

FIBER-FIBER BOND FORMATION AND FAILURE: MECHANISMS AND ANALYTICAL TECHNIQUES

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ABSTRACT

In this paper we give a literature overview on three different aspects of pulp fiber-fiber bonding. First we are reviewing how the adhesion between the pulp fibers is created by the capillary pressure during drying of a sheet. Second we are discussing the individual mechanisms relevant for fiber-fiber bonding. They can be grouped in three different groups: (a) The area in molecular contact, which also includes interdiffusion; (b) the intermolecular bonding mechanisms hydrogen bonding, Van der Waals forces and Coulomb interaction; (c) the mechanical bonding mechanisms which are capillary bridges and mechanical interlocking. The third and last part of the review discusses the failure process of fiber-fiber bonds and related single fiber-fiber bond testing methods. The general emphasis of the paper is set on providing a general understanding of the processes responsible for how bonds between fibers are created, how they work and how they are failing.

1 INTRODUCTION

The question which mechanisms are holding paper fibers together has been discussed for a long time, more recent literature reviews are given in [1, 2, 3, 4].

The aim of this paper is to give an overview on the processes taking place during development, existence and failure of fiber fiber bonds. Emphasis is put on a qualitative understanding of the fiber-fiber bonding- and bond failure procedure rather than on a quantitative analysis [5] of the individual bonding mechanisms.

A prevalent opinion still is that the adhesion in fiber-fiber bonds is caused by hydrogen bonding. However, it has also been proposed [1] that there are several bonding mechanisms that play an important role. Three of these mechanisms are interactions between surfaces on a molecular level, namely *hydrogen bonding*, *Van der Waals forces* and *Coulomb bonding* (electrostatic interactions between ionic species). Hydrogen bonding and Van der Waals forces only take place when the bonded surfaces are having a distance below a few Ångstrom. Regions close enough are thus forming the so called *area in molecular contact*, i.e. the region where all intermolecular bonding mechanisms can actually take place. *Interdiffusion* is a mechanism which increases the area available for intermolecular adhesion forces. In addition to these mechanisms taking place on the nanometer scale there are two other mechanical mechanisms contributing to fiber-fiber bonding on the micrometer scale, *mechanical interlocking* and *capillary bridges*.

In the following we will discuss how a bond between two individual fibers is created and the relevance of the area in molecular contact will be discussed. Then the individual bonding mechanisms will be reviewed followed by insights into the fiber bond failure. Finally conclusions and future challenges will be defined.

2 AREA IN MOLECULAR CONTACT

The interaction range for some of the molecular adhesion mechanisms like hydrogen bonding or Van der Waals forces is in the range of a few Ångstrom. Thus it is necessary to determine the contact area between bonded fiber surfaces on the Ångstrom size scale. In Figure 1, one can see that upon zooming in on the interface between two surfaces one will find non-bonded regions with increasing zoom. Regions that seem to have full contact may be separated under larger magnification. The actual area in molecular contact is the contact area at Ångstrom scale, i.e. the magnification that is able to resolve the relevant distance for short-distance molecular interactions. In this section we will first discuss the mechanism that brings the fiber surfaces close enough that molecular interaction occurs and the surface properties governing the area in molecular contact, an in-depth review on this topic gives [6]. Then the rather controversial literature on the actual degree of molecular contact in fiber-fiber surfaces is reviewed.

2.1 Obtaining adhesion between fiber surfaces

The degree of contact between surfaces on a molecular level is described by contact mechanics. Contact mechanics are relevant for phenomena like friction [8], sealing [9] and adhesion [7]. During the last years quantitative analysis of molecular contact area using different contact mechanics models has received increasing attention [9, 10, 11, 12].

In paper fibers the driving force to establishing molecular contact [13] are capillary forces, the same forces that are also responsible for paper wet web

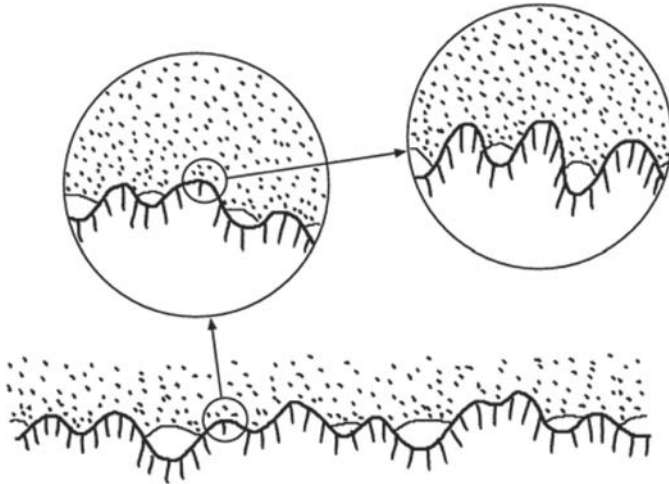


Figure 1. The contact area between two surfaces changes upon zooming into the interface. Regions that seem to have full contact may be separated under larger magnification. © IOP Publishing. Reproduced with permission from [24]. All rights reserved.

