

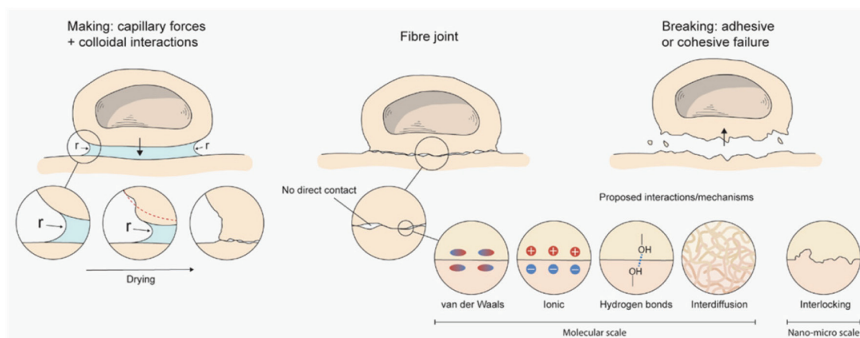
# FUNDAMENTALS OF INTERACTIONS BETWEEN CELLULOSE-RICH SURFACES

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The molecular mechanisms behind the interactions between fibres in fibrous networks, and their link to paper/network strength, have long been under intense scientific investigations and scientific debate (Wågberg and Annergren 1997, Lindström et al. 2005; Hirn and Schennach 2017) but still there is no unified view on how the strength of fibre/fibre joints and network strength can be linked to different molecular mechanisms (Wohlert et al 2022). Historically the interaction between cellulose-rich fibre surfaces was ascribed to hydrogen bonding and elaborate models were developed for linking mechanical properties of fibrous networks to the H-bonding between the surfaces (Nissan and Batten Jr 1997). This is however an oversimplification for several reasons. First of all, the H-bonds are very specific, which means that they are short-ranged and not implicitly additive over the material volumes engaged in the contact region between the fibres. Secondly the molecular interactions in the fibre/fibre contact zones are actively participating in the formation of the fibre joints, i.e. in the making of the fibre/fibre joints. The interactions in the wet state will hence affect the dimensions of the wet and dry contact zones and they will also create built-in stresses in the zones of contact in the dried fibre/fibre joint. The dry mechanical properties of the fibrous networks, i.e. the breaking of the joints and the fibres, will then be controlled by the molecular contact zone, the interactions in the contact zone, and also outside the molecular contact zone but within the molecular interactions range, the number of molecular contacts/network volume and the individual fibre strength. This is schematically illustrated in Figure 1 below.

During the past decades there has been a very interesting and important development of high resolution measuring techniques where both fibres (Lindström



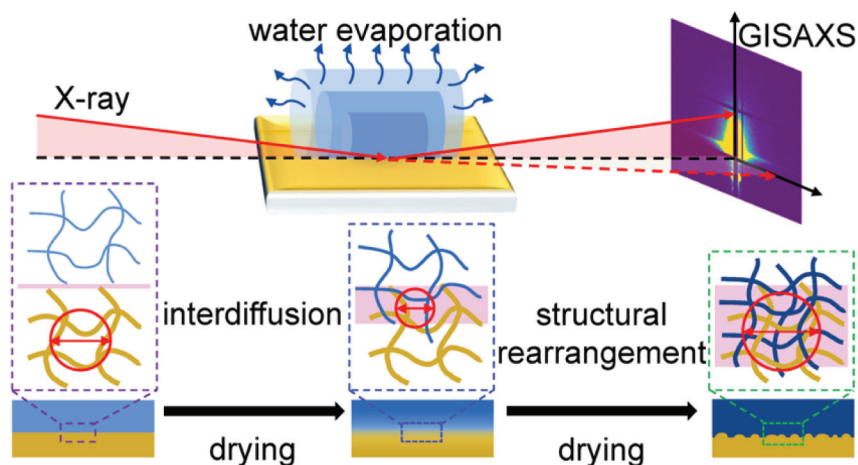
**Figure 1.** Schematic description of the making and breaking of fibre-fibre joints between cellulose-rich surfaces. The wet fibres are pulled together by the capillary pressure and the wet fibre wall will yield in the wet zone both due to the capillary forces and the molecular interactions, once the fibre surfaces are close enough. In the dry joint there will be areas in molecular contact and areas not in molecular contact but still close enough to allow for an interaction between the surfaces. Of the proposed mechanisms, only van der Waals and ionic interactions are significant when there is no direct molecular contact (during the making of the joints in the wet state). (Adopted from Wohlert et al, 2022)

