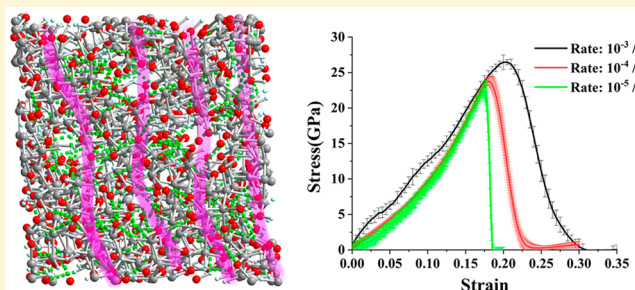


Crystalline Cellulose under Pyrolysis Conditions: The Structure–Property Evolution via Reactive Molecular Dynamics Simulations

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Supporting Information

ABSTRACT: As a primary component of cell walls of plants, algae, bacteria, and other natural biomaterials, cellulose has attracted research attention and is the key to effective conversion of natural biomaterial into processable advanced functional materials. From the chemistry point of view, a typical crystalline cellulose is composed of linear chains of hundreds of β -1,4-linker glucose units. Therefore, inter and intra hydrogen bonding interactions play a decisive role of the structure–property relationship of cellulose based materials. Despite research progress from past decades, the fundamental mechanism of how cellulose structure transforms under pyrolysis conditions and the practical guideline of how cellulose properties are finely tuned accordingly are still incomplete. In this work, a series of reactive molecular dynamics calculations has been designed to reveal the structural evolution of crystalline cellulose under pyrolysis treatments. Through the detailed analysis of cellulose configuration change, hydrogen bonding network variation, reaction and redistribution of carbon, oxygen and hydrogen elements, and Young's modulus, a molecule level insight of crystalline cellulose and its structural evolution under pyrolysis conditions has been constructed via reactive molecular dynamics simulations. We anticipate those theoretical results could effectively promote the design, the manufacture, and the optimization of cellulose based materials for relevant emerging applications.



1. INTRODUCTION

Cellulose exists in algae, bacteria, and other natural biomaterials as a basic building block. It is also a primary component of cell walls of green plants, along with hemicellulose and lignin. Cellulose based materials have been widely used in many applications, for example, biofuel productions,^{1,2} paper manufacturing,^{3,4} construction industry,^{5–7} energy related fields,^{8–11} drug delivery,^{12–17} and biomedical therapy,^{18–20} to just name a few. The unique properties of nontoxicity, good biocompatibility, high biodegradability, high water adsorption, and great mechanical properties make cellulose one of the most promising candidates to address the increasing challenges in environmental, ecological, and energy fields.

Chemically, cellulose is a polysaccharide that consists of a linear chain of thousands of repeating D-glucose units, which are interlinked with β -1,4-linkages. Hydroxyl groups of cellulose chains and the inter/intra hydrogen bonding (HB) networks are dominating structural factors to cellulose properties. The utilization of cellulose based materials largely depends on the effective manipulation of cellulose HB networks. Accordingly, various treatments have been proposed to process raw cellulose materials, which could be classified as the following categories: (1) mechanical treatments such as milling,^{21,22} grinding/refining,^{23–25} high-pressure homogenizers,^{26–29} cryocrushing,^{27,30,31} and high intensity ultrasonic

treatments;^{32–34} (2) hydrolysis treatments^{35–56} via the application of dilute acid, concentrated acid, enzyme, or autohydrolysis; (3) pyrolysis treatments^{57–61} through the steam, hydrothermolysis, or wet oxidation; (4) chemical treatments^{32,42,62–69} from oxidizing agents, alkali, acid, and organic solvents; (5) electrical, biological, and other treatments.^{70–79}

Most recently, producing cellulose based advanced materials via subtle treatment strategies has been brought to a new horizon. Exciting progresses include the milestone work of Hu⁶² and co-workers where they processed natural wood chemically to remove lignin, followed by a mechanical compressing to fine-tune the remaining cellulose structures into crumple and interlock. The transformed wood, mostly composed of structurally manipulated cellulose, is mechanically more than 10 times stronger than steel.⁶² Selectively removing hemicellulose and lignin has witnessed other promising progresses, including compressible carbon sponges and high surface area activated carbon for chemical and biosensor development and water/oil separations.^{63,80–83} Making use of

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the inherent structural and chemical properties is key to producing cellulose based advanced materials and maximizing their performance. It is worth noting that available results seem to suggest that having a proper amount of lignin is beneficial. The hypothesis is that the leftover lignin helps to bind cellulose fibers when further processed.

On the other hand, despite the importance and recent promising progress of the field, the theoretical understanding of cellulose based materials and their fundamental structure–property relationship are still far from complete. There is a pressing need to develop molecule level understandings of cellulose based materials and how their structure and property evolve under various treatments. To date, the majority of theoretical research efforts are from *ab initio* density functional theory (DFT) and classical force field based molecular dynamics (MD) simulations of crystalline cellulose structures and corresponding electronic properties.^{84–89} The breakdown of cellulose under solution (such as water, acid, or ionic liquid environments) or pyrolysis conditions has also been studied computationally. For example, classical MD simulations were used to simulate the surface of cellulose I β and its interactions with water.⁹⁰ Matthews and co-workers used molecular mechanics (MM) simulations to study the crystalline cellulose configuration changes with surrounding water.⁹¹ They found that the cellulose unit was expanded and twisted and that the formation of an adjacent water layer on the cellulose surface might delay the transitions of enzymes and further result in a slower hydrolysis rate in the enzyme-catalyzed hydrolysis approach.⁹¹ They also found⁹² that the twisting between cellulose chains results in the formation of a 3D hydrogen bond network inside hydrate cellulose I β microfibrils under high temperature (~ 500 K). *Ab initio* and MD simulations have also been used to understand the dissolution mechanism of cellulose in aqueous solutions. Janesko et al.⁹³ applied DFT calculations to study the interaction between cellulose and charged ions in ionic liquids (ILs). Payal and co-workers⁹⁴ carried out *ab initio* molecular dynamics (AIMD) simulations to study the dissolution of cellulose I β monomers in ILs. They found that the breaking of the hydrogen bond network was the key factor for cellulose dissolution. Similarly, Liu et al.⁹⁵ found in their MD simulations that the strong hydrogen bonding between anion and cellobiose could significantly impact cellulose dissolution. Moreover, other researchers^{96–98} have also reported that the changes of interchain and intrachain hydrogen bond network lead to cellulose dissolution in ILs.

