

Research Article

Interaction Effects between Cellulose and Water in Nanocrystalline and Amorphous Regions: A Novel Approach Using Molecular Modeling

Ali Chami Khazraji and Sylvain Robert

Département de Chimie et Physique, Centre de Recherche sur les Matériaux Lignocellulosiques (CRML),
Université du Québec à Trois-Rivières (UQTR), 3351 Boul. des Forges, C.P. 500 Trois-Rivières, QC, Canada G9A 5H7

Correspondence should be addressed to Sylvain Robert; sylvain.robert@uqtr.ca

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The hydrophilic/hydrophobic nature of cellulose is based on its structural anisotropy. Cellulose chains are arranged in a parallel manner and are organized in sheets stabilized by interchain OH–O hydrogen bonds, whereas the stacking of sheets is stabilized by both van der Waals (vdW) dispersion forces and weak CH–O hydrogen bonds. Cellulose has a strong affinity to itself and materials containing hydroxyls, especially water. Based on the preponderance of hydroxyl functional groups, cellulose polymer is very reactive with water. Water molecular smallness promotes the reaction with the cellulose chains and immediately formed hydrogen bonds. Besides that, vdW dispersion forces play an important role between these two reactive entities. They stabilize the cellulose structure according to the considerable cohesive energy in the cellulose network. Hydrogen bonding, electrostatic interactions, and vdW dispersion forces play an important role in determining the cellulose crystal structure during the cellulose–water interactions. As a result of these interactions, the volume of cellulose undergoes a meaningful change expressed not only by an exponential growth in amorphous regions, but also by an expansion in nanocrystalline regions. In addition, the volume change is associated with the swelling material expressed as a weight gain of the cellulose polymer. Molecular modeling using Accelrys Materials Studio allowed us to open a new horizon and is helpful for understanding cellulose–water interactions.

1. Introduction

Objective of This Study. In this paper, we studied the behavior of amorphous and nanocrystalline I α regions of cellulose when these two regions interact with water molecules. Furthermore, we highlighted the mechanism that governs their interactions.

Cellulose is a polymer of β -D-glucose units linked together by (1 \rightarrow 4) glycosidic bonds to form cellobiose residues that are the repeating units in the cellulose chain (Figure 1) [1]. Several reviews have already been published reporting the state of knowledge of this fascinating polymer [2–13].

The cellulose structure favors organization into bundles with the crystalline order held together by hydrogen bonds

and disordered or amorphous regions (Figure 2). In a previous study [14, 15], Flory stated that a polymer in a condensed amorphous state exists in a nonperturbed conformation in the conformational analysis of the polymer [16].

Native crystalline cellulose is generally found as a mixture of cellulose I α and cellulose I β polymorphic forms. The proportions of the two allomorphs of crystalline cellulose vary depending on the source of the cellulose. Higher plants such as trees and corn are believed to have a higher proportion of cellulose I β . Studies have determined that cellulose I β is more stable than cellulose I α , and the conversion from type I α to I β is irreversible. Electron diffraction patterns show type I α to have a triclinic unit cell and type I β to have a monoclinic unit cell. In both phases, the cellulose chains are organized in a parallel-up fashion. The I α phase has cell dimensions $a = 0.674$ nm, $b = 0.593$ nm, $c = 1.036$ nm

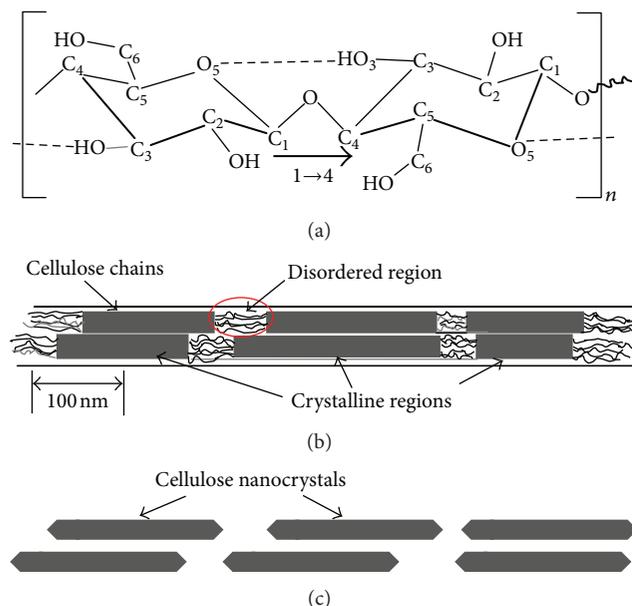


FIGURE 1: Schematics of (a) single cellulose chain repeat unit, showing the directionality of the 1→4 linkage and intrachain hydrogen bonding (dashed lines), (b) idealized cellulose microfibril showing one of the suggested configurations of the crystalline and amorphous regions, and (c) cellulose nanocrystals after acid hydrolysis dissolved the disordered regions.

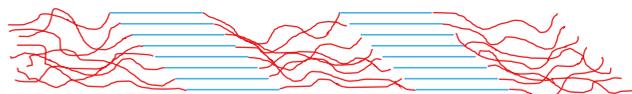


FIGURE 2: Cellulose chains consist of ordered regions or nanocrystalline (blue) and disordered regions or amorphous (red).