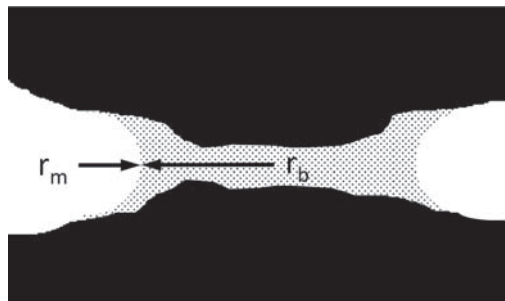


Figure 2. A capillary bridge of water between two fiber surfaces. The Laplace pressure due to the capillary force is shown in Equation 1.

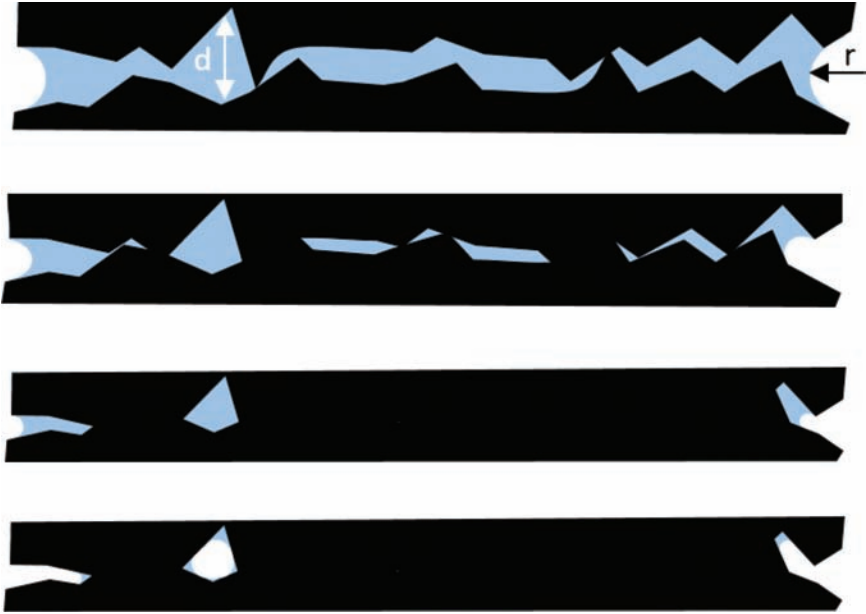


Figure 3. The capillary pressure during drying is pulling the fiber surfaces into contact (top to bottom image). As the water is removed the meniscus (R) of the capillary bridge decreases, increasing the Laplace pressure. The capillary pressure is promoting contact, surface roughness and material E-modulus are inhibiting contact.

strength [14]. The capillary forces in paper are created by bridges of water between the fiber surfaces, Figure 2. The meniscus in the capillary bridge is causing an adhesion pressure, the so-called Laplace pressure p

$$p = \gamma \left(\frac{1}{r_m} + \frac{1}{r_b} \right) \approx \frac{\gamma}{r_m}. \quad (1)$$

The Laplace pressure p is determined by the air-water surface tension $\gamma \approx 70\text{mN/m}$ and the two radii of curvature (m) in the meniscus r_m and r_b . As generally $r_b \gg r_m$ equation 1 can be approximated by $\frac{\gamma}{r_m}$. The key parameter determining the Laplace pressure pressing together the fiber surfaces is the distance between the surfaces $2r_m$. Large capillary forces occur if the distance between the surfaces is low and the resulting meniscus r_m of the liquid is small.

Figure 3 illustrates how molecular contact between two fiber surfaces is established. The driving force for contact development is the Laplace pressure due to

the capillary bridges. When the two surfaces are touching the peaks of both surface topography profiles are increasingly deformed. This deformation leads to a force counteracting the force pressing the surfaces together, the degree of contact between the surfaces is determined by the equilibrium between these forces. When the water is retracting the menisci in Figure 3 are moving inwards, thus decreasing the radius r which, according to Equation 1, increases the capillary pressure. So the capillary bridges become *stronger* as the water is removed between the fibers. This leads to an increase in the contact area and, at the same time an increase of the Laplace pressure because the reduced surface distance further decreases the radius r of the meniscus. The smoother the surface the smaller the menisci, and the stronger the Laplace pressure becomes. Consequently the degree of molecular contact between the fiber surfaces is determined by two factors. High surface smoothness and low stiffness (E-modulus) of the surface material promote molecular contact. One can imagine that very soft and smooth surfaces may even develop full molecular contact when pressed together by the capillary forces. However as the surface gets increasingly rough (or stiffer) there are regions that cannot be pulled in contact by the capillary forces, the force to deform the surfaces to full contact is larger than the Laplace pressure. So for a given material stiffness there is a critical distance between the fiber surfaces, if the combined surface topography of the fibers exceeds this critical distance no molecular contact between the surfaces will occur. This is illustrated by the region with distance d in Figure 3. In this region the gap between the surfaces is too large to be overcome by the capillary forces. A detailed discussion on the mechanisms outlined above can be found elsewhere [6, 7, 8, 15]

In conclusion this means that for a given stiffness of the fiber material there is a certain *critical distance* which is overcome by the Laplace pressure during drying. If the fiber surface topography is not exceeding this critical distance there is full molecular contact between the fibers, i.e. 100% of the fibers surfaces are actually in molecular contact. If the surface is rougher, some fraction of the surface that appears to be in contact under lower magnification actually is not having full molecular contact.