When it comes to pyrolysis treatments, Bergenstr hle et al.⁹⁹ reported via classical MD simulations that cellulose I β crystal changed its structure when the temperature was above 450 K. Assary et al.¹⁰⁰ and Mayes et al.¹⁰¹ performed DFT calculations to study the fast pyrolysis of cellulose. They both observed cellobiose depolymerization, epoxide formation, and the production of levoglucosan (LGA). Agarwal et al.¹⁰² performed both AIMD and Car–Parrinello molecular dynamics (CPMD) simulations to study cellulose decomposition pathways. They found that the cellulose decomposition to liquid intermediates started around 260 °C and LGA was produced from the fast pyrolysis between 400 and 600 °C, agreeing well with the results of Assary and Mayes. The authors also used classical MD to simulate the IR of cellulose I β crystal at 300–500 K.¹⁰³ The IR agreed with that of experiments, and high temperatures can weaken cellulose intrachain hydrogen bonds, eventually leading to the formation of a 3-D hydrogen bonding network.

In recent years, reactive force field (ReaxFF) based MD simulation (RxMD) has gained more and more attention from the cellulose research community. It is mainly due to the advantages that electronic/reaction details and large time/space scale computations can be achieved simultaneously in RxMD simulations. A number of RxMD simulations have been reported for cellulose, hemicellulose, lignin, and their mixtures. For example, Beste and co-workers¹⁰⁴ reported a RxMD study of the conversion of lignin at various temperatures, and they found that the 5–5 linkage was the weakest linker during the cyclization and dehydrogenation. Zheng and co-workers¹⁰⁵ studied the pyrolysis process of amorphous cellulose at temperatures from 500 to 1400 K. The reported pyrolysis products agree well with available experiments, which also confirms that the applied ReaxFF force field provides an accurate description of cellulose pyrolysis processes. Meanwhile, Paajanen et al.¹⁰⁶ studied the amorphous cellulose decomposition from 1400 to 2000 K. They observed that the breaking of 1–4- β bonds eventually leads to the cellulose decomposition and that the decomposition products are mainly glycolaldehyde, water, formaldehyde, and formic acid, which agreed with experimental results.

In this work, a series of RxMD simulations have been performed to reveal the structural evolution of crystalline cellulose I β via pyrolysis treatments under isolated conditions. By varying the pyrolysis temperature, the change of cellulose crystallinity, the variation of inter/intra HB networks, and the reaction and distribution of C, O, and H elements have been recorded and analyzed. In addition, the pyrolysis treated cellulose and its mechanical properties were also discussed in terms of Young's modulus and the yield tensile stress. Despite that the pyrolysis process was modeled under isolated conditions, that is, no contribution was considered from oxygen and water of the air, this work demonstrates a general computational protocol to study cellulose systems under reactive conditions. Furthermore, the constructed structure–property relationship could shed light on how to select pyrolysis conditions and achieve desirable structural, chemical, and mechanical properties of engineered cellulose based materials. This Article is organized as following: Section 2 presents a brief introduction to the ReaxFF reactive force field, a simulation protocol, and a list of computational characterizations. Section 3 contains the calculation results and discussion of structural evolution of crystalline cellulose I β as a function of time, the characterizations of inter/intra HB networks, and the mechanical properties of processed cellulose. Conclusions are finally provided in section 4.

2. MODEL AND SIMULATION DETAILS

2.1. Crystalline Cellulose. The initial cellulose I β crystal was generated by the cellulose builder from Gomes and co-workers,^{107,108} with the lattice parameters¹⁰⁸ of 7.784 Å, 8.201 Å, 10.380 Å, 90°, 90°, and 96.550° from experimental XRD and neutron fiber diffraction results at 293 K. In our RxMD simulations, a 2 $\times$ 2 $\times$ 6 supercell was constructed which produces a triclinic simulation box of 15.568 $\times$ 16.402 $\times$ 62.280 Å³. In this work, benchmark calculations on larger systems have been performed at the initial stage of this research. Quantitatively similar results were obtained about properties such as the hydrogen bonding network and the Young's modulus. Also, we followed the choice of simulation box size and used a similar total number of atoms in the cellulose model.^{105,106,109,110} Figure 1a shows characteristic

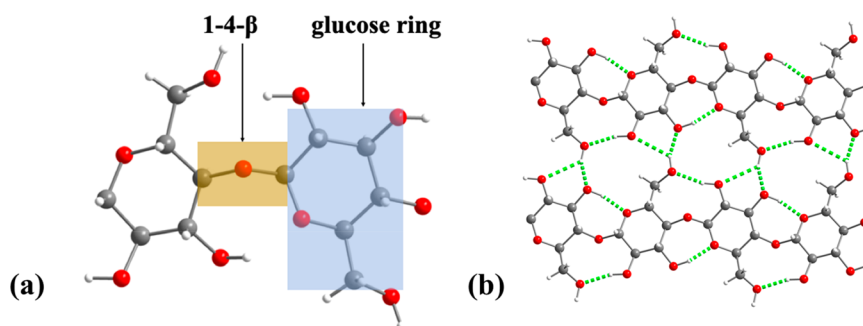


Figure 1. Initial configurations of the $I\beta$ crystalline cellulose: (a) two characteristic covalent bonds in a single cellulose chain; (b) the hydrogen bonding network from two parallel cellulose chains.

covalent bonds of crystalline cellulose, namely, the bonds of the glucose unit that hold the ring structure and the 1–4- β bonds that connect glucose units. It is expected that, at elevated temperatures, either the glucose ring structure or the 1–4- β bond would break down. Besides covalent bonds, the HB networking is also critical to cellulose properties. As shown in Figure 1b, hydrogen bonds (green dashed lines) come from both inter and intra cellulose chains. As the temperature increases, the crystallinity of the cellulose structure decreases, consequently producing a change of the inter and intra HB networks, which significantly affects the mechanical properties of the pyrolysis treated cellulose.