(chain axis), $\alpha = 117^\circ$, $\beta = 113^\circ$, and $\gamma = 81^\circ$ and one cellobiose moiety per unit cell [17]. The $I\beta$ phase is very similar to the model by Sarko and Muggli [18], with the cell dimensions $a = 0.801$ nm, $b = 0.817$ nm, $c = 1.036$ nm (chain axis), $\alpha = \beta = 90^\circ$, and $\gamma = 97.3^\circ$ and two cellobiose moieties per unit cell. The number of glucose units or the degree of polymerization (DP) is up to 20 000, but shorter cellulose chains can occur and are mainly localized in the primary cell walls [19].

2. Computational Methods

In this study, we used Accelrys Materials Studio 6.0 software [20]. In order to study the behavior of water in the disordered part of cellulose's so-called amorphous regions, we used the Amorphous Cell MS 6.0 module. This is a module to create 3D periodic structures composed of small molecules, polymers, and so forth. We construct a cell based on the density and the number and length of the chains. In the Amorphous Cell Construction, lattice type is cubic and lengths are the values of the lattice parameters a (Å), b (Å), and c (Å). Ramp density from: allows construction of the cell at the specified density, in g/cc, after which the density will be

ramped up to its final value as specified on the setup tab using a succession of geometry optimization and dynamics steps.

In addition, we used another module from Accelrys Materials Studio 6.0 called DMol³. This module helps us display electronic properties in amorphous cells of cellulose after interacting with water molecules. DMol³ is a modeling program that uses density functional theory (DFT) to simulate chemical processes and predict properties of materials both rapidly and accurately. The theoretical foundation is based on Schrödinger's equation. The Hamiltonian operates on wavefunctions of all electronic degrees of freedom. In practice, wave functions are expressed in terms of one particle function. The density functional theory is based on the Hohenberg-Kohn theorem, Kohn-Sham theorem, and Kohn-Sham equations.

We also used Forcite module from Accelrys Materials Studio 6.0. This module is an advanced classical mechanics tool that enables energy calculations, geometry optimizations, and dynamics simulations. We used this tool to calculate the cell parameters when cellulose chains in the ordered regions interact with water molecules. For cellulose polymers, using Forcite Plus with the COMPASS force field enables the prediction of properties such as mechanical properties, density, diffusion, and solubility parameters.

3. Results and Discussion

3.1. First Part of Study. Molecular modeling is a well-adapted technique to investigate the organization of the cellulose chains within the material [16]. Here again, most of the efforts have been devoted to modeling the crystal phases and performing the cellulose-water interactions. Modeling protocols go from simple minimization of finite-sized systems (without periodic boundary conditions) to molecular dynamics experiments performed on infinite solids with periodic boundary conditions. Former studies, called minicrystals, allowed prediction of the relative stability of the different cellulosic allomorphs [21–23]. Molecular modeling has been performed on three cellulosic systems: the amorphous phase and the two native crystalline phases ($I\alpha$ and $I\beta$).

The cellulose chains are composed of ordered regions (nanocrystals) and disordered regions (amorphous). We will start our study by interacting water molecules with cellulose chains in the amorphous regions and then in the nanocrystalline regions.

3.1.1. Creating a Cellobiose Molecule and a Water Molecule.

We will build an amorphous cell model in which there are cellulose chains and water molecules. The cellulose chain is composed of one cellobiose unit. The first task is to open a new 3D atomistic document in which we sketched a structure. Then, we have to draw a cellobiose unit and a water molecule in the corresponding files (Figures 3 and 4).

Now that our structures of cellobiose unit and water molecule are ready, we may start building an amorphous cell. In order to get a cell which is approximately $38.5 \times 38.5 \times 38.5$ Å, we used the Amorphous Cell MS Builder of Accelrys Materials Studio 6.0.

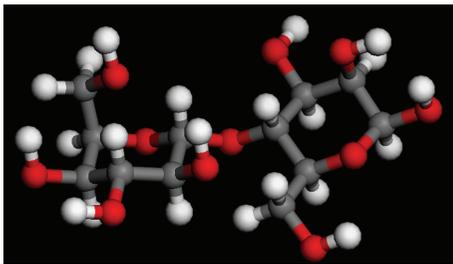


FIGURE 3: Cellobiose unit of cellulose chain.

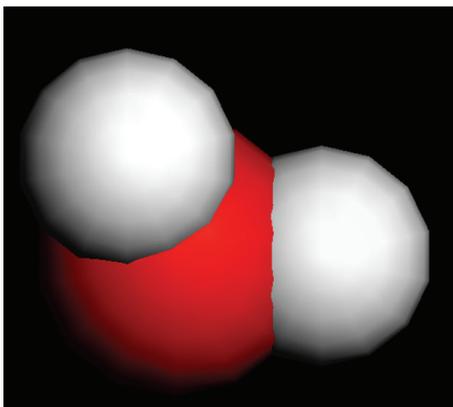


FIGURE 4: Water molecule to large CPK (Corey-Pauling-Koltun) spheres.

