Preferred citation: A. Paajanen, P. Penttilä, A. Zitting and J.A. Ketoja. New tools to study water interactions of microfibril bundles: molecular modelling based on nanoscale characterization. In *Advances in Pulp and Paper Research*, Cambridge 2022, Trans. of the XVIIth Fund. Res. Symp. Cambridge, 2022 (D. Coffin and W. Batchelor, eds), pp 483–494. FRC, Manchester, 2022. DOI: 10.15376/frc.2022.1.483.

NEW TOOLS TO STUDY WATER INTERACTIONS OF MICROFIBRIL BUNDLES: MOLECULAR MODELLING BASED ON NANOSCALE CHARACTERIZATION

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ABSTRACT

The picture of the smallest structural units of wood fibres, that is, cellulose microfibrils and their bundles, has become more accurate during the last couple of decades, when information gained from several experimental characterisations has been drawn together. This work has been supported by computational methods that allow one to test the behaviour of postulated structures on the nanometre scale, and thus help in interpreting the experimental data. Bound water is an essential component in these models, as it affects both the structural swelling and the mechanical properties of the fibre wall nanostructure. Moreover, mechanisms on this scale can be expected to drive similar properties of macroscopic fibres. We suggest that several large-scale problems in papermaking and converting could be approached with atomistic molecular dynamics simulations for varied chemical compositions and external conditions. We demonstrate this by first showing that simulated moisture diffusion rates agree with measured ones at room temperature, and then determine diffusion

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rates at elevated temperatures that lack reliable experimental data. These predictions provide key knowledge for further development of high-temperature drying and pressing processes. The results are important also when linking material performance at varied external conditions to the composition of the fibres.

1 INTRODUCTION

Many of the macroscopic properties of cellulosic fibres and fibre materials are sensitive to moisture. As bound water can be generally associated with the fibre wall nanostructure [1], we can expect the macroscopic properties to be also dominated by mechanisms at this scale. The smallest structural units of the fibre wall are cellulose microfibrils (diameter 3–4 nm) and their bundles, whose main components are crystalline and amorphous cellulose and different hemicelluloses. The chemical composition of the fibre wall determines the distribution of bound water, which affects both the structure and the mechanical properties of paper, including properties such as elasticity and creep.

Earlier experimental studies [2–4] have found both elastic modulus and creep to depend exponentially on moisture content (MC). A thorough explanation for this behaviour is still missing. [5] In earlier papers, the moisture-induced changes in mechanical behaviour have been often associated with softening of the amorphous polymer components as described by underlying glass transitions for lignin, hemicellulose and cellulose (see e.g. [6]). In his classic paper, Goring [7] considered sorbed water to act as diluent in plasticising the polymers. He reported a pronounced decrease of the softening temperature coming from sorption of water by isolated lignin and hemicellulose. Crystalline cellulose lacked a similar effect, and Goring concluded that water did not plasticise individual cellulose chains but would rather be adsorbed on the microfibril surfaces. Later Salmén and Olsson [8] refined the picture of the structural arrangement of the wood polymers within the secondary fibre wall. By studying delignified fibres, they found that xylan was responsible for the observed softening (at c.a. 75 % RH, 80°C), while attachment of glucomannan to the cellulose surface appeared to prevent softening of that hemicellulose.

Water diffusivity is another example of exponential dependence on MC. Topgaard and Söderman [9] used nuclear magnetic resonance (NMR) measurements to determine the self-diffusion coefficient of water absorbed in cellulose fibres, and they found the diffusivity to depend exponentially on MC in the range 0.15–0.2 g/g (water mass/dry mass). Quantitatively similar behaviour had been found indirectly by Gupta and Chatterjee [10] when modeling moisture diffusivity through paper samples. Perkins and Batchelor [11] carried out NMR diffusion measurements at an intermediate MC range of 0.2–1.2 g/g for varied pulps, and they found good agreement with a model of slow and fast diffusion components. The diffusion along the paper plane was described by the slow component up to about 0.5 g/g moisture level. For fully saturated fibres, the level of diffusion constant, $2–12 \times 10^{-10}$ m^2/s [11, 12], has also been obtained by molecular simulations of water bound to crystalline cellulose [13]. The speeding up of diffusion in saturated redwood at increased temperature was measured to be described by an activation energy of 28 kJ/mol in the range of 4–55°C. [12]