2.2. ReaxFF Reactive Force Field and RxMD Simulation. Proposed by van Duin and co-workers in 2001, the ReaxFF reactive force field has been actively developed to describe complex and large-scale reactive systems, which could contain hundreds to several thousands of atoms.¹¹¹ So far, ReaxFF has been applied to describe complex systems such as protein/DNA,^{112,113} membrane fuel cell systems,¹¹⁴ and very complicated coal structure and properties.¹¹⁵ ReaxFF has become a choice for multiscale modeling of systems with adsorption, dissociation, and complicated reactions.^{116–118} Unlike traditional definitions of bonds, angles, and dihedrals of classical force fields, a concept of bond order^{119–123} has been developed in ReaxFF to calculate atomic connections and system energies in order to describe the continuous bond formation and breaking and mimic the reaction pathway in the systems.¹¹¹ These advantages make ReaxFF a useful tool in predicting structural evolution, tracing intermediates, and analyzing final products.^{124,125} Recently, ReaxFF has been successfully used for the study of the mechanism of the pyrolysis process of cellulose, hemicellulose, lignin, and their derivatives.^{104–106,109,126,127} Generally speaking, ReaxFF is 1 order slower than the nonreactive force fields; the most expensive calculations part of ReaxFF have been the charge calculations that come from the electronegativity equalization method (EEM) by Mortier and co-workers.^{128–130} However, with the help of parallel calculations, a time scale of microseconds trajectory could be archived.¹¹⁷ More details of ReaxFF are available from recent reviews.^{131–133} The ReaxFF parameters used in this work have successfully described cellulose systems.^{106,109}

All RxMD simulations were performed by the LAMMPS package. The isothermal–isobaric (NPT) ensemble was applied where the pressure was maintained at 1 atm. The temperature was controlled via the temperature-programmed protocol, changing from 300 K slowly to targeted final temperatures (500, 800, 1000, 1100, 1200, and 1300 K).

The Berendsen method with a temperature damping coefficient of 100 fs was applied to maintain the system temperature. Initial velocity was assigned according to the Boltzmann distribution. A time step of 0.25 fs was adopted in all calculations. Each of the RxMD simulations in this work has a trajectory of at least 10 ns. For the cellulose decomposition distribution analysis, longer simulations have been performed for 60 ns for 1200 and 1300 K. For the Young's modulus analysis, after the 10 ns trajectory, an additional calculation of 1 ns was carried out to collect the data at a smaller time step (0.05 fs). Other calculations were performed at a time step of 0.25 fs. It is worth noting that identifying the true equilibrium state is always important and challenging for molecule simulations. Technically, the equilibrium state is justified via various analyses such as the total energy of the system, the root-mean-square deviation of atomic positions, diffusion coefficients, etc. Zheng and co-workers¹⁰⁵ have summarized that cellulose is thermally stable in the temperature ranges of 673–1073 K (experimentally) and 500–1400 K (computationally). The wide temperature range is mainly due to different cellulose resources and the treatment conditions (isolated, vacuum, with a mixture of gases or liquids). Our work shows that cellulose is generally stable up to 1000 K, which qualitatively agrees with other computational studies. In addition, we have tested the calculations for different time scales, from 25 ns up to 100 ns. No qualitative difference was observed. However, it is worth noting that the choice of simulation time depends critically on the property of interest; for example, to gain cellulose dissociation kinetics, longer calculations are recommended.

2.3. Monitored Properties from RxMD Simulation.

2.3.a. Hydrogen Bonding Network. The HB networking has been widely used to describe structural changes of crystalline cellulose $I\beta$ and is considered as a packing indicator when linear cellulose chains roll into highly ordered structures.^{108,134–138} In this work, the HB criteria proposed by Nishiyama and co-workers¹⁰⁸ were adopted

$$R_L^{O\cdots H} < R^{O\cdots H} < R_H^{O\cdots H}; \quad \theta^{O\cdots HO} < \theta_C^{O\cdots HO}$$

where $R^{O\cdots H}$ is the distance between the HB acceptor (O) and the HB donor (H). The low and high thresholds are 1.7 and 2.6 Å, respectively. $\theta^{O\cdots HO}$ represents the angle $O\cdots O-H$ for the HB formation where the threshold angle is 110° .

