Molecular modeling of interfaces between cellulose crystals and surrounding molecules: Effects of caprolactone surface grafting

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A technical problem in cellulosic nanocomposite materials is the weak interaction between hydrophilic cellulose and hydrophobic polymer matrices. One approach to solve this difficulty is to chemically graft monomers of the matrix polymer onto the cellulose surface. An important question is to understand the effect such surface modification has on the interfacial properties. Semi-empirical approaches to estimate work of adhesion based on surface energies do not provide information on specific molecular interactions. Details about these interactions were obtained using molecular dynamics (MD) simulation. Cellulose interfaces with water and caprolactone medium were modeled with different amounts of grafted caprolactone. The modification lead to an increased work of adhesion between the surface and its surrounding medium. Furthermore, the MD simulations showed that the interaction between cellulose, both modified and non-modified, and surrounding medium is dominated by Coulomb interactions, predominantly as hydrogen bonds.

1. Introduction

Bio-composite materials currently receive considerable scientific and technical interest. An important justification is the global warming problem. Replacement of petroleum-based polymers by materials from renewable resources would reduce the green-house effect by lowering the carbon dioxide emission [1].

An important reason for the wide-spread commercial interest in cellulose is its unique mechanical properties. Mechanical function is important in biological structures and cellulose is the main load-bearing constituent in plants [2,3]. The reason is its highly sophisticated fibril structure with an estimated longitudinal Young’s modulus of the cellulose crystal in excess of 100 GPa [4]. During bio-synthesis, cellulose is polymerized and solidified in the form of fibrils where the molecules are in an extended chain conformation and densely packed in semi-crystalline structures [5]. The interior of the crystals themselves are not accessible by small molecules such as water [4]. In contrast, the surface structure is somewhat less ordered and more accessible to the surrounding medium [6].

Recently, cellulose nanocomposites have entered as a new class of cellulosic materials. Boldizar et al. [7] produced nanostructured composites in the 1980’s, although reports on composites from tunicate whiskers started the strong development observed presently [8,9]. It is apparent that in this class of materials, the molecular interaction between the cellulose reinforcement and surrounding molecules is critical. This interaction will influence the rheology of nanocellulosic suspensions, and will also control interfacial adhesion in solid nanocomposite materials. In combination with the increasing interest in nanocellulotics [2,10], further study on the cellulose–polymer interactions is relevant. An interesting approach providing improved surface chemistry control is grafting of monomers onto the cellulose surface. For instance, caprolactone may be chemically grafted from surface hydroxyls on cellulose by ring opening polymerization [11].
In general, adhesion between two dissimilar materials may take place through a variety of mechanisms including inter-diffusion and adsorption. Inter-diffusion means that polymers become mixed in a diffuse inter-phase region. The potential for inter-diffusion between two polymers is frequently analyzed using the concept of solubility parameters [12,13]. The present study, however, focuses on the adsorption mechanism. Adhesion is assumed to take place at a distinct interface by molecular interactions across that interface. Interactions are short-range, and the term ‘contact adhesion’ is commonly used to describe this phenomenon [14]. The interactions include weak interactions, polar and induced polar forces. As contact adhesion is considered, we may assume ideal adhesion, that is, perfect physical contact between surfaces, only one adhesion mechanism and no presence of contaminants. The work of adhesion (WA), as defined in Section 2, is obtained by modeling and is used as a measure of the adhesive interfacial debond energy.

Previous efforts to predict interfacial adhesion between dissimilar solids are typically semi-empirical in nature [14]. Commonly, experimental data for contact angles between solid surfaces and a range of liquids are used to estimate the surface energy of the solids. The surface energies are then combined to estimate the WA between the solids. Experimental difficulties include effects from surface roughness, the need to establish equilibrium, and the difficulty to study solid surfaces of high surface energy (difficult to find probe liquids of high surface energy). An alternative technique is inverse gas chromatography (IGC) [15], and it has been successfully used to determine the dispersive part of the surface energy. In the case of cellulose–polymer adhesion, Coulombic interactions (including hydrogen bonds) are expected to be important. Existing semi-empirical approaches [14], including combinations with data from IGC, have not yet established predictive capabilities for interfacial adhesion involving Coulombic interactions because of their complexity. For instance, the interaction energy between two atoms or chemical groups depends on a number of factors including their orientations, separation distances and neighboring interactions. Furthermore, molecular interactions are dynamic.

