Revealing the Weak Interaction Mechanism of Crystalline Cellulose Iα by Molecular Dynamics Simulations[⋆]

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Abstract

According to our previous works on cellulose Iβ and Iα, the weak interactions, though easily ignored, play certain role in the stability mechanism of nature cellulose. These weak interactions should never be ignored or underestimated. In this work, a molecular dynamics study of cellulose Iα was reported to evaluate the weak interactions under various temperatures. The polar and non-polar solvation interactions and hydrogen bonding were taken into account. The Van der Waals, electrostatic, polar solvation and non-polar solvation energy per chain were estimated up to -131.68, -56.38, 29.16 and -41.76 Kcal/mol at room temperature. The weak interactions behaviors of cellulose Iα, including that of the cellulose Iβ and Iα reported previously, were compared. The results indicate that hydrogen bonding contribute obviously for the intrachain stability. The interchain electrostatic interaction maintain a reasonable level under 300 K but decreases rapidly with the ascending of temperature. The polar and non-polar solvation interaction plays an important role not only to interchain under high temperature but also to the intersheet stability. In addition, the hydrogen bonding in intersheet is weaker than that of intrachain and interchain. The result is same as cellulose Iβ that relatively weak hydrogen bonding and strong nonbonded interactions keep the intersheet stability collaboratively.

Keywords: Weak Interaction; Cellulose Iα; Molecular Dynamics; Hydrogen Bonding

1   Introduction

Serving as reinforcement of wood, glass, cotton, and ramie and so on, cellulose is widely recognized as a sustainable source for every trade [1, 2]. Cellulose is a linear polysaccharide, and always forms with high crystallinity ranging from 1 000 to 10 000 [3]. Because of its abundance and

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sustainability, cellulose has been under investigation since early years of polymer science [4-9]. Natural cellulose occurs as two different crystal phases, Iα and Iβ [4, 10]. Cellulose Iα is predominant in bacterial, algae, and fungi, whereas higher plants have a bigger percentage of cellulose Iβ [11]. According to the CP/MAS NMR spectra recording, the proportion of cellulose Iα was estimated to be 60-70 percent for Acetobater cellulose, 65 for valonia cellulose, and 60-70 percent Iβ within cotton fibres [4, 12]. Since then, a considerable part of cellulose research was devoted to decipher the atomic structure of the dimers. Roman and infrared spectroscopy was employed to uncover the meticulous details of a cellulose structure and it was discovered that cellulose Iα was less thermally stable than Iβ [3, 13, 14]. Nishiyama et laid down the basement of more accurate assessment of potential structure, and accurate positions of all atoms and hydrogen-bonding network were revealed with Synchrotron X-ray and electron diffraction methodology [15, 16]. The fine structure of native crystalline has important implications for understanding of physical properties within many other cellulose-based materials.

For the existence of the dimorphism, the thorough understanding of native cellulose requires the determination of both two, not only one. Therefore, the study of cellulose Iα is a favorable supplement of native cellulose. Various improved models were proposed to elucidate the hydrogen binding networks and molecular arrangement [3,17], and Nishiyama et proposed the re-orientation including the cell parameters and dihedrals of cellulose Iα [16]. According to the electron microscopy research, Cellulose Iα has a triclinic structure with one cellobiose in each unit cell of P1 symmetry, where a=6.717 Å, b=5.962 Å, c=10.4 Å (chain direction), $\alpha = 118.08°$, $\beta = 114.8°$, $\gamma = 80.37$, while cellulose Iβ crystallizes with a two-chains monoclinic unit of P2$_1$ symmetry [15,16]. Constituted by stacking cellulose sheets, cellulose Iα has linear chains along the c direction and the repeat unit has different glucose monomers. Hydrogen bonding bindings are widely perceived as the major reason for the stable structure of native cellulose. The most frequently occupied hydrogen bonds are intrachain O2HO2$\cdots$O6', O3HO3$\cdots$O5' and interchain O6HO6$\cdots$O3'. All of those are identified as the primary effect factors to keep chains rigid by Heiner et [18]. The hydrogen bonding interaction has been estimated that between 4.06 and 7.17 Kcal/mol [16]. Hydrogen bonding is experimentally most demonstrative, but insufficient to elucidate solvent resistance [19]. It is essential to reveal the intricate interplay of the relevant molecular interactions.

There is not much work focused on the weak interactions in cellulose before. French evaluated the energies of cellulose I with the MM3 force field, and found that the lattice energies is the major difference between celluloce I, while the lattice energies are mostly consituted with Van der Waals interaction [20]. The models they used were not based on high resolution experimental results. Heiner attributes the stability of cellulose I to intermolecular Coulomb interactions [18]. Our previous work shows that electrostatic interaction also play a certain role in cellulose Iα and Iβ [21,22]. The nonbonded interactions polar solvation and non-polar solvation should also be taken into account to acquire more comprehensive knowledge of the interaction network in native cellulose. The GLAYCAM 06 force field has been shown to be reasonably reliable in the prediction of structures and energies of saccharide [21,23]. GLYCAM 06 force field is a universal force field for biological macromolecules designed and developed by KIRSCHNER et al [24]. GLYCAM06 force field uses hydroxyl van der Waals parameter compatible with Amber, and fits the electrostatic potential energy calculated by quantum mechanics, so the GLYCAM 06 force field can express the interaction better between molecules. Considering the relationship between partial charge and molecular conformation, GLYCAM06 can reduce the influence of intersheet hydrogen bonding on cell parameter, then more reasonable cell parameters can be accuqed with