2.3.b. Computational X-ray Diffraction. X-ray diffraction (XRD) patterns are sensitive to spacings between layers or rows of atoms and are capable of determining the orientation of a single crystal or grain. XRD has been utilized to identify crystal structures and measure the size, shape, and internal

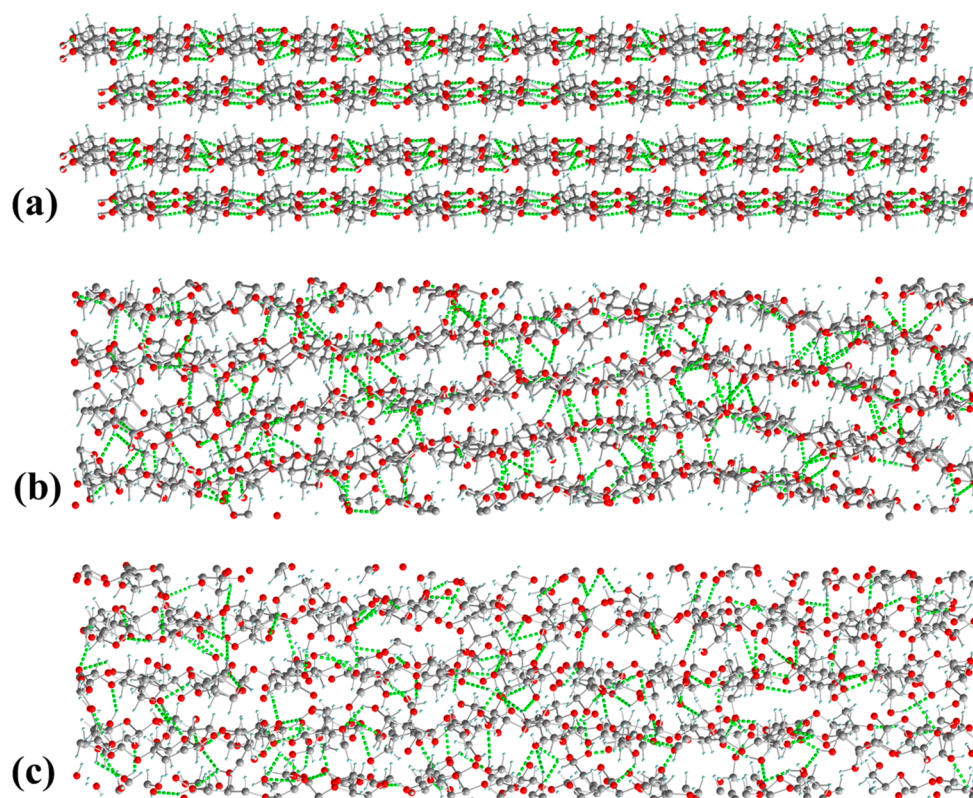


Figure 2. Cellulose configuration changes at different temperatures: (a) initial cellulose crystalline structure (exp. 293 K);¹⁰⁸ (b) cellulose structure at 300 K; (c) intermediate cellulose structure at 1100 K. When the temperature is higher than 1200 K, the cellulose structure will decompose. The hydrogen bonding network is shown in green dashed lines.

stress of small crystalline regions. It is also a primary tool for determination of nanocrystallite orientation in polymers. In this work, XRD plots were calculated to monitor the structural evolution of crystalline cellulose: the peak positions are determined by the lattice parameters, while the peak intensities are from the motif. XRD calculations were carried out by the Mercury and Diamond software; more information is available from the software manual.^{139,140}

2.3.c. Young's Modulus. Young's modulus defines the relationship between stress (force per unit area) and strain (proportional deformation) in the linear elasticity regime of a uniaxial deformation.¹⁴¹ A larger Young's modulus suggests a better stiffness of a material. Young's modulus could be experimentally determined via X-ray diffraction¹⁴² or Raman spectroscopy.¹⁴³ Computationally, several methods have been proposed to calculate this elastic modulus.^{143–146} One method is to enlarge the simulation box length repeatedly by a small amount, along the axis where the stress is applied. The simulation system is then reoptimized at each new fixed cell unit.^{110,146} Another method is to allow the simulation box to elongate continuously at a defined strain rate for a uniaxial tensile deformation. Several articles have adopted the second method to estimate the Young's modulus for amorphous polymers and metals.^{147–152}

This work also uses the second method to monitor the uniaxial tensile deformation at three different strain rates. In those simulations, the tensile stress is the negative value of pressure along the corresponding direction. The strain is then calculated by the amount of the length change for that direction. Young's modulus (E) is the ratio of tensile stress ($\sigma(\epsilon)$) and strain ϵ , $E = \sigma(\epsilon)/\epsilon$. From the stress–strain

diagram, the point of yielding is estimated by the offset yield method, also known as 0.2% offset yield strength. As shown in the following section, the yield strength is obtained by drawing through the point of the horizontal axis of $\epsilon = 0.2\%$, a line parallel to the initial straight-line portion of the stress–strain diagram.

3. RESULTS AND DISCUSSION

3.1. Cellulose Configuration under Different Temperatures. As shown in Figure 2, the temperature effect on cellulose configuration has been monitored. Figure 2a displays the final configurations from different temperatures, whereas the hydrogen bonding network of cellulose chains is illustrated by green dashed lines. In Figure 2b and c, the cellulose has been treated at 300 and 1100 K, respectively. The structure gets corrugated and twisted due to the pyrolysis process, which in turn could modify the hydrogen bonding network. Both traditional and ReaxFF force fields provide similar descriptions to cellulose conformation and its hydrogen bonding network. We analyzed and compared the cellulose unit cell predicted from this work and reported experimental and computational data from the literature. Nishiyama and co-workers¹⁰⁸ reported atomistic coordinates of cellulose crystal via XRD and neutron fiber diffraction at room temperature (293 K), which is adopted as the starting structure in this work. Matthews and co-workers^{91,92} used the CHARMM force field to discuss cellulose structures. Bergenstr hle⁹⁹ observed similar cellulose structural changes via the GROMOS, PCFF, MM3, and CHARMM force fields. In Table S1 of the Supporting Information, the equilibrium unit cell parameters are listed

from experiments and different computational studies, including this work.