Molecular dynamics (MD) simulation offers interesting possibilities to study molecular interactions at cellulose–polymer interfaces. Compared with the above mentioned semi-empirical approaches, MD provides much more specific and detailed information about the molecular interactions. The semi-empirical approaches are based on scalar values for surface energies of solids in combination with semi-empirical equations to estimate the surface energy of the interface itself. The underlying assumption is that even for Coulombic interactions such as hydrogen bonds, surface energies estimated from complex experiments can be plugged into a generally valid equation in order to determine the surface energy of a specific interface. In contrast, a MD simulation allows direct analysis of a molecular model of the interface. Instead of the scalar values for interaction energies used in semi-empirical approaches, MD is based on specific functions for pairwise force potentials between chemical groups or atoms. The force-field can also be independently evaluated by comparing modeled and experimentally obtained characteristics of structure and of mechanical and physical properties as exemplified by studies on cellulose [16,17]. A previous study on cellulose–polymer interfaces investigated native cellulose together with poly(ethylene-co-vinyl acetate) of different compositions [18]. Data for the structure at the interface and the work of adhesion between polymer and cellulose were obtained and the strategy was to select the best polymer among several candidates that shows the highest work of adhesion with cellulose.

Another strategy, as mentioned above, is to chemically modify cellulose to maximize the work of adhesion for a given matrix. The present work is a pilot study for evaluating the predicting capacity of MD applied according to this strategy. Cellulose–caprolactone and cellulose–water interfaces are being studied. The (110) and (110) surfaces are the most abundant surfaces of the cellulose I/ crystal [19]. Here, the (110) surface is grafted with caprolactone with different degrees of substitution. Grafted and non-grafted cellulose surfaces are exposed to water and to caprolactone. Water is studied due to its presence in all practical bio-composite systems. The work of adhesion is estimated directly from the simulated interface model. The different energy contributions (weak interactions and electrostatic interactions) are specified and compared to the total interaction energies revealed at cellulose–water and cellulose–caprolactone interface. The effects of grafted, and specific interactions such as hydrogen bonds with the surrounding molecules, on cellulose crystal structure and surface chain conformations are investigated.

2. Methods

Molecular dynamics simulations were carried out using the GROMACS simulation package [20]. The simulations were performed on six different interfacial systems. All simulated systems and details about their composition are listed in Table 1.

2.1. Molecular models

Cellulose is a linear polymer with glucose units linked together by β-1,4-glucosidic bonds, two glucose units form a cellobiose as depicted in Fig. 1. The crystalline cellulose I/ model consisted of 8 × 8 glucan chains giving a cross section of 4.6 nm × 4.7 nm. Each chain had 8 glucose units, with a total length of 4.2 nm and was covalently bonded to its own periodic image, mimicking chains of infinite length.

The 64 chains were placed in a periodic computational box with the chain axis parallel to the Z-axis of the box. The initial structure for crystalline cellulose I/ was constructed from X-ray diffraction data [21], and the force field was the GROMOS96 45A4 parameter set [22]. This particular model has been described in detail in an earlier study [17] where 10 ns bulk simulations were performed and the obtained results showed good agreement with experimental data for the cellulose structure, Young’s modulus and thermal expansion. It has also been used in a study of surface dynamics at cellulose–water interfaces,
showing good agreement with NMR relaxation data [23]. For water, the simple point charge (SPC) model [24] was employed. Instead of a polymeric matrix caprolactone was modeled as a system with open monomeric units, its correct chemical name would be 6-hydroxyhexanal. For simplicity, it will be referred to as CL. Each monomer has the structure shown in Fig. 2. Cellulose and CL were modeled with united atoms, excluding aliphatic hydrogens but having explicit hydroxyl hydrogens. The bonded and Lennard–Jones parameters from the GROMOS96 45A3 force-field [25] were used also for CL, whereas the charge distribution as derived from ab initio calculations and reported by Gardebien et al. [26] was applied. Bulk simulations were performed on CL and water separately for 10 ns. Water density was well reproduced, only deviating 2.5% from the experimental value [27] of 997 kg/m$^3$. The CL bulk system, with 6-hydrohexanal molecules, had a density of 879 kg/m$^3$, 7% less than the predicted value [28] of 949 kg/m$^3$.