We expect all these phenomena, including equilibrium bound water content [8], moisture diffusion and fibre softening to originate from the same nano-scale structural level. In this paper, we discuss this idea by using water diffusivity as an example of the interplay between fibre wall nanostructure and the studied macroscopic property. The rate of moisture diffusion is important for many phenomena in paper physics such as drying processes [14] and dimensional stability in printing [15, 16]. This relevance is caused mainly by slow diffusion at a low MC, which often becomes either a bottleneck for water transport (like for the final stage of web drying) or causes unwanted interactions with the process time scales (like for subsequent printing units). For uneven moistening, the impact can be multiple: increasing MC speeds up moisture diffusion that exponentially accelerates the relaxation of a fibre network causing severe cockling or curling of the paper web. Thus, it is important to understand how the fibre ultrastructure and chemical composition and external parameters like temperature affect the molecular diffusion rate.

Molecular simulations have been recently introduced to the study of the fibre wall nanostructure. [17] Their main advantage is the capability to probe molecular-level structures and processes that are difficult to observe experimentally. In the present work, we use models of cellulose microfibril bundles to study the effects of water sorption on their structure and on the mobility of bound water. We assume that hemicelluloses are bound to the fibril surfaces and thus present within the bundles. Similarly, we assume that the bound water of the fibre wall resides on the fibril surfaces. A previously developed nanoscale structural model (Figure 1) [17–19] is taken as a starting point for diffusion simulations at room temperature at varied MCs. The idea is to confirm that our simulations are able to describe the earlier experimental diffusion results with sufficient accuracy. The model is then used for taking a closer look at how bundle swelling and surface interactions affect the observed dynamics. Moreover, we repeat the simulations in a wide temperature range of 27–407°C and compare the results with simple activation models.

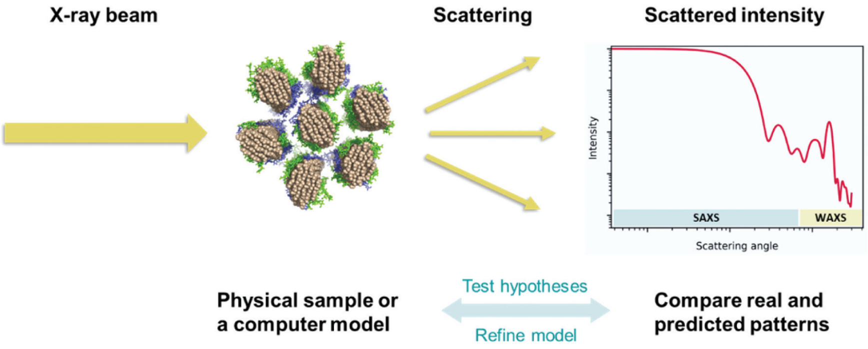

Figure 1. The models of cellulose microfibril bundles are based on previous work that combines molecular simulations and X-ray/neutron scattering measurements to study the moisture behaviour of the fibre wall nanostructure. [17, 18, 19] The molecular visualisation represents a cellulose microfibril bundle with hemicelluloses adsorbed on the fibril surfaces.

2 SIMULATION METHODS

Molecular models of cellulose microfibril bundles were used to study the effects of MC on bound water diffusivity within fibre walls. A recently proposed model for the nanostructure of spruce secondary cell walls [20] was used as the basis for model building.