2.2 Measuring the area in molecular contact

Measurement of the area in molecular contact in fiber-fiber bonds is difficult. A detailed review and discussion on the various approaches and methods is given in [6], here we give a brief overview. As explained in the previous section, even if contact is observed between two surfaces at a given magnification it may very well turn out that a measurement under higher magnification reveals that there is only partial contact. This is particularly a problem for all imaging based measurement techniques, because the imaging resolution is limited by half the wavelength of the

radiation used in the imaging process. For light microscopy techniques the limiting resolution is half the wavelength of light, about 200 nm. Furthermore, surface gaps smaller than this distance are not affecting light traversing through the fiber-fiber bond. This leads to the situation that all light optical methods investigating the contact area in fiber-fiber bonds are not able to spatially resolve the area in molecular contact on a sub micrometer scale. Nevertheless, they provide valuable tools to inspect the bonded region on a larger length scale. Most relevant here is polarized light microscopy [16, 17, 18] and sectioning methods [19]. Higher resolution analysis is possible with x-ray micro tomography [20, 21] due to the lower wavelength. Contact on the nanometer scale has only been evaluated qualitatively using TEM [22] or in terms of relative differences [23, 24] using FRET microscopy.

For a contact model based analysis of the area in molecular contact in fiber-fiber bonds [6, 15, 25] first, the surface roughness of the two interacting surfaces needs to be measured. Second, the surface hardness needs to be evaluated. Based on these two input parameters the contact mechanics model can be used to calculate the area in molecular contact. This was done in [15, 25] using surface roughness data obtained from AFM measurements and surface hardness data obtained from AFM based nanoindentation [26].

Results for the contact area in individual fiber-fiber bonds are not conclusive. Results for unbleached softwood kraft pulp fibers were reported to have a high degree of contact [17, 19, 27] using light microscopy and contact mechanics simulations of one group [25]. Also strength testing of single fiber-fiber joints manufactured with different drying pressure indicate a high, maybe even full degree of molecular contact in softwood kraft pulp fiber bonds [6]. However low degrees of molecular contact were reported from x-ray nanotomography [21] and from contact mechanics simulations of another group [15].

Clarifying the degree of molecular contact in fiber-fiber bonds is a key factor in understanding and improving fiber-fiber bonding and thus paper strength for low density paper grades. If it turns out that there is in fact only a low degree of molecular contact in fiber-fiber bonds, then improving fiber bonding is probably most efficiently addressed by improving the molecular contact area between fibers. If it is found that the degree of molecular contact is high, close to full contact, there is only little room for improvement there. Then other approaches must be sought, like increasing interdiffusion or trying to tap the potential of strong intermolecular mechanisms like Coulomb interaction.

3 BONDING MECHANISMS

In section 4 we will be showing and discussing in detail that the fiber-fiber bond failure process is *not* governed by the specific bond strength (strength per unit

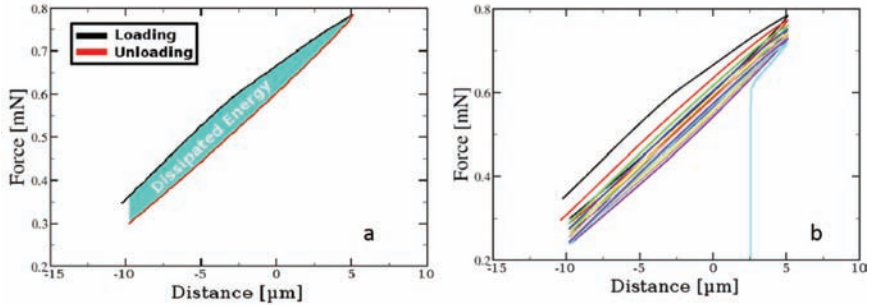


Figure 4. Force distance curves measured by mode 1 experiments using an AFM. (a) single experiment, (b) cycled experiment. (Reproduced with permission from [28].)

area) but instead it is governed by the *fracture toughness*, which is the energy consumed to grow a crack in the bonded region. We thus believe that the bonding energy of the adhesion between the surfaces is a much better parameter describing bond strength than the frequently used specific bond strength. This is why the bonding mechanisms are consequently analyzed in terms of bonding energy.

By cyclic loading and unloading of an individual fiber bond the energy dissipated between loading and unloading can be measured. All the elastic energy stored during loading is released during unloading, thus the dissipated energy corresponds to the area between the force–distance curves for loading and unloading. The cyclic loading can be repeated until the fiber bond fails. Figure 4 shows the loading-unloading curves for a mode 1 testing setup for fiber-fiber bonds [28]. Such experiments can also be done in mode 2 and mode 3 configurations [29]. The such measured dissipated energy is the sum of the bonding energy plus the energy consumed by plastic and viscoelastic deformation of the fibers, the bonding energy thus is *lower* than the dissipated energy. Nevertheless measurement of the dissipated energy gives an upper bound for the bonding energy.