Compared with results from traditional force fields,^{89,92,99,153–155} ReaxFF described the cellulose structure similar to that of the experimental value at 293 K.¹⁰⁸ It is worth noting that the unit cell angle γ is smaller than the experimental result, which is probably due to the underestimation of cellulose chain–chain dispersion interactions via the ReaxFF force field. A smaller γ value is also reported from calculations with traditional force fields at 300 K.^{92,99} In our calculations, when the temperature was increased to 500 K, larger unit cell parameters were observed, also similar to results from traditional force fields.⁹⁹ As discussed in the literature,^{92,99} the change of unit cell shape (α and β angles) indicates the interchain sliding of cellulose crystal. When the temperature increased from 500 to 1100 K in this work, the unit cell change became more significant, suggesting the increasing distance between cellulose chains. Such a configurational change eventually leads to the structural collapse of cellulose at high temperatures, around 1100 K according to RxMD simulations in this work. In RxMD calculations, the cellulose structure was stable up to 1000 K. At 1100 K, cellulose was stable for a few nanoseconds, but then it gradually decomposed. Even though cellulose is not thermally stable at 1100 K, the observed stability transition is important. When the temperature was beyond 1200 K, the cellulose structure quickly decomposed. Reaction products such as H₂, CO, H₂O, and very little CO₂ were observed, as shown in the Supporting Information. These pyrolysis products were also reported by previous work.^{105,109}

3.2. XRD of Cellulose Structures. XRD is a useful method to identify crystalline, semicrystalline, and amorphous structures. Here we calculated XRD to qualitatively determine the crystalline phase of cellulose under pyrolysis conditions. Since the initial cellulose crystal was built up based on experimental XRD data,¹⁰⁸ we used its XRD here to represent experimental XRD results from Nishiyama and co-workers. The green region represents the peak ranges of experimental XRD results that were reported by other authors.^{156–158} The cellulose structures at 300, 1000, and 1100 K were used to study the structure phase change under different pyrolysis temperatures. As shown in Figure 3, cellulose structures at 300

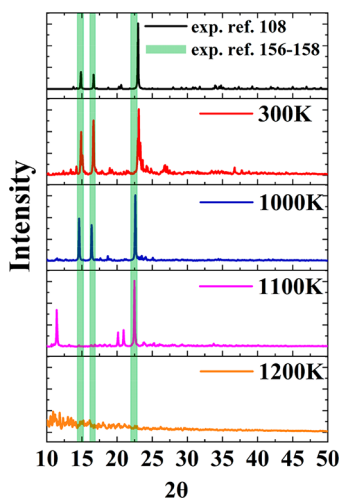


Figure 3. XRD of cellulose structures at different pyrolysis temperatures.

and 1000 K have similar XRD patterns as those of the experimental results (exp.¹⁰⁸), for both peak position and peak intensity. This suggests that I β crystalline cellulose has a relatively good thermal stability. When the temperature increases to 1100 K, there is a noticeable XRD peak shift when we calculate the XRD of the cellulose intermediate crystalline structure. From 300 to 1000 K, the calculations revealed cellulose structural changes, such as the corrugations and the twists of cellulose chains. However, the chains were generally still parallel to each other, and the distance between chains did not change too much. Therefore, no significant XRD peak shifting was observed between the initial crystalline cellulose and cellulose at temperatures from 300 to 1000 K. When the temperature was further increased to 1100 K, an obvious increase in cellulose chain–chain distance occurred. In addition, the twist of individual cellulose chains was more significant. Both contributed to the shift of XRD peaks from this temperature (1100 K) and up. It is also worth noting that the increased chain–chain distance reduced the total number of HBs between cellulose chains and eventually led to the collapse of cellulose structure. At 1200 K and above, XRD results showed an amorphous cellulose structure, suggesting the structural collapse at those higher pyrolysis temperatures.

3.3. Cellulose Decomposition and Element Distribution Analysis. Under pyrolysis temperatures of 1200 and 1300 K, the crystalline cellulose structure could fully decompose. The categories of pyrolysis products have already been studied, and one of the classifications¹⁰⁹ was adopted in this work: (a) organic gas composites which contain 1–4 carbon atoms; (b) light tar which contains 5–13 carbon atoms; (c) heavy tar which contains 14–39 carbon atoms; (d) char which contains more than 40 carbon atoms. As shown in Figure 4a, cellulose started to decompose into tar or heavy tar at the beginning of the simulations. After the crystalline structure was decomposed, several light tar products were detected, as well as light gas molecules such as CH₄ and CO. RxMD simulations with the same ReaxFF force field have been performed to understand the pyrolysis decomposition of cellulose, hemicellulose, and lignin.^{105,106,109,159} From an experimental point of view, pyrolysis temperatures could be divided into the following ranges:¹⁶⁰ (1) 550–950 K (slow pyrolysis); (2) 850–1250 K (fast pyrolysis); (3) 1050–1300 K (flash pyrolysis). We adopted the concept and qualitatively treated temperatures from 500 to 800 K as slow pyrolysis, temperatures from 800 to 1000 K as medium pyrolysis, and temperatures of 1100 K and above as fast pyrolysis. It is also worth noting that cellulose pyrolysis at high temperatures has been investigated via the ReaxFF force field.^{105,109} In this work, we mainly focus on cellulose structural evolution under low and medium pyrolysis temperatures. Cellulose decomposition products depend on the pyrolysis setting, that is, the initial cellulose structure (crystalline vs amorphous), the pyrolysis temperature (medium vs high), and the pyrolysis atmosphere (isolated vs ambient with CO₂, O₂, or H₂O). For the isolated condition and under a high temperature (>1200 K), we observed that cellulose should decompose completely into light products of H₂, CO, H₂O, and very little CO₂ after a sufficiently long RxMD calculation (~60 ns).