The basic structural unit is the cellulose microfibril (Figure 2a). The microfibrils were chosen to consist of 18 cellulose chains arranged in the hexagonal 2-3-4-4-3-2 stacking (Figure 2a) [21]. Each chain consists of 34 glucose units, and the last unit of the chain is bonded to the first one across the periodic boundary of the simulation box. The fibril model was generated based on the cellulose Iβ unit cell [22]. Eight models of hemicellulose coated fibrils were then created by simulating the adsorption of galactoglucomannan (GGM) and glucuronoarabinoxylan (GAX) chains on the fibril surfaces (Figure 2b). The hemicelluloses were assumed to be aligned with the microfibrils and to reside on their surfaces. Cellulose-GGM mass ratio was chosen to be roughly 9:2, and the cellulose-GAX mass ratio roughly 9:1. The mass ratios and the chemical structures of the hemicelluloses were chosen to mimic those found in spruce secondary cell walls (see [18] for further details). Both the GGM and the GAX chains consist of 30 repeat units.

The hemicellulose-coated fibrils were then used to build a periodic model of a fibril bundle. Four such fibrils were arranged in a periodic simulation domain to form an infinite hexagonal lattice (Figure 3). The initial inter-fibril distance was chosen to be 5 nm. The space between the fibrils was then filled with water, which resulted in a system with an MC of at least 100% ($m_{\text{water}}/m_{\text{dry}}$).

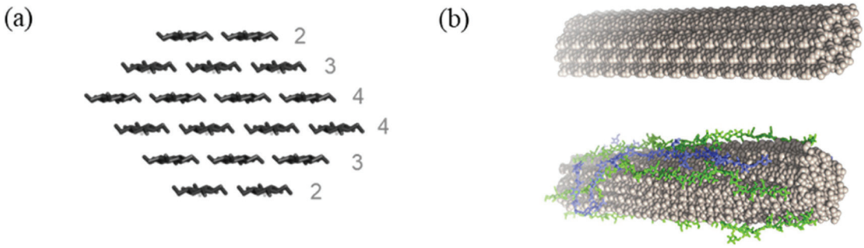

Figure 2. (a) Cross-section of an 18-chain microfibril model. Cellulose chains are shown in the stick-representation of covalent bonds. The hydrogen bonded layers of cellulose I_β are labelled according to the number of constituent chains. (b) Space-filling representation of a microfibril segment of 30 anhydroglucose units with and without adsorbed hemicelluloses. Cellulose chains are coloured brown, GGM chains green and GAX chains blue. The hemicellulose-coated fibril displays a helical twist.

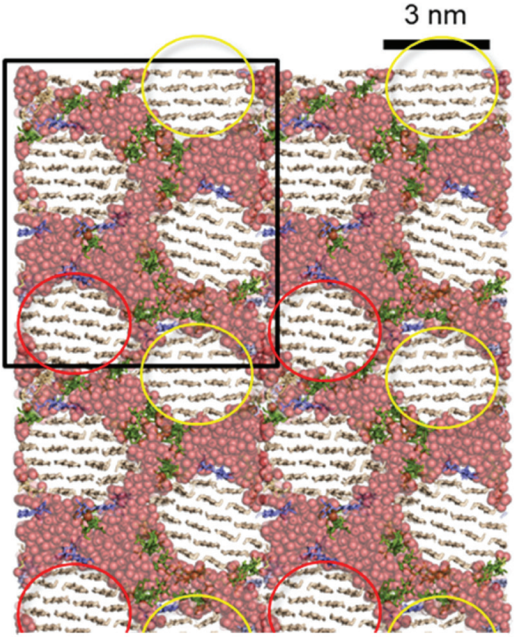

Figure 3. Cross-sectional view of the microfibril bundle model. The periodic simulation domain is outlined in black. Periodic images of two of the fibrils are highlighted by red and yellow outline. Cellulose chains are coloured brown, GGM chains green and GAX chains blue. Water is coloured red. The MC of the system is 40 % ($m_{\text{water}}/m_{\text{dry}}$).