The experimentally derived values for dissipated energy now can be compared to a quantitative model of the bonding mechanisms. Such an approach was used in [5]. Here the bonding mechanisms proposed in the literature earlier [1] were investigated in terms of their quantitative contribution to the overall bonding energy. The results are shown in Figure 5. Please note that the uncertainties are large. Coulomb, Van der Waals and hydrogen bonding seem to have the strongest contribution to the overall bond energy followed by mechanical interlocking. However, Coulomb bonding has a particularly high uncertainty. According to Figure 5, hydrogen bonds and capillary bridges play a less important role. The sum of all the mechanisms is quite well comparable to the overall energy dissipation for separating a bond. As this energy dissipation is also including plastic and

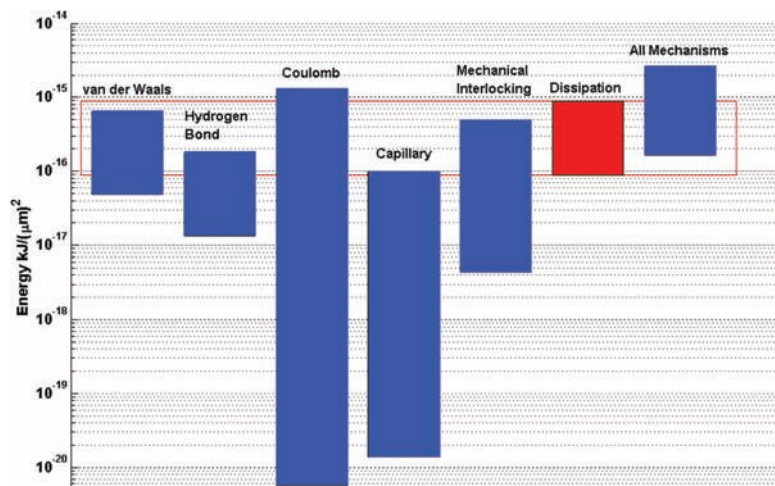


Figure 5. Contributions of the different bonding mechanisms to the bond energy of a single fiber bond. The height of each bar represents the uncertainty. The red part shows the experimental results from mode 1 measurements. (Reproduced with permission from [5].)

viscoelastic deformation during the mechanical testing it becomes clear that the calculated value is higher than the actual bonding energy.

3.1 Interdiffusion

In contrast to [1] where interdiffusion is listed as one of the bonding mechanisms, it is missing in Figure 5. This is due to the fact that interdiffusion is increasing the area in molecular contact. This effect was added to the uncertainties given in [5]. Interdiffusion will happen when polymer chains partly diffuse in the bonding region from one surface into the other. This is facilitated by the fact that the fiber surface in the wet, swollen state actually can be considered as a swollen hydrogel [30]. Interdiffusion has already been mentioned a rather long time ago [31], some authors even believe that this is the key mechanism for fiber-fiber bonding [32]. A literature review on this topic is given in [2].

Recently the effect of interdiffusion on adhesion energy was directly measured for PCL-grafted cellulose spheres using atomic force microscopy in colloidal probe mode. A time dependent increase in bonding energy and bonding force was found, stabilizing after roughly 10 seconds [33]. Interdiffusion, like the area in molecular contact, is a multiplier to the inter-molecular bonding mechanisms of Van der Waals forces, hydrogen bonding, and Coulomb interaction. It increases the contact surface between the fibers and thus the area of molecular interaction. The well known

Table 1. Energies of hydrogen bonds, Van der Waals bonds and Coulomb bonds

<i>Bonding mechanism</i>	<i>Bond Energies for one individual bond in [kJ], taken from [5]</i>
Van der Waals	6.8×10^{-24} for cellulose molecules from DFT
Hydrogen Bond	1.9×10^{-23} from DFT
Coulomb	1.2×10^{-20} between COO^- and Na^+

relation between increased fiber swelling and stronger bonding [34] can also be interpreted as an effect of interdiffusion. Higher dilution in the gel layers leads to faster interdiffusion, thus creating a larger surface for molecular interaction between the surfaces. There are several publications dealing with the diffusion of polymers. The diffusion process strongly depends on the molecular weight and generally two different diffusion regimes for high and for low molecular weight are proposed. More details about polymer diffusion can e.g. be found in [35, 36, 37, 38]. Stadlmeier and Köhler [38] for example give a thermal and a mass diffusion coefficient for long and short polymer chains of $13.76 \times 10^{-12} \text{ m}^2/\text{sK}$ and $1.36 \times 10^{-10} \text{ m}^2/\text{s}$, respectively.