From the materials perspective, it is desirable that the pyrolysis process only produces necessary changes to the structural and chemical properties of cellulose and maintains the maximum use of the elements of cellulose. If a large amount of gas-phase species, such as CO₂, CO, CH₄, H₂, and

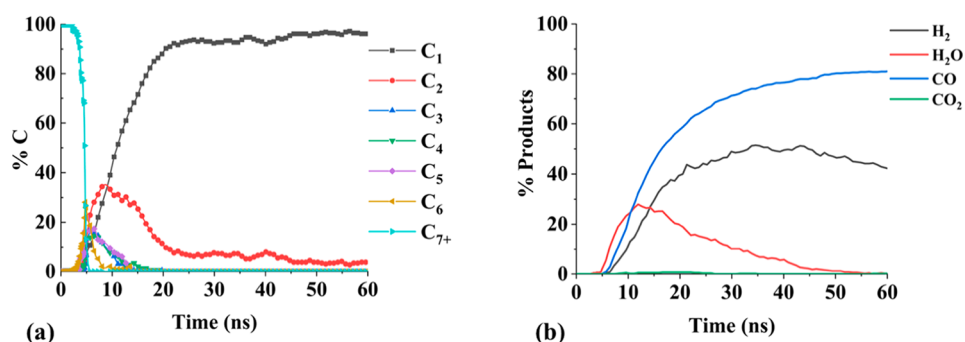


Figure 4. Analysis of cellulose decomposition at 1200 K: (a) The redistribution of carbon elements; C₁, C₂, ..., C₇₊ denote decomposition products having 1 carbon atom, 2 carbon atoms, ..., and 7 or more carbon atoms, respectively. (b) Light gas-phase molecules during the isolated pyrolysis process.

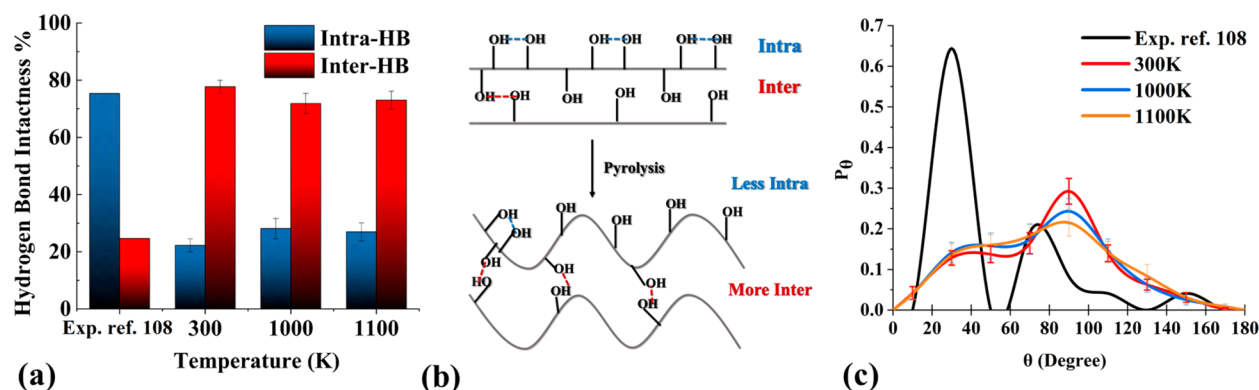


Figure 5. (a) The intrachain HB and interchain HB distributions at different pyrolysis temperatures. (b) A schematic illustration of the inter and intra HB network change due to pyrolysis temperature. (c) The HB angular distribution, which is through the analysis of the angle formed between the HB bond and the positive Z axis.

H₂O, is released during the pyrolysis process, the efficiency of converting cheap biomaterials to cellulose based advanced materials would be rather low. For the isolated pyrolysis conditions in this work, the calculations reveal that the release of CO₂ is negligible, see Figure 4b, and that CO and H₂ are the dominating gas-phase species. It is worth noting that gas-phase H₂O is released during the early stage of the pyrolysis process. At the studied high temperatures, the vapor water can further interact with cellulose and produce more CO and H₂.

3.4. Cellulose Hydrogen Bonding Network. The cellulose configuration in Figure 2 shows that the corrugation and twist can lead the linear cellulose chains to a more complex three-dimensional hydrogen bonding network. To further monitor this change, the two types of hydrogen bonds have been distinguished, namely, the intrachain HBs that are formed between hydroxyl groups of same cellulose chains and the interchain HBs that are formed between hydroxyl groups from different cellulose chains. The percentage of hydrogen bond intactness is defined as the number of intra (or inter) HBs over the total number of HBs. Figure 5a shows the numerical analysis of the two hydrogen bonds where more interchain HBs exist under those studied pyrolysis conditions. For the pristine initial cellulose crystal, the majority is the intrachain HBs. In addition, comparing the initial model and cellulose at 300 and 1000 K, the total number of HBs is 292, 247 ± 10, and 183 ± 11, respectively. This indicates that the studied Iβ cellulose is thermally stable from 300 to 1000 K.

A scheme in Figure 5b illustrates the comparison of the hydrogen bonding network between the pristine Iβ cellulose

crystal and the cellulose after the pyrolysis treatment. In the initial crystal state, all cellulose chains are linear and highly ordered, with most hydroxyl groups on a cellulose chain pointing to the same directions. As a result, forming intrachain HBs is easier than forming interchain HBs due to the structural hindrance. On the contrary, under pyrolysis treatments, the corrugation and twist of cellulose chains prevent the formation of intra HBs but promote those inter HBs. At finite temperatures, cellulose chains rotate, twist, and corrugate to form a three-dimensional hydrogen bonding (HB) network. Figure 5a reveals a significant difference between experiment (XRD and neutron fiber diffraction data) and RxMD simulations. This is likely due to the fact that, in RxMD simulations, all hydrogen atoms are expressed explicitly. Their interactions contribute significantly to the HB network. However, XRD and neutron diffraction experiments cannot determine the exact locations of hydrogen atoms, which might lead to the incorrect description of the HB network. This explains the overestimated intra HB and the preferential HB angular distribution in Figure 5c: peak positions around 30, 70, and 150°. The HB angular distribution is through the analysis of the angle formed between the HB bond and the positive z axis. In this work, the RxMD results show that inter HB bonds are critical to the 3D network. It is also the main reason why cellulose is stable even at high temperatures (for example, 1000 K in this work). The 3D HB network and its change due to temperature have been investigated also by classical force fields, with qualitatively similar results.^{91,92,99,161} It is worth mentioning that the total number of hydrogen bonds should