In the amorphous cell calculation dialog, the setup tab contains a construction task, the quality is medium, the density is 1 g/cc, and the output is 10 frames. The composition table, including cellobiose unit and water molecules, is represented in Table 1. Each experiment between cellulose chains and water molecules in this table is independent of the other.

At the beginning, we set the number of cellulose chains, and we varied the number of water molecules. We started the modeling with 100 cellulose chains, and in each chain, there is one repeating unit (cellobiose) and one water molecule. We loaded them into amorphous cell. After that, we varied only the number of water molecules as shown in the following Table 1.

Amorphous cell is a comprehensive model building tool for creating a wide range of amorphous materials. Its flexible approach to force field choice, combined with several different construction techniques, enables the building of bulk structures of a wide range of systems including polymers and glasses, as well as nanostructures. Amorphous cell can also be used to generate layered structures to enable calculations on interfaces.

In the energy tab of the amorphous cell calculation dialog, we change the force field to COMPASS. After running the calculation, we obtained something like the model shown in Figure 5 as an example, including 100 cellulose chains and one water molecule.

COMPASS is a powerful force field that supports atomistic simulation of condensed phase materials. COMPASS

TABLE 1: Cubic cell composition of 100 cellulose chains fixed (one cellobiose unit) and a varying number of water molecules.

Molecules	Loading	Weight%
Cellobiose	100	99.9
Water	1	0.1
Cellobiose	100	95
Water	100	5
Cellobiose	100	90.5
Water	200	9.5
Cellobiose	100	82.6
Water	400	17.4
Cellobiose	100	70.4
Water	800	29.6
Cellobiose	100	54.3
Water	1600	45.7
Cellobiose	100	37.3
Water	3200	62.7
Cellobiose	100	22.9
Water	6400	77.1

TABLE 2: Volume of cubic amorphous cell composed of 100 cellulose chains fixed (one cellobiose unit) and a varying number of water molecules.

Water molecules	a (Å)	b (Å)	c (Å)	V (Å ³)
1	38.456	38.456	38.456	56871.1915
100	39.112	39.112	39.112	59831.5251
200	39.753	39.753	39.753	62821.706
400	40.977	40.977	40.977	68805.0761
800	43.227	43.227	43.227	80772.8279
1600	47.132	47.132	47.132	104700.223
3200	53.434	53.434	53.434	152564.348
6400	62.852	62.852	62.852	248288.901

stands for condensed-phase optimized molecular potentials for atomistic simulation studies. The COMPASS force field aims to achieve high accuracy in prediction for a broad range of systems. The goal is to be able to predict properties of molecules, both in isolation and in the condensed phase, with accuracy comparable to an experiment. It is an *ab initio* force field because most parameters are initially derived based on *ab initio* data. Following this step, parameters are optimized to yield good agreement with experimental data. In particular, thermophysical data for molecular liquids and crystals are used to refine the nonbonding parameters by using molecular dynamics simulations.

When this experiment ended, we repeated the same experiment by changing the number of water molecules and keeping the number of cellulose chains fixed at 100 as shown in Table 2. This table represents the cubic cell parameters. The experiments were done on systems with 100 cellulose chains composed of one cellobiose unit and progressive amounts of water molecules.

TABLE 3: Amorphous cell composed of 100 cellulose chains fixed (5 cellobiose units) and a varying number of water molecules.

Molecules	Loading	Weight%
Cellobiose	100	99.9
Water	1	1.0
Cellobiose	100	98.9
Water	100	1.1
Cellobiose	100	97.8
Water	200	2.2
Cellobiose	100	95.8
Water	400	4.2
Cellobiose	100	91.9
Water	800	8.1
Cellobiose	100	85.0
Water	1600	15.0
Cellobiose	100	74.0
Water	3200	26.0
Cellobiose	100	22.9
Water	6400	77.1

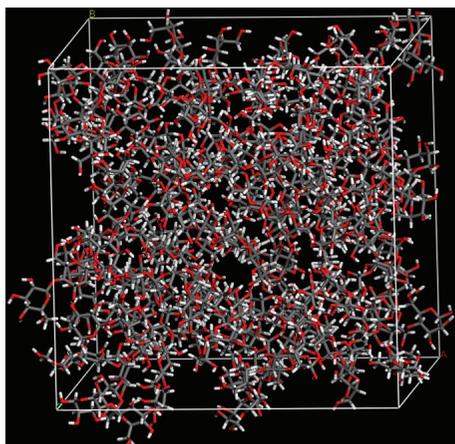


FIGURE 5: Cubic cell of amorphous region representing 100 cellulose chains of one repeating unit or cellobiose and one water molecule.

We repeated the same procedure, but now we increased the polymerization degree of the cellulose chains. This time, we took a chain cellulosic that contains five repeating units of cellobiose. The cubic cell composition including cellobiose unit and water molecules is represented in Table 3.

After running the calculation, we obtain the model shown in Figure 6 as an example representing 100 cellulose chains which are formed by five repeating units or cellobiose and 6400 water molecules.

We set the number of cellulose chains, and we varied the number of water molecules. Table 4 shows the results of the experiments that were performed with 100 cellulose chains composed of five repeating units or cellobiose with a varying number of water molecules.