Thomson *et al.* have adapted Förster Resonance Energy Transfer (FRET) microscopy for analysis of cellulosic fiber-fiber surfaces. FRET is a technique capable to quantify the degree of molecular contact (10 Å to 100 Å) between two surfaces. They studied the degree of contact of individual fiber-fiber bonds from pairs of viscose fibers and pulp fibers [23]. Furthermore, they analyzed the development of bonding during drying [39] and due to pressing [24]. For individual softwood pulp fiber-fiber bonds they found an increase in the FRET signal [39] which they attributed to interdiffusion of the surface molecules.

Interdiffusion might be an important binding mechanism, as it increases the molecular contact and therefore the microscopic bonding mechanisms (Van der Waals, Hydrogen Bonds, Coulomb interaction). However, it needs a lot more experimental research in order to get an at least semiquantitative value of its contribution to the overall bond strength. As the degree of interdiffusion seems to depend on the polymer chain length it will depend on the diffusing species (cellulose, hemicellulose, lignin) making quantitative statements even harder. Overall, it is unclear if diffusion is playing a relevant role for the industrial papermaking process as dewatering is taking place there rather very quickly, which could inhibit significant interdiffusion.

3.2 Hydrogen bonds and Van der Waals bonds

Hydrogen bonding has for decades been viewed as the most important binding mechanism in paper [40]. As sugar polymers have quite a lot of OH– groups this

notion is not surprising. However, recent calculations of the bonding energy have identified Van der Waals forces as the most important bonding mechanism, Figure 5. When looking at table 1 we see that the difference in the bonding energy for individual bonds between Van der Waals bonds and hydrogen bonds is only about a factor of 3. Considering a cellulose unit cell it can be seen that there are 4 hydrogen bonds along the (010) surface [5]. Van der Waals interaction occurs between all atoms, thus there are 41 atoms per unit cell which can interact via Van der Waals. Additionally Van der Waals is a more far-reaching interaction than hydrogen bonding. The Van der Waals interaction force between two atoms is proportional to $1/r^6$, r being the distance between the particles. For two flat surfaces approaching each other the van der Waals force – distance relationship according to Lifshitz theory is proportional $1/r^3$ [8]. In contrast, hydrogen bonds are very local interactions with hydrogen bonding distances between water molecules of about 0.18 nm, the force distance relationship, however, is proportional to $1/r^3$, as hydrogen bonds can be regarded as interactions between permanent dipoles. Accordingly calculations then lead to the result that, assuming single crystalline cellulose surfaces, Van der Waals is the more important bonding mechanism [5]. From recent studies of the crystalline structures of cellulose several other groups also argue that Van der Waals interactions are more important than hydrogen bonding between cellulose molecules in the crystalline structures [41, 42, 43, 44].

The role of hydrogen and van der Waals bonding has also been investigated experimentally. Recently, Przybysz *et al.* [45] argued in favor of hydrogen bonding. They conducted handsheet forming using water and increasingly apolar alcohols as solvents, paper strength increased with increasing polarity. The authors conclude that the reduction in paper strength is due to a decrease in the energy of hydrogen bonds between the fibers due to the decreasing polarity of the solvents and claim that their results reflect the prevalent importance of hydrogen bonding for the adhesion of pulp fibers in paper. One can also, however, explain the effect of changing the solvent in terms of reduced swelling and reduced softness of the fiber surface. As discussed in the section on area in molecular contact, reduced fiber swelling leads to a harder surface which impedes the formation of a large molecular contact area between the fibers, which leads to the well known correlation between fiber swelling (in terms of fiber saturation point) and paper strength [34]. In fact, in the work of Przybysz *et al.*, the swelling decreased continuously with increasingly apolar solvents [45], which led to the reported loss in strength. Additionally the stiffer fibers caused higher bulk [45], which also leads to decreased paper strength.

Other experimental investigations on the relevance of polar and apolar interaction for fiber-fiber bonding has been conducted by Pelton [46]. He had modified dry strength agents like starch by substituting an increasing amount of apolar

during kraft pulp productions these acid functions dissociate and the fibers retain negative charges. At least partial dissociation will also take place at lower pH values. Of course paper is electrically neutral, which is due to cations from the solution that attach to the acid function and compensate the negative charges of the fibers [34]. If the charged species on the fibers in a fiber bond are in the right geometry they will lead to strong bonds, as Coulomb interactions are very strong (three orders of magnitude stronger compared to Van der Waals and Hydrogen bonds; see Table 1). In addition, Coulomb interactions are far reaching, as the force decreases with $1/r$. However, the geometry can also be unfavorable if two positive or two negative charges come close together in the bonded area. This is shown in the sketch in Figure 6. Both, repulsive [13] and attractive [49] Coulomb interaction has been reported.