A hybrid Monte Carlo and molecular dynamics (MD) scheme [23] was used to study the response of the fibril bundle to changing MC. In the simulation protocol, 10 randomly chosen water molecules were removed from the system in between 100 ps simulations of molecular dynamics. After each percentage point decrease in moisture content, a longer 1 ns simulation was carried out. This procedure was followed until the system was completely dry. Sampling simulations of 200 ns were then carried out for chosen moisture contents. After this, molecular configurations for MCs 5–65 % at 300 K were heated to 480 K over 200 ns to obtain corresponding configurations at 360 K, 420 K and 480 K. Lastly, sampling simulations of 200 ns were carried out for these configurations at the corresponding temperatures. All simulations were performed in the isothermal-isobaric ensemble at 1 atm external pressure.

The simulations were performed using GROMACS [24] and the GLYCAM06H force field [25]. Water was described using the TIP3P model [26]. Temperature control was implemented using a stochastic variant of the Berendsen thermostat [27]. Pressure control was implemented using the Berendsen barostat [28]. Damping parameters of 200 fs and 2 ps of were used for temperature and pressure control, respectively. The equations of motion were integrated using the velocity-Verlet algorithm with a 2 fs time step. Trajectory analysis was performed using GROMACS utilities. Molecular models of the hemicelluloses were generated using the doGlycans tool [29].

3. RESULTS AND DISCUSSION

Changes in moisture content affect the microfibril bundles in a number of ways. Our previous work using non-periodic models shows that water molecules penetrate the fibril bundles, which causes changes in the inter-fibril spacing and the bundle diameter. [18, 19] Comparison against models without hemicelluloses [30] indicates that the amorphous polysaccharides have a key role in the swelling. The periodic models with hemicelluloses predict a moisture-dependent inter-fibril spacing that is in quantitative agreement with small-angle X-ray and neutron scattering experiments (Figure 4). [18, 19] Changes in moisture content also affect the internal structure of the fibrils. Most notably, the hydrogen-bonded layers of cellulose chains move further apart at low moisture contents and the chain length slightly contracts. Structural changes to the microfibril bundles are discussed in detail in [19]. In what follows, we focus on the effects of moisture content and temperature on bound water diffusivity.

We determined the diffusion coefficients at each MC and temperature based on the Einstein relation, which links molecular diffusivity with mean-square displacement:

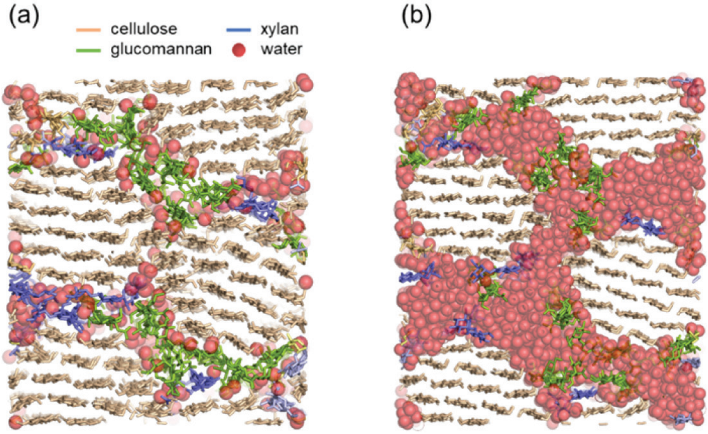

Figure 4. Microfibril bundle at (a) MC 5 % and (b) MC 40 % (water mass/dry mass). [18]

$$\left\langle r_i^2(t)\right\rangle = \frac{1}{N}\sum_{i=1}^{N}[r_i(t)-r_i(0)]^2 = 6Dt \tag{1}$$

where $r_i(t)$ is the position of water molecule i at time t, N is the total number of water molecules and D is the diffusion coefficient. Figure 5a shows the predictions for the axial direction of the bundles. Diffusion in the transverse direction is markedly slower. The limiting behaviour is particularly interesting. At MCs below 15–20%, the diffusivity grows exponentially with MC:

$$D \sim e^{\mu MC} \tag{2}$$

The value of the exponent μ at room temperature, 0.28, is in agreement with the result of Topgaard and Söderman for water absorbed in cellulose fibres, approximately 0.24 (see Figure 15 of [9]). The rate of change decreases above MC 25–35%, and the diffusivity ultimately reaches a level of 50–75% of the self-diffusivity of water. Our results for room temperature are similar to those of Kulasinski et al. [31], who studied water diffusion in amorphous polysaccharides and aggregated cellulose microfibrils. Inspection of the molecular trajectories shows that the exponential increase in diffusivity coincides with the formation of nanoscale channels of water, in which the water molecules are not in direct contact with the interfacial hemicelluloses.