Analysis of the results is presented in Figure 7. This graph shows what happens when water molecules interact with cellulose in amorphous regions. These regions are influenced by

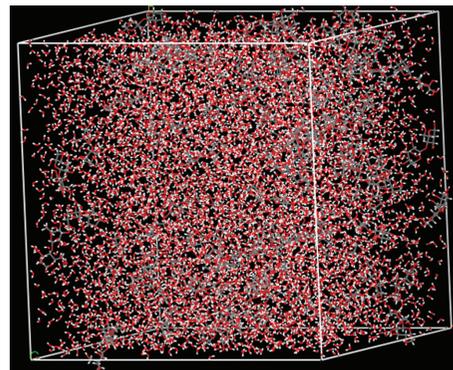


FIGURE 6: Cubic cell of amorphous region of 100 cellulose chains of five repeating units or cellobiose and 6400 water molecules.

TABLE 4: Volume of cubic amorphous cell composed of 100 cellulose chains fixed (5 cellobiose units) and a varying number of water molecules.

Water molecules	a (Å)	b (Å)	c (Å)	V (Å ³)
1	64.813	64.813	64.813	272261.587
100	65.047	65.047	65.047	275221.156
200	65.282	65.282	65.282	278214.880
400	65.747	65.747	65.747	284202.454
800	66.657	66.657	66.657	296167.426
1600	68.406	68.406	68.406	320097.725
3200	71.658	71.658	71.658	367954.440
6400	77.400	77.400	77.400	463684.824

the presence of water molecules. Consequently, the volumes of the amorphous regions undergo an exponential growth.

Now, look what happened to the electronic levels. In general, carbohydrates are hydrophilic and tend to strongly interact with water. Water can act as a plasticizing agent changing the key mechanical properties and depressing the glass transition temperature of an amorphous carbohydrate. Figure 7 clearly shows the volume variation of the amorphous regions of cellulose as a function of the water molecules variation. The amorphous regions are unstable when they interact with the water molecules.

In order to elucidate the mechanism that governs the interactions between the cellulose chains and water in the amorphous regions, we reacted only few molecules (Figure 8). The water molecules are interacting with the cellulose chains. Consequently, we found an immediate formation of a hydrogen bonding network occurring between cellobiose and water molecules dispersed in the amorphous regions. The polar bonding can occur between cellobiose (intermolecularly), within different parts of a single cellobiose (intramolecularly), or between cellobiose and water molecules. The hydrogen bond is often described as an electrostatic dipole-dipole interaction. However, it also has some features of covalent bonding. It is directional and strong, producing interatomic distances shorter than sum of the van der Waals radii.

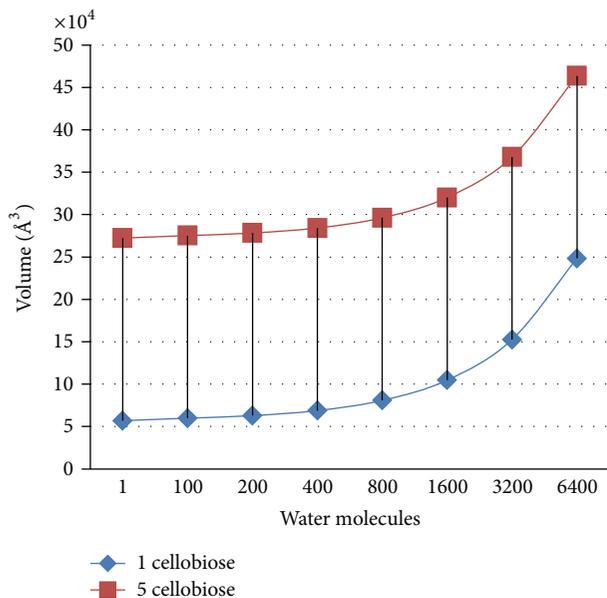


FIGURE 7: Volume increase of cellulosic amorphous regions during cellulose-water interactions.

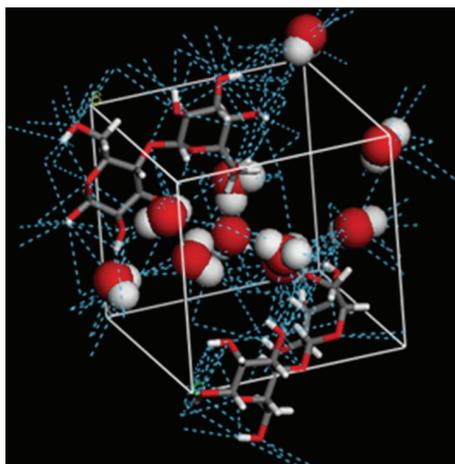


FIGURE 8: Hydrogen bonds between cellulose chains and water molecules (CPK style) in the cubic cell of the amorphous region.