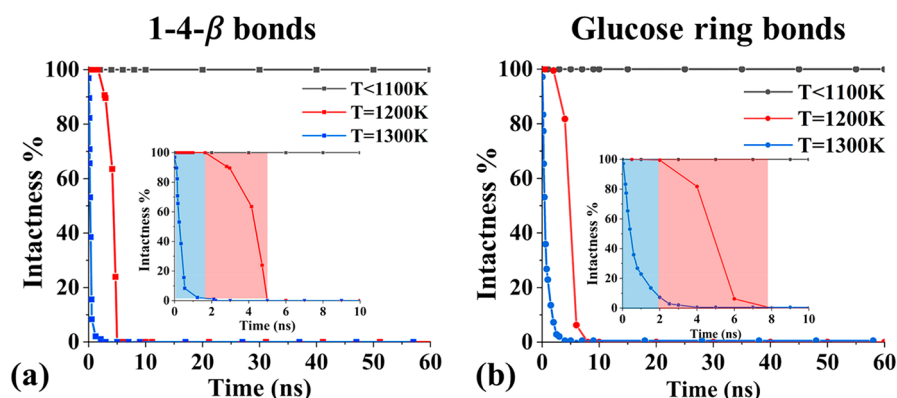


Figure 6. Intactness analysis of cellulose covalent bonds: (a) the 1–4- β bond; (b) the glucose ring. The red and blue regions respectively correspond to the time scales that 1–4- β bonds and glucose rings are detectable during the RxMD simulation.

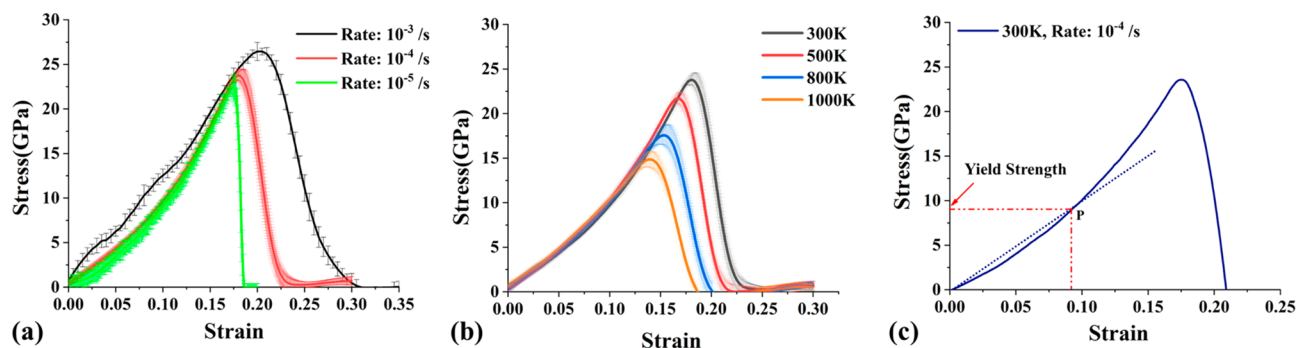


Figure 7. (a) The stress–strain diagram of cellulose at 300 K. The strain rate of 10^{-3} /s is in black, the strain rate of 10^{-4} /s is in red, and the strain rate of 10^{-5} /s is in green, respectively. (b) The stress–strain diagram of cellulose at 300, 500, 800, and 1000 K. The strain rate is kept at 10^{-4} /s. (c) The determination of cellulose yield stress at the strain rate of 10^{-4} /s and 300 K.

decrease under even higher pyrolysis temperatures. This is because the distance between cellulose chains gets slightly enlarged under higher temperatures, and eventually those interchain HBs would disappear.

3.5. The Breakdown of Cellulose Structures. In order to gain the fundamental insight of when and how the cellulose structure breaks down, the two characteristic covalent bonds of Figure 1a have been monitored, and the definition of bond intactness is defined as follows: (1) for a 1–4- β bond, the oxygen atom remains connected with the exact same two carbon atoms during the pyrolysis process; (2) for the glucose ring structure, all bonds from the ring structure are monitored, as well as the C–OH and C–CH₂OH groups that are connected with the ring structure. Each carbon in the glucose unit should remain bonded with the neighboring atoms during the pyrolysis process; in this work, the bond intactness is evaluated as a function of interatomic distance, to monitor the type, the breaking, and the formation of bonds via ReaxFF.¹⁶² With the bond order information, the intactness of a molecule or structure is further evaluated to see whether and for how long atoms of the molecule/structure remain connected.