Our results at elevated temperatures display the expected increase in diffusion rate. Otherwise, the diffusion behaviour remains similar to that observed at room

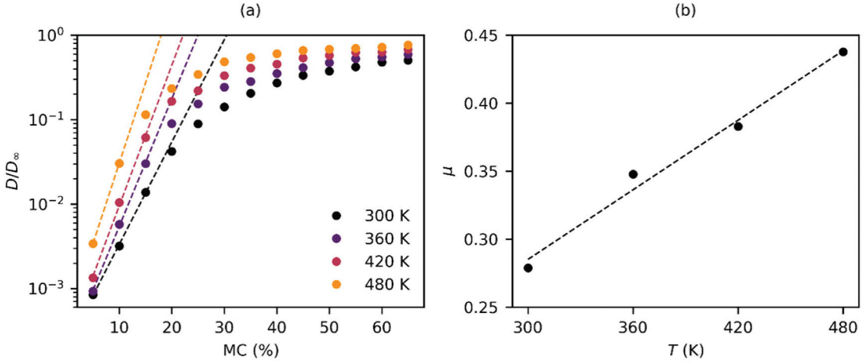

Figure 5. (a) Water diffusivity within the periodic microfibril aggregate at different moisture contents and temperatures. The diffusivity is normalised by an estimate for the self-diffusion coefficient of water D_∞ (to account for systematic over-estimation due to the TIP3P water model). (b) Exponential factor μ of Eq. (2), determined at low moisture contents, as a function of temperature.

temperature. The exponential growth becomes more pronounced with increasing temperature, and the onset of deviation from simple exponential behaviour shifts towards lower MCs. The value of the exponent μ depends roughly linearly on temperature, as shown in Figure 5b. Figure 6a shows Arrhenius plots of the logarithmic diffusivity versus inverse temperature for the MC range 15–65 %. Diffusivities for the lower MCs are omitted, since they clearly deviate from an Arrhenius-like temperature dependence

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

where E_a is the activation energy and R is the gas constant. We determined the apparent activation energy and prefactor D_0 for the above MC range through linear least squares fits, as shown by the dashed lines in Figure 6a. Figures 6b and c show the activation energy and the prefactor as a function of MC, respectively. The obtained activation energy has a similar level as the one measured earlier for saturated redwood [12].

Eqs. 2 and 3 can be used to estimate how moisture and temperature affect the paper web drying processes. The water removal is limited by the diffusion of bound water inside fibres during the final falling-rate phase of drying. The associated decay in drying rate originates from the exponential dependence of diffusion on moisture content as depicted by Eq. (2). However, the diffusion can be greatly