Within the plant cell wall matrix, water molecules are subjected to a number of interactions caused by the chemical and physical composition of the cell wall. Structure and composition of the cell wall produce states and locations of water molecules. Further, cellulose chains have a strong affinity toward themselves and toward materials containing hydroxyl groups. Cellulose chains are inter-connected by OH–O-type hydrogen bonds to form flat sheets with CH–O hydrogen bonds. Nonbonding interactions are involved in these interactions, especially electrostatic, hydrogen bonds, and van der Waals dispersion forces. Water is a good polar solvent. Among its properties, water molecules are solvent ionizing and dissociating molecules. Cellulose polymer is hydrophilic and tends to strongly interact with water. Also, water molecules interact easily with cellulose chains. At the

cellulose chain interface, several hydrogen bonds are lost. However, these losses of intermolecular hydrogen bonds within the cellulose chains are compensated with new hydrogen bonds from water molecules. Large anti-bonding electron clouds exist around the glycosidic bonds in the cellulose polymer. These anti-bonding electron clouds produce an induced polarization at the approach of the water molecules. Electron clouds can be distorted and thus create an electrostatic dipole. From the concept of polarizability, a wave dipole is created. The properties of the hydrocarbon chains dominate and define the interactions. A repulsion component resulting from the Pauli principle prevents the collapse of the chains. Different types of interactions could exist—attractive or repulsive interactions between permanent dipoles within the cellulose polymer and water molecules, induction interactions between permanent poles of water molecules and induced multipoles of cellulose chains, and any pairs of molecules arising from the interactions on instantaneous multi-poles.

Water molecules could penetrate between the fibers through capillary forces and interact with the cellulose chains. Formation of hydrogen bonds at the water/cellulose interface is shown to depend sensitively on the adsorption site, for example, above the equatorial hydroxyls or OH moieties pointing out of the cellulose chains. Also, the van der Waals dispersion forces contribute significantly to the adsorption energy. All intermolecular/van der Waals dispersion forces in the cellulose polymer are anisotropic. Electrostatic interactions change sign upon rotation of the molecules. Electrostatic forces can be attractive or repulsive depending on the mutual orientation of the molecules. Moreover, weak interactions also allow the dispersion of cellulose chains in water.

In addition, we must consider another factor which is the swelling. The term swelling is usually associated with volume increase of the material due to liquid uptake. This term is expressed as weight gain of the cellulose material.

Each molecule from cellulose and water has an electron density that measures the probability of an electron being present at a specific location. We reacted a few molecules of cellulose and water so that we can show clearly their reactive effects that occur between them. Through their valence electrons, we can show the effects using molecular modeling software DMol³ from Accelrys Materials Studio 6.0.

3.1.2. Modeling Interactions between Cellulose and Water Using Quantum Mechanics. We used DMol³ tool from Accelrys Materials Studio 6.0 to display electronic properties after interactions between cellulose chains and water molecules. We set the Task to Geometry Optimization. The Quality is set to Medium. The Functional is set to GGA and BLYP. In the Electronic Tab we set the Basis Set to DNP.

Electron clouds are often found around atoms. Molecular modeling software provides graphical images of electron density (Figure 9). Graphically, the electron density surface also serves as a canvas upon which other electronic properties can be displayed. The electrostatic potential map provides an indicator for charge distribution in cellulose

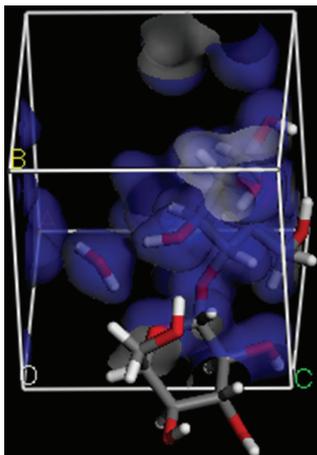


FIGURE 9: Electron density in the cellulosic amorphous region when water molecules interact with cellulose chains.

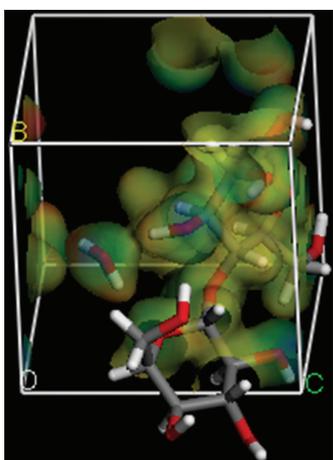


FIGURE 10: Electrostatic potential in the cellulosic amorphous region when water molecules interact with cellulose chains.

and water molecules (Figure 10). The electrostatic potential is mapped onto the total charge density isosurface using color to represent the variation. Conversely, we have built an interactive model between these two entities cellulose-water interactions. Consequently, in this region, cellulose and water molecules can interact easily between themselves, and they finish by forming one entity with the electronic clouds mixed up together.

The Amorphous Cell module from Accelrys Materials Studio 6.0 allows us to highlight a way in which the cellulose and water react. The Ewald summation method is for both electrostatic and van der Waals nonbonds terms. In other words, the default methods are Ewald summation for van der Waals interacting and for Coulombic interactions (Figure 11).

This experiment clearly shows what happens when cellulose chains and water molecules get together—cellulose chains and water molecules react quickly and without any obstacles. In other words, cellulose is a hydrophilic interface. In addition to the hydrogen bonds, van der Waals dispersion forces are present during the cellulose-water interactions.