After the bulk simulations were finished, the computational box surrounding the equilibrated cellulose bulk crystal was enlarged in the Y direction (see Fig. 4) in order to create (110) faces. The topography of this surface is elucidated by a density map shown in Fig. 3. Surface chains were then modified by attaching CL monomers onto the O6 atoms instead of the H6 atoms in Fig. 1 with a covalent bond. The grafting was done with 0%, 50% and 100% degree of substitution of H6 atoms (DSH6). We chose to graft only from the O6 atoms in this demonstrative study, since they are protruding the most from the cellulose surface.

A surface with 100% DSH6 was created by exchanging every H6 atom protruding from the surface for a CL monomer, which means 4 CL monomers on each surface chain. In a similar way, the surface with 50% DSH6 was created but here every second protruding H6 atom was exchanged for a CL monomer. Thereby, after the 50% modification every cellulose surface chain had 2 grafted CL monomers, and the grafts were evenly distributed over the surface.

For each DSH6, the empty space around the cellulose crystal was filled with randomly oriented water molecules. Subsequently, the systems were equilibrated and simulated for 5 ns. Next, the water was exchanged for CL.

<table>
<thead>
<tr>
<th>System</th>
<th>DSH6 [%]</th>
<th>Surr. med. [substance]</th>
<th>Cellulose</th>
<th>Surr. med.</th>
<th>Grafted monomers [#molecules]</th>
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<tr>
<td>CL0</td>
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<td>64</td>
<td>512</td>
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<tr>
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<td>50</td>
<td>CL</td>
<td>64</td>
<td>510</td>
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<td>64</td>
<td>510</td>
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<tr>
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<td>1802</td>
<td>—</td>
</tr>
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<td>50</td>
<td>Water</td>
<td>64</td>
<td>1955</td>
<td>32</td>
</tr>
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<td>100</td>
<td>Water</td>
<td>64</td>
<td>1398</td>
<td>64</td>
</tr>
</tbody>
</table>

Fig. 1. Glucose unit with atom names. For non-modified units $R = H$ whereas for units modified with caprolactone $R = \text{the structure in Fig. 2.}$

Fig. 2. Caprolactone model. For free CL, $R = H$, whereas for grafted caprolactone $R = \text{O6 in Fig. 1.}$

Fig. 3. Density map showing the cellulose (110) crystal surface in the Water0 simulation. The number density over the XZ box surface is mapped with a scale from zero density (white) to 100% of maximum density (black).
The CL system already equilibrated in bulk was used and put into the box. Again, after equilibration, simulations were extended for 5 ns each.

Pressure was kept constant at 1 atm using the Berendsen algorithm [29], and a temperature of 300 K was maintained with a Nosé–Hoover thermostat [30,31]. The simulations used the Leap Frog algorithm with a time step of 1 fs. A cut-off of 1 nm was used for the non-bonded interactions, but long range contributions were included by the Particle Mesh Ewald (PME) method [32,33] for electrostatics, and an analytical dispersion correction for Lennard–Jones interactions. Bonds were kept rigid throughout the whole simulation using the linear constraint solver LINCS [34].

2.2. Estimating contact adhesion

One objective of this study was quantification of the contact adhesion between the cellulose crystal and its surrounding medium in order to evaluate the effect of surface modifications. Here, the method used to estimate the adhesion between the two components is described in detail. The cellulose surfaces (modified as well as non-modified) are termed medium A and the surrounding medium (water or CL) medium B (reconsider Fig. 4 for a pictorial view of the systems). The modeled interaction energy, $E_{AB}$, in a simulation of an interface between A and B was divided into two components within the force-field:

$$E_{AB} = E_{\text{Coulomb}} + E_{\text{LJ}}$$

The $E_{\text{Coulomb}}$ part contains the electrostatic interactions described by a Coulomb potential and it consists of one short range contribution from atom pairs within the cut-off of 1 nm and one long range contribution including atoms at distances larger than the cut-off. The $E_{\text{LJ}}$ part was modeled with a Lennard–Jones potential which describes the weak non-bonded interactions between two atoms as a combination of attractive van der Waals forces and steric repulsion. The Lennard–Jones interactions outside a cut-off of 1 nm are excluded. When A and B are separated from contact to infinity the reversible work required is termed work of adhesion or $W_A$. If this separation takes place in vacuum, $W_A$ will correspond to the sum of free energy per surface area of two free surfaces A and B minus the interfacial surface energy of the interface $AB$ as follows:

$$W_A = \gamma_A + \gamma_B - \gamma_{AB}$$  \hspace{1cm} (2)$$

The surface energy $\gamma$ is the change in free energy when a unit area is created:

$$\gamma = \frac{\partial F}{\partial A}$$  \hspace{1cm} (3)$$

To calculate Eq. (2) we need to know $\gamma_A$, $\gamma_B$ and $\gamma_{AB}$. We estimate surface energies by using the values of potential energies in the systems. An alternative would be to calculate surface energy from the differences in normal and lateral pressures using the pressure tensor obtained from simulations. This approach would require additional simulations of free interfaces against vacuum in order to calculate work of adhesion. The advantage is that both energetic and entropic contributions are taken into account with this method. The infinite cellulose crystal surface has very small possibilities to change its conformation, and the assumption is that entropy changes will be small for the crystal and in principle cancel out for the surrounding media. An energetic consideration is straightforward and assumed to be sufficiently correct when comparing the nature of the different interfaces of interest.

Moreover, the GROMACS simulation package provides the possibility to extract energy contributions between pre-specified groups in one single simulation. Instead of combining results from several different simulations, $W_A \approx \frac{E_{\text{inter}}}{\text{Area}}$ from the interaction energies across the interface in one interfacial simulation is calculated. This approximation is justified by substituting the terms in Eq. (2) with the expressions from Eqs. (4)–(6), where $E_A$ and $E_B$ correspond to energy differences between a bulk system and a system with a free surface.

$$\gamma_A \approx \frac{E_A}{\text{Area}}$$  \hspace{1cm} (4)$$

$$\gamma_B \approx \frac{E_B}{\text{Area}}$$  \hspace{1cm} (5)$$

$$\gamma_{AB} \approx \frac{(E_A + E_B - E_{AB})}{\text{Area}}$$  \hspace{1cm} (6)$$

The calculation of $W_A$ is also highly dependent on the definition of interfacial area. In the context of practical adhesion, the main interest is to increase the adhesion of a given interfacial area between cellulose and matrix polymer. Therefore, it is here more relevant to use the nominal area of the entire cellulose crystal rather than the accessible surface area, which takes into account that the surface is not completely flat on the molecular level. The accessible area would increase with increasing degree of substitution, but in the nominal surface area is fairly constant in the different systems. The area used here is defined as time average of the XZ box area which corresponds to the interfacial area between the cellulose (110) crystal surface and its surrounding medium.

Fig. 4. Graphical representation of systems with from the left, 0%, 50% and 100% degree of substitution with H6 atoms exchanged for grafted caprolactone. The medium (water or CL) surrounding the cellulosic surfaces is represented in the upper and lower parts of each interfacial system.
3. Results and discussion

Here, results from the analysis of the MD simulations are presented and discussed. The interfaces are analyzed with respect to system structure as revealed by density profiles, interfacial energies, hydrogen bonds between cellulose and surrounding medium and conformation of hydroxyl groups.

3.1. Density profiles

Figs. 5 and 6 show density profiles in the surface normal direction (Y direction in Fig. 4) of the interfacial parts of the different systems. Density is depicted as a function of distance from interface, where the interface is set to be where cellulose and surrounding medium densities are equal. The cellulose crystal density profile in the interior of the interfacial systems is similar to a bulk crystal profile. Both water and CL structure is affected by the interface. At the non-modified surface, water shows one peak of much higher density at about 2.5 Å from the surface and one less distinct peak at 5 Å after which the bulk density seems to be reached. The behavior is similar also at modified cellulose surfaces. On the other hand, the CL systems in Fig. 6 show a difference with increasing DSH6. At non-modified cellulose surfaces, the CL shows a layered structure with clear density peaks even at a distance of 25 Å from the surface, where the system ends. In contrary, at the modified surfaces the grafted caprolactone seems to affect the surrounding CL so that it reaches bulk structure earlier, at a distance of about 15–20 Å.