Charged species in the pulp fibers play an additional role beside forming Coulomb bonds, they are highly relevant for fiber swelling. As discussed above fiber swelling is strongly associated with surface hardness and therefore with the area in molecular contact. This connection was also discussed in [50] where cellulose films with and without Xylan were swollen in different aqueous solutions. In [50] it is clear that Coulomb interactions increase swelling (softening the surfaces which increases the area in molecular contact) and induce stronger bonding (due to the electrostatic interactions of the charged species). There have been many discussions if charged species really increase bond strength by Coulomb bonding, or if they only increase swelling [1, 13, 51]. It was shown on viscose fibers that one can distinguish between the impact of swelling and the impact of Coulomb interactions [49]. In this paper it was shown that a pure viscose fiber swells as much as a viscose fiber containing cationic charges. However, while the viscose fibers did not form a bonded sheet the viscose fibers containing cationic charges formed sheets with a breaking length of about 500 m [49]. In the same work it was also shown that two viscose fibers with different amounts of added negative charges showed rather similar swelling. However, the viscose fibers with the higher amount of negative charges showed a significantly higher breaking length as compared to the fiber with less negative charges [49]. These results make it clear that charged species not only increase swelling they also lead to significant bonding due to attractive Coulomb interaction. Also Laine and coworkers [52] showed that a high surface concentration of carboxyl groups increased the specific fibre-fibre bond strength, in their case they created it by grafting CMC on the fiber surface.

Figure 6 shows that carboxylic groups must be present on *both* surfaces to enable Coulomb bonding. Assuming random distribution on the surface a first order approximation for the probability for a Coulomb bond is the squared surface coverage of carboxylic groups [5]. In the literature there are large differences in the reported values for the surface charge of pulp fibers, compare [53, 54, 55].

These large differences in surface charge lead to a huge uncertainty in the contribution of Coulomb interaction in Figure 5. Furthermore it is unclear if, and if yes to what extent, besides attractive Coulomb interaction there is also repulsive Coulomb interaction taking place between fiber surfaces, as sketched in Figure 6.

The fact that the carboxylic groups are promoting fiber swelling leads to the situation that the ionic strength (salt concentration) of the surrounding liquid has an impact on fiber-fiber bonding. If the concentration of charged species in the solution is higher than in the swollen fibers, osmotic pressure will lead to de-swelling of the fibers. This will lead to an increase in surface hardness (see, e.g. [50, 56]) which will decrease the area in molecular contact leading to less bonding.

We can conclude that carboxylic groups on the fiber surface lead to increased bonding between the fiber surfaces. They are promoting two bonding mechanisms which are contributing independently: increased swelling leading to an increased area in molecular contact and predominantly attractive Coulomb interaction.

3.4 Mechanical interlocking

Mechanical interlocking is not a bonding mechanism on a molecular scale, it is taking place on the micrometer scale. It refers to the idea that the surfaces of the bonding fibers are mechanically entangled, which leads to an increase in bonding strength between the fibers.

This type of entanglement is mostly taking place by fiber surface fibrils produced by refining of the pulp. The formerly bonded area of fiber-fiber joints looks different for refined and unrefined fibers, see Figure 7. For unrefined fibers it is fairly smooth, while for refined fibers broken fibrils are found in the bonding region. Investigation of the strength of individual fiber-fiber joints for refined and unrefined fibers are supporting the idea of mechanical interlocking. For mode II testing of softwood fiber joints an increase of bonding force has been found regularly for refined fibers compared to the unrefined ones. The increase was 15% for Saketi [58], up to 50% for Jajcinovic [59], 20% for Mayhood *et al.* [60], and finally 8% for Stratton and Colson [61]. For some of these results the increase was statistically not significant, however the trend is consistent. Also for mode I testing a higher bonding force was found for refined fibers [62].

Please note that Figure 7 is *not a direct evidence* for mechanical interlocking as strong bonds from unrefined fibers also show fibril bundles torn off the surface, similar to refined fibers [61]. However, it is likely that the mechanism of strength increase in refined fiber-fiber bonds indeed is entanglement of external fibrils rather than increased area in molecular contact or interdiffusion.

Sometimes in publications on fiber-fiber bonding the bonded fiber surface is sketched as having considerable roughness on the micrometer scale [1, 63] which