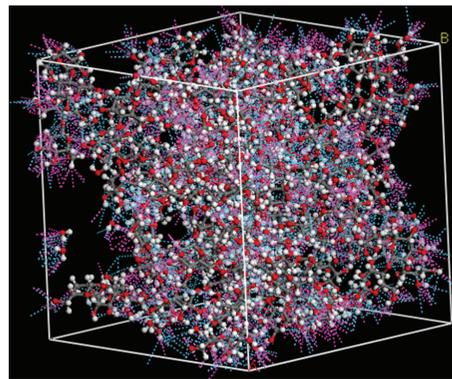


FIGURE 11: Hydrogen bonds (blue dashed lines), and van der Waals dispersion forces (pink dashed lines) between cellulose chains and water molecules.

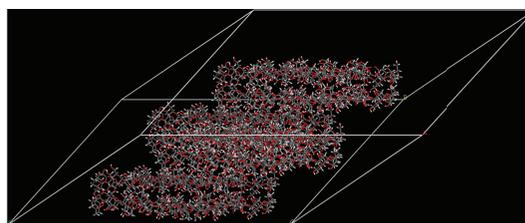


FIGURE 12: Nanocrystalline cellulose I α without water molecules.

In our previous papers, we showed in detail several phenomena that govern the interactions between cellulose and water.

3.2. Second Part of the Study. In the second part of this work, we will study the cellulose chains in the nanocrystalline regions when they interact with water molecules using molecular modeling from Accelrys Materials Studio.

3.2.1. Building and Optimizing the I α Structure of Cellulose.

In the I α structure, cellulose chains adopt parallel configurations. We built a model of nanocrystalline cellulose I α . We used the Forcite Molecular Modeling of Accelrys Materials Studio 6.0. The first structure of nanocrystalline cellulose I α is without water molecules (Figure 12). The lattice parameters are defined as following. The lattice type is 3D triclinic 1 P1 ($a = 91.031 \text{ \AA}$, $b = 54.677 \text{ \AA}$, $c = 84.934 \text{ \AA}$, $\alpha = 128.610^\circ$, $\beta = 115.950^\circ$, and $\gamma = 80.470^\circ$). In the second structure of nanocrystalline cellulose I α , we inserted water molecules (Figure 13). We also defined the follows lattice parameters of the crystal. The lattice type is 3D triclinic 1 P1 ($a = 90.444 \text{ \AA}$, $b = 54.788 \text{ \AA}$, $c = 85.189 \text{ \AA}$, $\alpha = 128.150^\circ$, $\beta = 115.770^\circ$, and $\gamma = 80.580^\circ$). After that, we compared the effects of water molecules in these two models of nanocrystalline cellulose I α . From Forcite calculation, in the setup tab the task is geometry optimization, and in the energy tab the force field is COMPASS.

The results that we obtained are presented in Figure 14. We find that the effects of water molecules on the cellulose chains are not negligible on the volume. The nanocrystalline

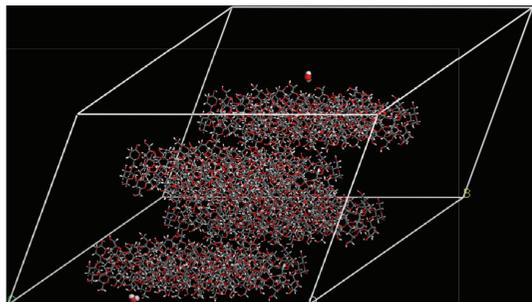


FIGURE 13: Nanocrystalline cellulose I α with water molecules (CPK style).

TABLE 5: Dimensions of nanocrystalline cellulose crystal I α before and after interacting with water molecules.

	Cell parameters		
	a (Å)	b (Å)	c (Å)
Initial structure	94.038	59.620	72.800
No water molecules	91.031	54.677	84.935
1 water molecule	90.444	54.787	85.189
~200 water molecules	92.165	56.496	85.548

cellulose I α regions undergo a meaningful expansion. In the global volume, there is much change. However, these changes in volume did not prevent a slight variation along all the sides of the cube. The volumes of nanocrystalline cellulose I α have been changed undergoing narrowing or enlargement of their sides, as shown in Table 5. All the sides varied so that the whole crystal volumes do not remain constant.

We have only taken a low polymerization degree because the reaction takes a long time and, in the end, did not lead to completion. We will try in the next work to increase the polymerization degree according to the performance of the molecular modeling in Accelrys Materials Studio 6.0.

Using the Accelrys Materials Studio 6.0 allows us to formulate the following approach (Figure 15). Molecular modeling allowed us to demonstrate in this experiment, for example, that water molecules could penetrate through cellulose fibers that consist of multiple cellulose chains. These cellulose chains interact through hydrogen bonds, van der Waals (vdW), and electrostatic interactions. Cellulose chains have a strong affinity toward themselves and toward materials containing hydroxyl groups. At the surface of chains, several intermolecular hydrogen bondings are lost, but they are compensated by water molecules hydrogen bonds. Hydrogen bonding and vdW dispersion forces stabilize the cellulose chain structures in the water media. Hydrogen bonds dominate interchain energy, and vdW dispersion forces are mostly responsible for holding the chains together, although with relatively weak CH–O interactions. The large antibonding electron clouds surrounding the glycosidic bonds in the cellulose chains produce an induced polarization at the approach of water molecules. Electrostatic potential added to electronic density gives an insight into the cellobiose and