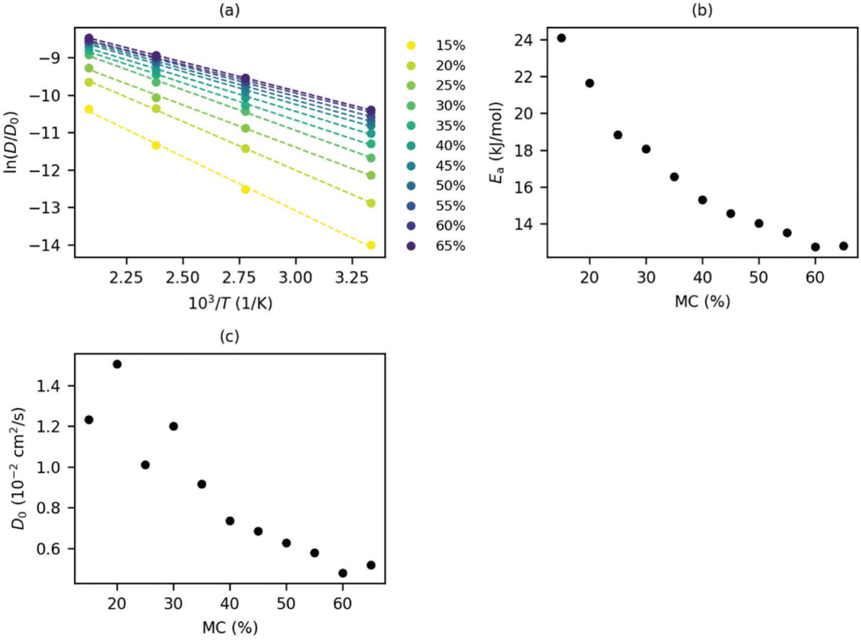

Figure 6. (a) Arrhenius plots for water diffusivity at different moisture contents. Linear least-squares fits are shown as dashed lines. (b) Apparent activation energy and (c) pre-exponential factor as a function of moisture content.

speeded up by increasing the temperature. For example based on Eq. (3), water removal at a temperature of 200°C, which is typical for hot-pressing [32] or heatset printing, can be expected to be an order of magnitude faster than in conventional cylinder drying [14] at temperature of 80°C (here we assume that MC < 20%). Direct measurements of the diffusion rate at such high temperatures would be extremely difficult.

Analysis of the molecular trajectories shows that a significant amount of water is confined within the hemicellulose-coated surfaces of the fibrils. In addition, the simulations predict the existence of two bound water populations with distinct diffusion behaviour. The presence of distinct water populations in wood cell walls has been observed in both two-dimensional low-field NMR and neutron scattering studies. [33] Similar behaviour has also been reported in a previous molecular modelling study of water diffusion in amorphous hydrophilic polymers. [31]

CONCLUSIONS

We have introduced a molecular model that describes the internal structure of microfibril bundles within wood fibre walls. The essential structural features of the model agree with X-ray and neutron scattering results on the crystal lattice parameters of the microfibrils and the packing of the microfibrils in bundles at varied MC. This structural level is expected to be the origin of many central phenomena in paper physics, such as bound water content, chirality, swelling, stress relaxation, and water transport. The model was applied to predict moisture diffusion rate at varied temperature and MC, and the results were linked to interactions of water molecules with cellulose and hemicelluloses and to changes in the bundle structure. We found good agreement with earlier discovered experimental trends, which makes the simulation results highly interesting at conditions where diffusion experiments are difficult or even impossible.

The above example shows that modern characterisation and simulation tools enable moving from phenomenological models to direct molecular descriptions of the phenomena underlying measured fibre properties. The atomistic models can be further extended to coarse-grained models that describe a higher level of the fibre wall structural hierarchy. Information from such models can then be used at the fibre network level. This kind of approach not only helps in getting a more coherent picture of the phenomena at various scales but also removes unknown parameters from the models, improving their predictability.

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Steve Keller Miami University

Assuming they are wood fibres that you are modelling, you are dealing with cellulose I. Am I correct?

Antti Paajanen

Yes.

Steve Keller

What are your thoughts about the penetration of water for something such as Cellulose I or Cellulose II? That is a sulfite pulp has Cellulose I structure, and kraft would contain Cellulose II. How would that influence your perception of how the water penetrates the different crystalline structures?

Antti Paajanen

I actually do not know the microstructure of these regenerated celluloses very well. So obviously, it will depend on the conditions in which they crystallise. But when you are talking about fibres, crystallites are obviously somehow elongated, but they are probably not like the ones in native cellulose, and at least would not have the hemicelluloses in them. So, in some of our previous work, we have observed that, if we assume this type of aggregate structure, the hemicelluloses are absolutely central for water to be able to penetrate the fibril interfaces. So, that would at least be one difference. Also, a quite interesting thing is that our models seem to imply that the crystallite size needs to be more or less what we have used. If they were bigger, the fraction of surface chains would become smaller, and the surface effect would not produce those kinds of shifts in peak locations anymore. So, the fibril needs to be that small to produce that kind of shift. This might also be something that could be observed with regenerated cellulose.