et al 2005, Hirn and Schennach 2015, Schmied et al 2015) and model surfaces have been used to elucidate the molecular nature of the formation of and the nature of the fibre/fibre joints (Li et al 2020, Li et al 2021). By using wood-based fibres it is difficult to establish the true molecular contacts area since the fibres are very rough (on a nano-meter scale) and the polydispersity of fibre properties is immense. Therefore, the use of smooth and well-characterized model-surfaces provides a very promising route for establishing the relative importance for different molecular mechanisms provided that the model materials show similar properties as cellulose-rich fibres regarding swelling properties and wet mechanical properties. A similar swelling behaviour as cellulose-rich fibres has indeed been found for regenerated cellulose beads and filaments from cellulose nanofibrils (CNFs) (Karlsson et al 2020). It has also been found that films from Cellulose II, prepared from regenerated cellulose (Fält et al 2003), and cellulose beads (Carrick et al 2014), containing non-ordered cellulose, have a nanometer-smooth surface which allows for precise studies of the molecular mechanisms behind the interaction between cellulose-rich surfaces.

Recently it has been shown that a combination of these model surfaces and high-resolution Grazing Incidence Small Angle X-Ray Scattering (GISAXS) techniques for characterizing the development of the structure between model

surfaces of cellulose renders a totally new insight on how the surfaces are affecting each other (Li et al 2021). The results show that there seems to be an intermixing of the molecules in the external surfaces of the cellulose materials as the surfaces are approaching each other during water removal and that this will have a large influence on the development of the interaction between the dried surfaces. The results also showed that there seems to be a roughening of the surfaces at very small length scales during the drying of the surfaces. This is schematically summarised in Figure 2 where the GISAXS evaluation of the interaction between the two cellulose model surfaces is shown.

By using these model surfaces and careful covalent or physical modification techniques it will be possible to isolate how different treatments will affect the adhesion and the structure of the interface both during making and breaking of the joints. These types of investigations will indeed also lead to a better understanding of the molecular interactions at cellulose-rich interfaces and how these interactions can be controlled and optimized. It would also be very useful and desirable if the scientific community could spend more time on using similar model systems, similar techniques and similar modelling procedures in order to collectively isolate the molecular mechanisms behind fibre/fibre interactions.



**Figure 2.** Schematic representation of how well-characterized cellulose model surfaces can be combined with high resolution structure measurements in order to determine how the structure of the interface between the materials is developed during drying, how surface molecules can mix at the interphase and how this in turn will affect the dry properties of the formed joint between the materials. (Adopted from Li et al 2021)

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*Robert Pelton*     McMaster University

What is special about hyaluronic acid and why does it have such unusual properties?

*Lars Wågberg*

I have been trying to read up on it but I have no final answer. First of all it's a change in molecular structure of the polyelectrolyte. You change the ionic strength, and I also think that this leads to a stiffer dry material as the HA is combined with PAH. So, if you form a polyelectrolyte complex between PAH and HA and dry it, it forms a very stiff material which is probably important for its final effect in the dried paper or as a link between model surfaces. I guess much more can be understood from the polyelectrolyte properties of the HA but I haven't had time to read up on all of it. Maybe we can do it together.

*Gil Garnier*     Monash University

You showed us some beautiful filaments of the two polymer surfaces. The filaments that you show, are they individual polymer coils that are extended or are they assemblies of polymer chains diffusing one into the other?

## *Discussion*

### *Lars Wågberg*

When we are preparing the filaments we first have to dry them before treating them with the layer-by-layer technique. Following this, we are forming the joint, drying it and then testing the dry stress at break of the joint.

### *Gil Garnier*

Is it a single polymer coil that you stretch to 1 micron or the assemblies?

### *Lars Wågberg*

No these are polyelectrolyte complex structures that form after forming layer by layer. At an average, these layers are around 25 nm for 10 layer-by-layer assemblies they are really very thin. However, the strands that are strained emanate from the complexes where a lot of polyelectrolytes are present, NOT a single strand of polymer.

### *Gil Garnier*

Let's go back to the fibre-fibre cellulose bond together. Can you extrapolate these mechanics of diffusion; are we basically thinking that we have diffusion of individual cellulose chains into there from fibre to fibre?