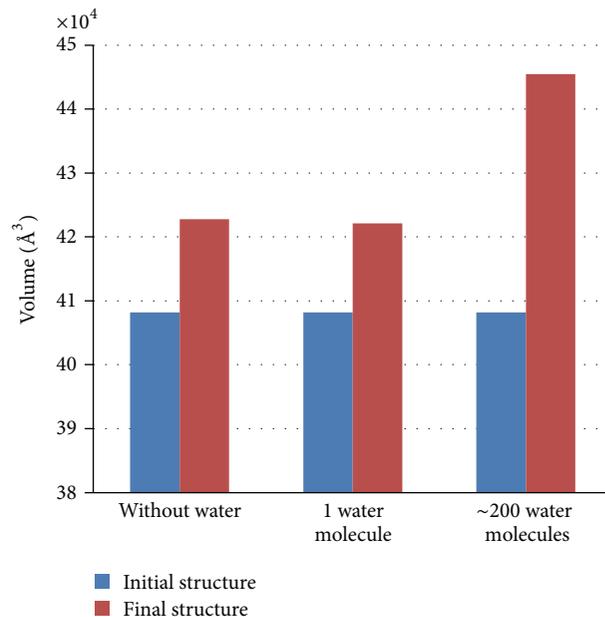


FIGURE 14: Volume increase in nanocrystalline cellulose I α regions when cellulose and water molecules interact.

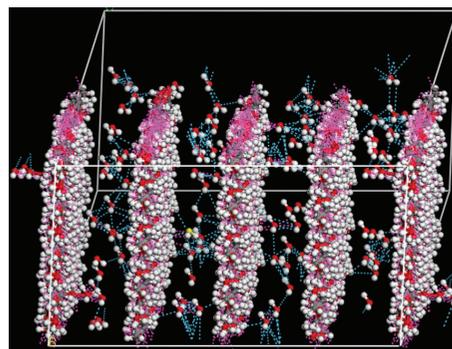


FIGURE 15: Hydrogen bonds (blue dashed lines) and vdW dispersion forces (pink dashed lines) in cellulose-water interactions.

water molecules. In other words, water molecules cannot enter between the cellulose chains because the chains form strong aggregations. On the contrary, water molecules could seep between the fiber bundles. Water molecules may surround cellulose chains forming at least one layer of water.

We seek to understand the interactions between water molecules and cellulose polymer. This study takes us a little closer to reality. The following images help us a little to clarify the phenomenon of the behavior of water molecules when they come close to the cellulose polymer. That is to say, how they might behave in the fiber matrix. These images allow us to explain our approach.

The cellulose chains have a hydrophilic character and tend to aggregate with other cellulose chains as shown in Figures 16, 17, 18, and 19. Water molecules have the tendency or power to enter into the cellulose fibers, for example, through capillary attraction, capillarity, or capillary motion.

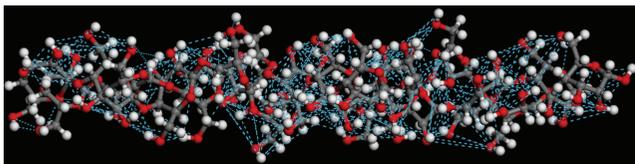


FIGURE 16: Aggregation between two cellulose chains and hydrogen bonds (blue dashed lines).

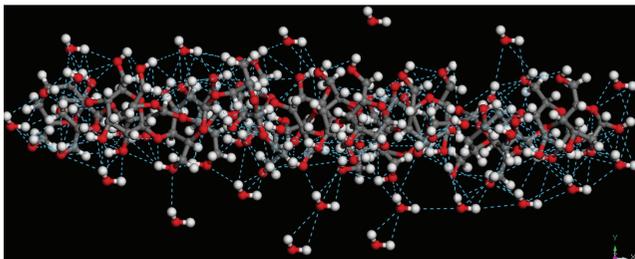


FIGURE 17: Hydrogen bonds network between water molecules and cellulose chains with hydrogen bonds (blue dashed lines) after interactions between them.

However, it is so difficult or almost impossible for water molecules to break the strong bonds that exist between the cellulose chains, except perhaps by an external effect which could weaken such strong chemical bonds. On the contrary, the water molecules are largely free of interactions with the external cellulose chains.

Table 5 shows the cubic cell parameters of the volume of cellulose $I\alpha$ into the nanocrystalline regions when the cellulose chains have been interacting with water molecules. These cells parameters show that the volumes of nanocrystalline cellulose changed after interacting with water molecules. As the water molecules increase, the volumes of nanocrystalline cellulose regions increase. Therefore, the water is able to react with cellulose chains in these regions, causing an increasing in the volume.

We tried to produce patterns through changes in the volume of the cellulose chain sheath-binder when they interact with water molecules. We achieved this diagram in which it shows the approximate change in the volume of the polymer cellulose when it comes into contact with water. We wanted to show pattern variations in volume when the cellulose chains and water molecules react with each other. Figure 20 shows the expansion of the cubic cell parameters from the initial structure to the final structure of nanocrystalline cellulose $I\alpha$ when the cellulose chains and the water molecules interact.