For the studied conditions, both 1–4- β and glucose ring bonds remain intact for the temperature range from 300 to 1000 K. When the temperature increased to 1200 K, 1–4- β bonds started to break down within 2 ns, and by the end of the 5 ns in the trajectory, all 1–4- β bonds were decomposed, as shown in the inset of Figure 6a. Meanwhile, the breakdown of glucose ring structures was also detected at 1200 K. Compared with the 1–4- β bond, the decomposition of the glucose ring was slightly delayed, and it took until 7.5 ns in the trajectory to

break all glucose rings. This suggests that the glucose ring is more thermally stable than the 1–4- β structure. At 1300 K, the breakdown was expedited: within 2 ns, all 1–4- β were decomposed, while the complete breakdown of glucose rings was achieved within 5 ns. However, no temperature range is identified where 1–4- β bonds are decomposed and the glucose rings remain intact. It is probably due to the dangling bonds of broken 1–4- β structures, which can further induce the breakdown of glucose rings. Under different conditions, that is, instead of isolated pyrolysis, with liquid or gas mediated pyrolysis processes, the 1–4- β bond breakdown does not spontaneously lead to the decomposition of glucose rings. Thus, the cellulose structure could be modified selectively, by removing only those 1–4- β bonds. It is also interesting to note the collective contributions from the 3-D HB network. At 1200 or 1300 K, where both 1–4- β bonds and cellulose rings were decomposing, the 3-D hydrogen bonding network was still able to hold together partial crystalline cellulose chains. It is worth pointing out that the dissociation energies for characteristic structural changes are 0.2–40 kcal/mol for the hydrogen bonded (HB) network, 51–76 kcal/mol for the glycosidic (1–4- β) bond cleavage, and 78–191 kcal/mol for the glucose ring dissociation.^{163–165} In our calculations, when temperature was increasing from 300 K, the first structural change was from the 3-D HB network. At 1100 K, the thermo energy was able to further break down 1–4- β bonds and induce partial structural collapse of cellulose. In addition, the total number of HBs also decreased at 1100 K, which is more evidence of cellulose structural collapse. The simulation results also revealed that it is challenging to identify a temperature region where glucose

rings stay intact but the H-bonding network and 1–4- β bonds are broken. This is probably due to the fact that 1–4- β bonds and glucose rings alternate to form cellulose structures; see Figure 1. When 1–4- β bonds start to break down, the neighboring glucose rings become unsaturated and could easily interact with molecules or other parts of the partially collapsed cellulose. Between the covalent and HB bonds, is it possible to selectively remove the HB network and keep covalent bonds intact? More theoretical and experimental efforts are needed to validate the two hypotheses.

3.6. Young's Modulus Analysis. The configurational change of cellulose leads to the HB network variation, which inevitably affects cellulose mechanical properties. In this work, the uniaxial tensile deformation along the z direction has been calculated to evaluate the Young's modulus of cellulose. The deformation was carried out at 300 K at three different strain rates, namely, $10^{-3}/s$, $10^{-4}/s$, and $10^{-5}/s$. During the calculation, the stress (pressure) was only considered along the z direction and the pressure of the x and y directions was kept at zero. A time step of 0.05 fs was applied, and a total of 1 ns RxMD calculation was performed for each case. A smaller time step here was employed to avoid the error in calculating atom motions or any unstable structures. The Young's modulus was averaged using the data from the last 10% of the simulation trajectory. At 300 K, the calculated Young's modulus was about 113.24 ± 3.85 GPa (see Figure 7a) at the strain rate of $10^{-4}/s$, which agreed well with other calculations.¹¹⁰ From the literature, the Young's modulus of cellulose has been reported to be $(110\text{--}220) \pm 50$ GPa experimentally,^{142,166–169} or in the range 110–173 GPa by computational studies.^{99,110,143,144,146,153,155,170,171} The relatively small Young's modulus is probably coming from the adopted ReaxFF force field and the I β crystalline cellulose structure. In Figure 7b, we plotted the deformation curves for temperatures from 300 to 1000 K with a strain rate of $10^{-4}/s$. We observed a Young's modulus of 99.03 ± 2.16 , 95.67 ± 3.65 , and 94.34 ± 3.08 GPa at 500, 800, and 1000 K, respectively. When the temperature increases, the Young's modulus decreases. This is because cellulose can deform easily at higher temperatures, leading to the drop of Young's modulus.

In addition, as shown in Figure 7c, at the strain rate of $10^{-4}/s$, via the aforementioned proportional limit method, the yield stress was determined to be about 8.75 GPa, which is in excellent agreement with experimental and other modeling results.^{110,172,173}

4. CONCLUSION

While the classical force field has been adopted to study cellulose properties and cellulose interaction with other materials, chemical reaction and thermal decomposition of cellulose are beyond the reach. In this work, via ReaxFF based reactive molecular dynamics (RxMD) simulations, we observed bond breaking and structural change of cellulose at elevated temperatures. By changing the pyrolysis temperature from 300 to 1300 K, we are able to analyze the overall configuration, the covalent bonds of 1–4- β and glucose ring units, the inter and intra hydrogen bonding networks, and the element distributions systematically. XRD and Young's modulus have also been computed to compare with available experimental and previous modeling results. Key results include the following: (a) Cellulose is able to hold the general crystalline structure for temperatures up to 1000 K. The good

thermal stability is assisted by the interchange of inter- and intrachain HB networks. (b) When the pyrolysis temperature is beyond 1200 K, both 1–4- β bonds and glucose ring units will decompose. Light gas-phase molecules, such as CO and H₂, are detected as major decomposition products. (c) Through the analysis of XRD, Young's modulus, and elements distribution, we show that the ReaxFF reactive force field is capable of describing both stable and dissociative properties of cellulose under isolated pyrolysis processes. Ultimately, this work provides an atomic level fundamental understanding of cellulose structural evolution via pyrolysis treatments. More studies of cellulose under real pyrolysis conditions, that is, instead of isolated conditions but via liquid or gas mediated pyrolysis processes, are worth pursuing. Moreover, the detailed mechanism of how cellulose, hemicellulose, and lignin respond differently to pyrolysis treatments could lead to a subtle manipulation and a successful conversion of biomass into advanced functional materials.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.9b00701.

- (1) A table of comparison of unit cell parameters, angles between experiments, traditional force fields, and our models; (2) the configuration plots of 500, 800, 1000, and 1200 K; (3) the XRD plots of 500 and 800 K and element distribution of 1300 K; (4) the comparison of the stress–strain diagram for different strain rates at 300 K; (5) force field parameters we used in our work (PDF)

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Notes

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