### *Lars Wågberg*

When we are talking about layer-by-layers and monolayers, I think, based on our results, that the added polyelectrolytes are dominating the interdiffusion of polyelectrolytes at the interface. At the moment we are studying the hornification between cellulose surfaces and here the movement of glucan chains at the fibril surface can have a significant effect. We cannot detect any chemical reactions, regardless of how hard we try. So for nanocellulose based papers we can detect a significant hornification and this, I think, can be related to a diffusion of glucan chains across the interface.

### *Gil Garnier*

So, am I understanding that the mechanism of hornification can include both a permanent development hydrogen bond and a diffusion mechanism?

### *Lars Wågberg*

Yes, definitely and, depending on what you have adsorbed at the surfaces, these diffusion processes are more or less important. With the techniques I describe it

will also be possible to test the importance of H-bonding in comparison with other interactions if somebody can come out with an ingenious idea how to make the surfaces more or less prone to form hydrogen bonds. Based on our results and our understanding I do believe more in the diffusion in glucan chains from the less ordered outer layers of cellulose nanofibrils than the formation of “irreversible” hydrogen bonds. It needs to be critically tested though.

*Gil Garnier*

On your third slide you discussed the capillary forces and you showed two fibres coming in contact and the effect of roughness. Do you think roughness plays a critical role on the capillary force and is it something that we can use to control the bond strength?

*Lars Wågberg*

When it comes to the fibre level, I think that there is definitely no hydrogen bonding involved in the formation of the joints, it's not relevant at all. However, once the surfaces are brought closer together some hydrogen bonding can form. As to your other question the capillaries are all important and the cavities located at the surface would be very important for holding the surfaces together. Considering the geometry at the interface the capillary pressures are huge.

*Markus Biesalski*      Technical University of Darmstadt

Can you comment on the influence of molar mass of your polyelectrolytes that you use in the layer-by-layer technique? I assume at some point chain entropy also kicks in of the polymer chains that you searched, those must be multiple chains to stretch apart?

*Lars Wågberg*

As you saw the PAH, used in one of the examples, with a  $M_w$  of 56 kDa showed the best effect, but we haven't tested a very large range.

*Markus Biesalski*

At some point interdiffusion is very much dependent on molar mass?

*Lars Wågberg*

Yes, their  $M_w$  will have a large influence on their diffusion. In addition to this, their location at the surface, the removal of water in combination their  $M_w$  will

## *Discussion*

determine how fast they can diffuse. To form strong entanglements they they must have a certain molecular size so there is probably a maximum in  $M_w$  for forming strong intermixing and strong joints.

*Jon Phipps*      FiberLean Technologies Ltd

Microfibrillated cellulose (MFC) suppliers are very interested in wet web strength because we observe that MFC is particularly effective at increasing it. The wet web comes out of the papermachine press section at about 50% solids content, which we understand is much too wet for hydrogen bonding to occur; we assume the strength is enhanced by some other mechanism such as entanglement friction. So my question is whether any of the other bonding mechanisms that you have discussed could be active when the paper is still that wet?

*Lars Wågberg*

Yes, for the interaction between wet surfaces the dispersive interactions are active but still the surfaces have to be close for them to play a role. As a rule of thumb the surfaces have to be around 10 nanometres, and less, apart for the dispersive interactions to play a role which is probably the case when water has been removed in the press section and would hence be of importance for the initial wet web strength. However, I also think it's also that the entanglement and friction becomes very important for this property. When you have a significant amount of water present the effect of the hydrogen bonding is definitely insignificant.

*Ulrich Hirn*      Graz University of Technology

Obviously we were also looking into interdiffusion as a bonding mechanism, and I would like to hear your opinion on this. If interdiffusion would play a large role we should see an increase in the strength of fibre-fibre joints when they are formed slowly, or at higher temperature, and hence allowing for more interdiffusion. But we cannot observe this. In the paper machine, the process is very fast and in different labs the process can be arbitrarily slow, yet we always end up with similar joint strength. So this is why we came to the conclusion that maybe interdiffusion is not playing such a large role?

*Lars Wågberg*

You might very well be right in the standard papermaking situation. However, when we are preparing nanopapers and subsequently heating them for different times we see an enormous time dependence. So, I guess it's a question of how



close the surfaces are coming together, the mobility of the molecules on the surface and how much time you have for interaction before complete dryness. So, maybe in a paper machine this interdiffusion does not play such a big role but for hornification of cellulose materials it does.