The density profiles for the grafted caprolactone monomers show no difference between the water and the CL interfaces. The grafted monomers seem to protrude just as much from the cellulose surface when interacting with water as when they interact with CL.

3.2. Contact adhesion

In a polymer matrix reinforced by cellulose fibers, the interfacial adhesion should ideally be very strong in order to provide efficient load transfer across the fiber-matrix interface. If the interfacial adhesion is poor, the fibers will debond from the matrix at low strain. Here, contact adhesion is considered as calculated from electrostatic Coulomb interactions and weak Lennard–Jones interactions over the interfaces.

Work of adhesion ($W_a$), calculated as described in Section 2, for the six interfaces is presented in Fig. 7. The cellulotic surfaces in our systems consist of either pure cellulose or cellulose and grafted caprolactone. Thus, the
total interaction energy, as defined in Eq. (1), in a system with modified cellulose can be further divided into contributions from interactions between cellulose and surrounding medium, and between grafted caprolactone and surrounding medium. Therefore the bars are divided to show the contributions from the two surface components cellulose and grafted caprolactone monomers, respectively. One observation is that $W_A$ is in general higher between water and the celluloseic surfaces compared to CL. The figure also shows an increase in the total $W_A$ with increasing amount of grafted caprolactone monomers onto the surface, at both CL and water interfaces. This increase in $W_A$ can be assigned to the fact that the grafted monomers will increase the effective surface area available for molecular interaction since the data in Fig. 7 is based on calculations with the nominal ‘flat’ surface area. The importance of the interactions between the grafted caprolactone monomers and the surrounding medium is clearly visible in Fig. 7, since at 100% DSH6 the $W_A$ is completely dominated by these contributions. Simultaneously, the interaction between cellulose molecules and the surrounding medium decreases with increased DSH6.

The relative amounts of contributions from Coulomb and Lennard–Jones interactions within the work of adhesion is shown in Fig. 8. The $W_A$ was found to be dominated by Coulomb interactions in all systems. Nevertheless, the weak Lennard–Jones interactions at cellulose–CL interfaces were found to be more important than for the more polar cellulose–water interfaces. In each system the relative amount of contributions from Lennard–Jones interactions increased slightly with increased DSH6.

### 3.3. Hydrogen bonds at interfaces

Further interfacial details can be obtained by investigating the hydrogen bonds between the cellulose surface and the surrounding medium. Hydrogen bonds were here detected by geometric criteria. A hydrogen bond is present if the distance between donor and acceptor oxygen falls within a cut-off distance of 0.35 nm and the angle donor–hydrogen–acceptor is larger than 150°. The average number of hydrogen bonds between different groups of the cellulose surface molecules and the surrounding medium are presented in Table 2. The time average of the total number of hydrogen bonds was calculated and divided by the number of available groups on the surfaces. Values higher than 1 indicate frequent occurrence of shared hydrogen bonds.

The figures in Table 2 indicate that the O3H3 hydroxyl group is only involved in a few hydrogen bonds with the surrounding medium, whereas both O2H2 and O6H6 (when present) are more inclined to interact with foreign molecules (see Fig. 1 for definition of atom names). This is not very surprising, since the glucan chains in cellulose have strong intra-molecular hydrogen bonds between all O3H3 and O5 in the chains [21], whereas O2H2 and O6H6 in bulk only form inter-molecular hydrogen bonds, which were lost when the (110) surface was created. The ring oxygen O5 and the oxygen located between two glucose units, O4, seem to be barely accessible to surrounding medium. Since water molecules are small, mobile and consist of only oxygen and hydrogen, cellulose–water interfaces have more hydrogen bonds than cellulose–CL interfaces. At modified surfaces (Water50, Water100, CL50 and CL100) the major share of interfacial hydrogen bonds is formed between the grafted caprolactone monomers and the surrounding medium. Increasing the DSH6 from 50% to 100% reduces the mobility of both the grafted monomers and the surrounding medium near the surface. This may cause the observed decrease in the number of interfacial hydrogen bonds at 100% compared to 50% DSH6.