Artem Kulachenko Royal Institute of Technology (KTH)

That was a very interesting presentation from the point of view of what you could achieve with molecular scale simulations. You resolve water explicitly. Could you elaborate on how you remove the water molecules? What are the conditions? Because it’s always a problem with this approach.

Antti Paajanen

You can do it, in practice, in two ways. The brute force way is just to remove water molecules randomly, which then is perhaps a bit far away from what happens in the real system. Of course, we have to keep in mind that we have no consideration of any larger-scale effects regarding how water moves away from such a system, so our models represent more or less a sequence of equilibrium structures. The other way to remove the water molecules is to consider the potential in which they are sitting in the system. In other words, take out those water molecules that you would expect to be removed based on where they are sitting. We did the brute force approach. In this “quick and dirty” approach, we removed water molecules by force and then equilibrated the system. So, that is one place where this can be made more accurate. Others have done it for similar systems using both ways, and their results do not differ that much. What they get from the more sophisticated approach is actually a kind of simulated water sorption isotherm. So, using that approach, we could study a kind of sorption hysteresis phenomenon – what happens when you go up and down in the moisture content, what kind of path the system takes.

Artem Kulachenko

My next question is whether you can look at effects such as hornification of the fibre using this technique.

Antti Paajanen

Well, of course, then you have to do some assumptions about what hornification exactly is, but if we take it to be the loss of interfacial surface area, you could do a simulation of a bit larger system. You could really go down in the moisture, even to zero, and then try to push water in and see whether it goes in and what kind of structures it leaves, and if it is reversible or not. So that is doable, but then the challenge is how to interpret what you get from the model.

Lars Wågberg KTH Fiber and Technology

I would like to continue what Artem asked about hornification. One of your slides shows that at higher moisture contents, you showed that there is an increased mobility of the surface fibrils. Was that interpreted from the change in the 200 signal of the cellulose, or what was it based on?

Antti Paajanen

The scattering interpretation was taken from both the experimental and the simulated scattering curve. But since that does not yet tell us where that shift in the signal comes from, we then based it on the similarity between the experimental and simulated scattering intensity. We assume that the model is working more or less right, so we can look deeper into the model to find out where this shift comes from. And we saw that the core chains of the crystallite or fibril remained more or less unaffected, and that the shift in the 200 direction, for instance, came from the surface chains. And also, we saw the distribution of these distances change. Not only are the chains moved further apart, but there are some chains that are far removed and others that sit more tightly on the surface. Then we further looked into the chain conformations, hydrogen bonding statistics, and just looked at the visualisations to figure out what happens. Our best guess is that the effect comes from fibrils colliding in orientations where they cannot crystallise. So, you form a grain boundary between the fibrils, and that causes the distortion.

Torbjorn Wahlstrom Stora Enso

I was thinking about the water removal and the dimensional changes. There is some work available where people have been looking directly and measuring the transversal shrinkage of the fibre versus moisture, and it is found that a vast majority, actually almost all, of the shrinkage happens at the very end of the drying. That is obviously not seen here. Is there an opening in your model for such an effect? Or is that maybe happening on some other structural level, or what are your thoughts around this?

Antti Paajanen

This is regarding the fibril bundles, so obviously in the fibre we have higher-scale structures. We have the porosity there, so I am not really sure. From our models, you can at least see the scale of the effect in the nanoscale structures. So, from 4 to 3 nanometre spacing – approximately 1/4th of shrinkage. I am perhaps not in the position to say what that means at the fibre level. I don't know. Maybe some of my colleagues who work with me have thoughts on this?

Jukka Ketoja VTT Technical Research Centre of Finland Ltd

I have no idea.