*Ulrich Hirn*

Exactly, so I am not saying that it's not playing a role at all. I just wanted to bring up that we should be able to observe an influence of time and temperature if interdiffusion is relevant.

*Lars Wågberg*

Yes, I understand and what we are creating with different additives is that we are simplifying this joint formation between the fibres surfaces and the time scale for these processes is obviously of relevance for the time scales for water removal and drying in the paper machine.

*Ulrich Hirn*

Another thing I wanted to bring up is that when we study bonding on the molecular scale we can learn a lot, but in between molecular scale and fibre scale there are three orders of magnitude in size. In this size scale in between is where the fibre-fibre contact is formed, so in this size scale between nanometre and micrometre that is where we need to measure the (nanoscale) contact area, which controls hydrogen bonding and van-der Waals interaction.

*Lars Wågberg*

Yes, and I indeed know that you have been active in this area. It's a demanding task and you have done a fantastic job in that area. However, in Malin Erikssons work (*Ind. Eng. Chem. Res.* 2006, 45: 5279–5286) we measured the change in specific surface area with nitrogen gas absorption and the detected decrease in specific surface area with increased amount of additive was very large, but the measurements were repeatable and reliable and shows that the contact area in the sheets is largely increased without a macroscopic densification of the sheets. So, there we see when you add more layers we see a dramatic decrease in the specific surface area of the sheet, which indicates that you get a very very much tighter joining between the fibres and also the number of joints. So, I think that what you do with these additives is that you remove weak spots, you create new joints and you need to measure the BET area to be able to see them. You won't see them with light scattering as shown in our study.

## *Discussion*

*Ulrich Hirn*

That is for sure but the thing with BET is that you have a huge internal surface area and it is so difficult to interpret. Is this just a change of density or are we closing the pores because it all depends on BET for all absorption methods. They all depend on that you have access to the surface where it absorbs and that access can be closed and there is still a huge surface area, but the measurement is not responding any more.

*Lars Wågberg*

To repeat, what we detected was that, at a certain density, we got a large change in specific surface area which made us conclude that the area in contact between the fibres was increased in combination with the formation of new joints. It is though necessary to consider both the network level and the details in the fibre/fibre joints separately and draw the correct conclusions BUT one of the take home messages from my presentation is that the polyelectrolyte inter-diffusion is important for the fibre joint formation.

*Gil Garnier*

If we go with the polymer diffusion mechanism, is it more kinetically or more dynamically controlled? And my specific question is, have you investigated the effect of temperature and as you are further away or closer to  $T_g$ , and is there a difference in additional strength?

*Lars Wågberg*

No. We just measured the influence of contact time at ambient temperatures and we did not check the influence of temperature.

*Gil Garnier*

So is it thermodynamically or kinetically controlled, what is your vision?

*Lars Wågberg*

It's really hard to say. The end-situation is naturally controlled by thermodynamics but the way there is naturally determined by the kinetics. We do not know if this is a kinetically locked state.

*Torbjorn Wahlstrom*      Stora Enso

You mentioned several times that you have neglected the influence of the joint formation, and I was thinking what made you say this. We neglect so many things before we come to a ready paper and we have to simplify things to understand the mechanics, do you have reason to suspect here that the relative effects of chemical treatments will change depending on this?

*Lars Wågberg*

This question has many aspects, but to start by the first one, where I mentioned that I neglected the influence of the making of the joints. I convinced a PhD Student, Andrea Åman Träger, to make layer by layers with polymeric nanoparticles where the softening temperature was  $-10$  degrees. We got fantastic wet adhesion, even stronger than with the hyaluronic acid, and a very poor dry strength. It's therefore obvious that with this low  $T_g$  the polymer shows no resistance as the surfaces are pulled apart resulting in a very poor dry strength. So wet adhesion is important but once dried the low  $T_g$  is very negative, showing the importance of treating the making AND the breaking of the surface contacts together. I think we have a lot to learn about the softening of the fibre surfaces for the formation of certain end use properties of the network. For example, one thing that I have neglected is the influence of the cationisation of fibres which has an enormous effect on the swelling of the fibres, even though it contains nitrogen atoms (with reference to Bob Peltons presentation). So, yes, there are probably some factors that I have forgotten but naturally but I can't pinpoint them at this moment. I just talked about what I have understood.