### 3.4. Conformation of hydroxyl groups

Changes in hydrogen bonding pattern for the different surface hydroxyl groups also imply a change in their conformations. Two torsional angles specify the orientation for the cellulose hydroxyl groups O2H2 and O3H3 (see Fig. 1 for atom names), namely $\tau_2$ (C1–C2–O2–H2) and $\tau_3$ (C2–C3–O3–H3). The orientation of the hydroxymethyl group is commonly defined by the torsion angle $\omega$ (O5–C5–C6–O6). These angles were determined for all groups at different distance from the surface.

Time averages were calculated from MD simulations for groups located on surface chains pointing outwards (L10), surface chains pointing inwards (L1i) and the cellulose layer located just beneath the surface layer (L2). The occurrences could in principle be divided into three categories of conformations at about 60°, 180° or 300°. Relative conformational distributions for $\tau_2$ and $\omega$ in the different layers are presented in Fig. 9. The data for $\tau_3$ is not shown since...
it preserved its bulk conformation (about 180°) even for hydroxyls protruding from surface chains. This is expected from both experiments on cellulose reactivity [35] and our observation that O3H3 is not involved in hydrogen bonds between cellulose and surrounding medium.

The hydroxymethyl conformation ω is known to be ω = 180° in cellulose Iβ [21], this conformation is often referred to as tg. At cellulose crystal interfaces with water, the conformation has been found to be a mixture of the other two conformations, ω = 60° (gt) and, ω = 300° (gg) with different preferences. Our results show a preference for the gg conformation which is in agreement with NMR experiments [36]. The preference for ω seems to be 180° at all surfaces while the bulk conformation about 60° is found for all other layers.

One important conclusion from Fig. 9 is that only the conformation of the protruding groups are affected by the surrounding medium. Hydroxyl groups pointing inwards from surface chains seem to stay in their bulk conformations and the crystal bulk structure beneath the surface layer is preserved.

4. Conclusions

Molecular dynamics (MD) computer simulations provide an interesting alternative route to investigate interfaces between cellulose and polymers. Although other semi-empirical approaches can predict interfacial contact adhesion for material combinations dominated by Lennard–Jones interactions, the Coulomb interactions have proved to be much more difficult to analyze. Rather than scalar values for surface energies, MD uses physics-based energy functions where the parameters instead correspond to force constants and distributions of electric charges. The energies are thereby obtained as simulation results instead of being assumed in advance.

Work of adhesion as calculated from interaction energies increased with increasing amount of grafted monomers onto a cellulose surface, either the surrounding medium was water or CL. In general, the adhesion between water and the surfaces was larger than between CL and the surfaces. One explanation for this is that the grafted monomers increase the accessible surface area, whereas the flat surface area was used for the calculations of work of adhesion.

It was possible to analyze the proportions between Lennard–Jones and Coulomb interactions between cellulose and surrounding molecules. Non-modified cellulose surfaces interact with water and CL predominantly through its surface hydroxyl groups. The groups that are most inclined to participate in hydrogen bonds with a surrounding medium are the O2H2 and O6H6 groups. These groups also change their conformation on the surface. Only hydroxyl groups protruding from the surface changed conformation, all the other hydroxyls stayed in their bulk conformation. At cellulose interfaces with water, the hydroxymethyl conformation is predominantly gg, in agreement with experimental NMR data. Surfaces with modified 06H6 groups and a DSH6 of at least 50% interacted with the surrounding medium mainly through the grafted caprolactone.

The type of interactions was then principally Coulomb interactions, although the importance of weak Lennard–Jones interactions was larger when the surrounding medium was CL instead of water. Hydrogen bonds were formed extensively between the grafted caprolactone and the surrounding medium.

The overall goal with surface modification is to increase the interfacial adhesion between cellulose and polymer. The work of adhesion between cellulose and water is high, even higher than the work of adhesion between cellulose and the monomeric CL system studied here. When the cellulose surface was modified with grafted monomers, the work of adhesion increased both for water and CL showing that this form of modest modification with monomers grafted onto a cellulose surface is not enough to improve the adhesion between cellulose and CL when water is present. Increasing the degree of polymerization for the grafts would probably be more advantageous.

Density profiles at the interfaces show that CL at cellulose surfaces grafted with caprolactone reached bulk
density faster than at non-modified surfaces, whereas the structure of water was the same both at non-modified and modified surfaces.

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