. Their results indicated that φ and the *gauche-gauche* conformation of two models are different [7]. They have done another molecular dynamics simulation by Gromacs 4.5.5 with the CHARMM 35 force field. The model of cellulose II was finite-crystal and consists of 36 chains. The degree of polymerization was 10 and TIP3P water models was adopted [8]. However, the simulation only run for 10 ns at high temperature. Their results revealed that the reasons for the formation of crystal structure is that the glucopyranose rings are stacked with each other by a hydrophobic interaction. In our work, we used the same finite-crystal. Amber software was used to perform molecular dynamics simulation with GLYCAM06h force field. The simulation time was extended to 100 ns. The hydrogen-bonding model of cellulose II was analyzed from different perspectives. The main analysis was that the HO2 and HO6 hydroxyl groups and the torsional angles [9]. Kroon et al. compared the HBs networks of cellulose I with cellulose II by MD simulations with GROMOS force field [10]. Much work shows that cellulose II has a 3D HBs network and the transition of hydroxyl groups is easier. However, the simulation is at 300 K [11, 12].

In our previous work, the cellulose II model has been constructed and the HBs have been analyzed at 300 K [13, 14]. In this paper, we focused on the change of glycoside angles and the behavior of hydroxyl groups and hydrogen bonds at 300-500 K. Moreover, the type, angle and probability of HBs were considered. This work also provides information regarding the behavior structure in the cellulose II crystal model.

2 Methods

The MD simulation is based on Newton's law of atom motion to make statistical analysis, then to discuss the properties of the system [15]. In this paper, the structure behavior of cellulose II was analysed by the trajectories of the MD simulation. The initial model of cellulose II was constituted