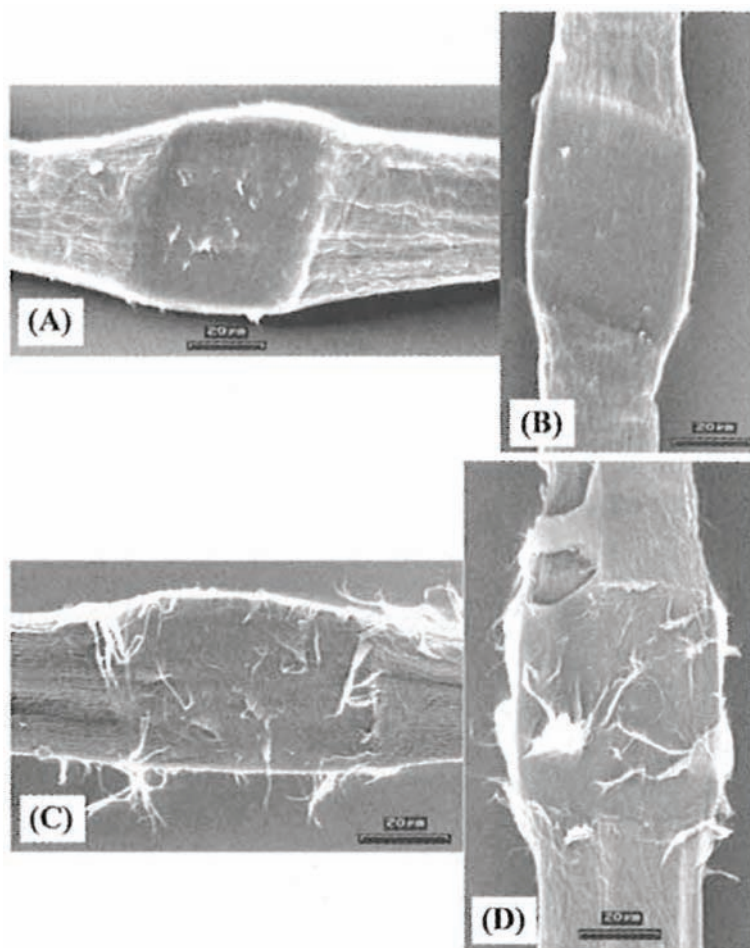


Figure 7. The bonding surface of individual fiber-fiber joints after breaking (reproduced with permission from [57]), unrefined (A, B) and 30 minutes Valley beating (C, D). For the refined fibers fibrils have been torn out of the fiber surface during breaking of the fiber-fiber joint.

might lead to the idea that mechanical interlocking could also be promoted by the surface roughness. High resolution LVSEM imaging of the formerly bonded area of broken fiber-fiber joints [64] however reveals that the surfaces are fairly smooth on the micrometer scale. This does not rule out entanglement due to roughness on the nanometer scale, nevertheless on the micrometer scale this mechanism is not playing a relevant role.

3.5 Capillary bridges

Capillary bridges will play an important role during bond formation as has been shown above in the discussion about the area in molecular contact. However, capillary bridges could also contribute to paper strength in ‘dry’ conditions. The main reason for that is that pulp fibers at a relative humidity of 50% actually have a water content between 6% and 8% [3]. This is enough water to still form capillary bridges. As the water is removed from the fiber surface the Laplace pressure bringing the two surfaces together in a capillary bridge increases because the radius r_m decreases, compare equation 1. Molecular dynamics simulations [65] suggest that the equation for the Laplace pressure still holds for very thin water films in the range of a nanometer, which for water leads to a capillary pressure around 70 MPa. Such capillary bridges, even when they increase the contact area between the fibers only a little, can significantly increase the adhesion between surfaces [66]. It is quite likely that capillary bridges are persisting through the drying section, because the vapor pressure over a curved surface (in this case the capillary bridge) increases according to the Kelvin equation [25, 66]. This leads to the effect that capillary bridges with very small capillary radius are not evaporating under low vapor pressure. Also from high vacuum technology it is known that even in the presence of ultra-high vacuum for long time there is still water present on solid surfaces. One reason is the high sticking coefficient of water on hydrophilic surfaces, e.g. [67]. This is the reason why water vapor limits the obtainable vacuum in high vacuum systems [68].

Considering the above it is not unlikely that capillary bridges also contribute to fiber-fiber bonding in dry paper. Empirical evidence has yet not been given to confirm this idea. Paper strength was investigated under ultra high vacuum at room temperature [69]. Using this approach the authors attempted to proof the existence of capillary bridges by changes in the paper strength between high- and ultrahigh vacuum. However the results were inconclusive.

4 FIBER BOND FAILURE

The failure of materials under load occurs in three different modes, Figure 8. Cracks may propagate in the plane perpendicular to normal stress (mode 1, peeling), in the plane with shear stresses with the crack line perpendicular to the stresses (mode 2, sliding) or in the plane with shear stress with the crack line parallel to the shear stress (mode 3, tearing). Depending on the loading situation and the material, failure may occur due to normal or shear stresses. In order to understand the failure of fiber-fiber joints we thus need to analyze the stresses in the bonding region.

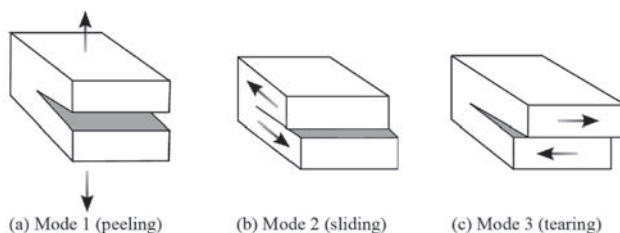


Figure 8. The three modes of failure in fracture mechanics.

A fiber-fiber joint in the configuration as a lap joint is shown in Figure 9 (*left*). The stress distribution in such a type of joint gives Figure 9 (*right*). One can see that the stresses in the center of the joint are low and that the peak stresses are occurring at the edge of the bond. Button [71] has extensively studied the failure of lap joints. Due to the high peak stresses occurring at the edge of the joint, the failure starts at the edge and moves inwards [71, 72, 73]. The failure of the joint is thus governed by the *peak stress* at the edges of the joint. As a consequence the length L of a lap joint has only a minor influence on its strength, its thickness t and the E-modulus E of the material instead have a large influence [71], compare Figure 9 (*left*). This basic idea also holds for all other configurations and loading situations of individual fiber-fiber joints, the failure is always driven by the peak stresses at the edges of the bond.