We note that this work is a continuation of two previous studies. The one study is entitled “Molecular modeling of cellulose-water interactions: qualitative studies of water on cellulose structure and properties”. other study is entitled “Self-assembly and intermolecular forces when cellulose and water interact using molecular modeling”. All these studies showed the phenomena that may exist in the interactions between cellulose when it comes into contact with water.

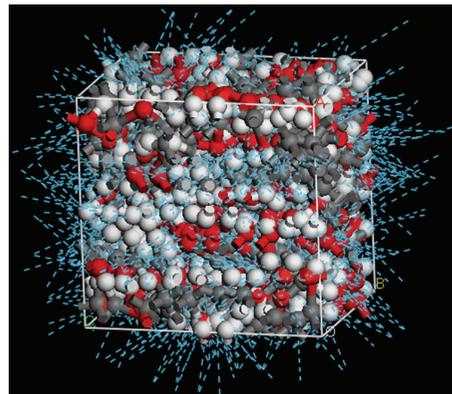


FIGURE 18: Cellulose chains aggregations with hydrogen bonds (blue dashed lines) in the cellulose chains (blue dashed lines).

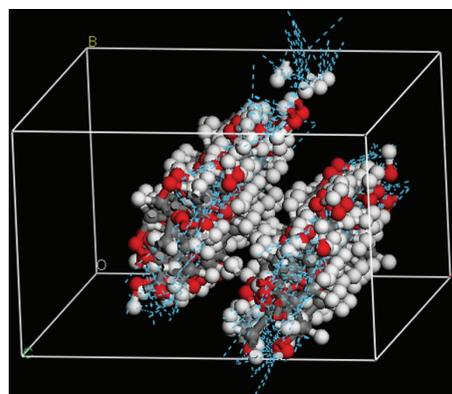


FIGURE 19: Spaces between cellulose chains aggregated and hydrogen bonds in the aggregations (blue dashed lines).

4. Conclusions

In summary, understanding the interactions of cellulose with water and the state of water in cellulose are of a great interest. This study shows, using molecular modeling software from Accelrys Materials Studio, the hydrophilic nature of the cellulose polymer, especially, in aqueous media. Cellulose polymer is formed of several chains packed together. Such cellulose chains are strongly bonded between them, and it is so difficult for water molecules to break these bonds.

In fact, water molecules interact rapidly with cellulose chains either in nanocrystalline cellulose $I\alpha$ regions outside of the chains or in the amorphous regions. After interacting, these two reactive species form one single entity together. However, this new state has an effect on cellulose structures, especially, in volume. The nanocrystalline cellulose $I\alpha$ and amorphous regions are influenced after the interactions with water molecules. Consequently, this effect is reflected in the volume change in these two cellulose regions that are amorphous and nanocrystalline $I\alpha$.

The volume change of both nanocrystalline cellulose $I\alpha$ and amorphous regions is manifested in its dimensions. Their volumes become larger. Consequently, this change in volume is the result of the interactions between cellulose and water

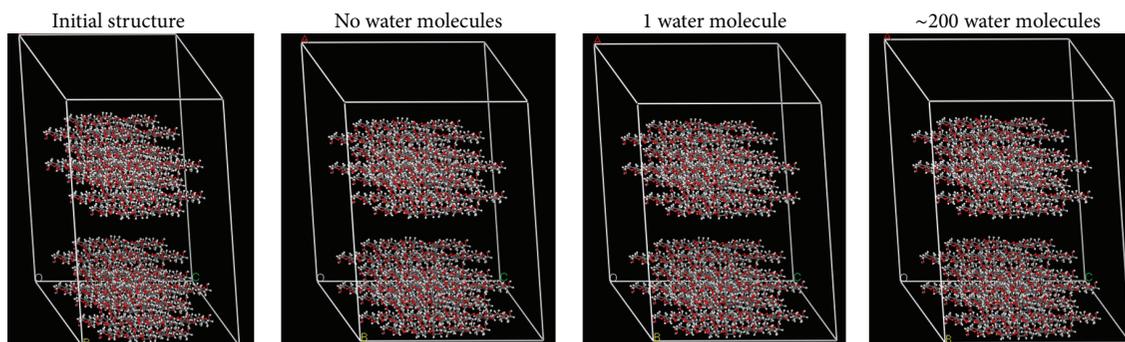


FIGURE 20: Approximate representation of the cubic cell parameters from Table 5 according to their dimensions.

molecules. Besides that, the interactions between the water molecules and the cellulose chains result in the electronic reactions. These reactions between the cellulose and water lead to the formation of hydrogen bond networks between water molecules and cellulose chains, perfect fusion of electron densities of these two reactive species, and creation of single electrostatic potential fields that can combine these matters into one reactive entity. In the amorphous regions, when water molecules come into contact with cellulose chains, it produces a molecular orbital combination of the cellulose chains with those of water molecules according to the linear combination of atomic orbitals (LCAO) theory. In addition, the swelling factor following the interaction with the water molecules is another factor that causes the increase in the volume of the cellulose chains. In other words, the swelling factor is usually associated with volume increase of the material due to liquid uptake (expressed as weight gain of the material).

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