Progressive failure from the edges to the center of the bond has been observed in fiber-fiber joint testing, where sudden drops in loading force indicate local failure of the bond [62, 72, 74]. There is considerable evidence that failure in paper also occurs due to progressive failure of fiber-fiber bonds. Nordman *et al.* [75] observed that the light scattering coefficient of paper increases upon straining. The increase in light scattering can be attributed to new surface area created in the paper due to the separation of previously bonded fiber regions [73]. Investigations of fiber-fiber bonds in paper using polarized light microscopy have shown that the bonds indeed fail progressively under dynamic load [76] as well as under constant load, i.e. creep testing [77]. Further direct evidence for progressive failure for fiber-fiber bonds was found in the AFM based mode 1 breaking of fiber fiber joints [62]. It revealed sequential failure of the joint with distinctive, sudden drops in the debonding force of refined fibers, whereas no such force discontinuities have been found for unrefined fibers [62]. The sudden force drops can be interpreted as the failure of individual, fibrils, fibril bundles and parts of the S1 fiber wall breaking away.

In general the increase of fiber wall damage increases with the strength of the fiber-fiber bond. Stratton and Colson [61] have investigated the amount of fiber wall damage for single fiber-fiber joints of differently treated pulps. The joint

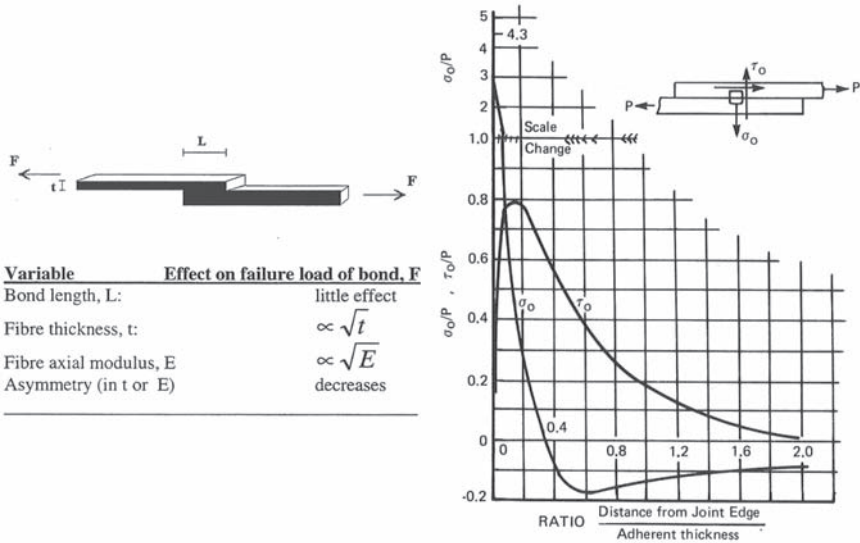


Figure 9. Idealized configuration of a fiber-fiber bond as a lap joint (left) [70, 71]. The stress distribution in a lap joint (right). (Reproduced with permission from [72].) τ_0 is the shear stress, σ_0 is the normal stress and P is the mean tensile stress in the joined pieces.

strength of fibers treated with a dry strength agent showed significantly higher breaking strength and exhibited fibrils and larger parts torn off the fiber wall, very similar to the refined fibers shown in Figure 7. They concluded that, independent of the mechanism of strength increase, weak bonds are failing at the interface between the bonded fibers, whereas for strong bonds the locus of failure shifts to the region between S1 and S2 which leads to tearing out of material from the surface.

In the literature the strength of fiber-fiber bonds is often described to be the product of the bonded area and the so called *specific bond strength* [78] given in N/mm². The specific bond strength is employed as the parameter describing the strength of the bonding per unit area. However, the assumption that the strength of a fiber-fiber joint increases linearly with the bonded area can neither be observed in single fiber joint testing experiments [79, 80], nor by simulations [81]. The concept of specific bond strength is assuming evenly distributed load carrying in the bonded area, which is not the case. The material property determining the resistance to the progressing growth of a crack in the failing fiber-fiber joint is the fracture toughness [71]. The fracture toughness is defined as the amount of energy required to generate the new surface created by the growth of a crack. It is related to the bonding energy per bonded area as discussed in the previous sections.

We thus conclude that the concept of specific bond strength is not suitable to understand the failure process of fiber-fiber joints. That is the reason why measuring the bond strength of individual fibers and comparing the results to the specific bond strength obtained via the Page equation does not work. Weber *et al.* [79] measured the specific bond strength via determining the optically bonded area using polarization microscopy [82] and the bonding force necessary to open individual fiber-fiber joints, from these values they calculated the specific bond strength. Simultaneously they determined the specific bond strength using the Page equation [78]. It was found that the values did not match [79]. Instead of specific bond strength the failure process of fiber-fiber joints is driven by two factors. The first factor is the peak stress in the joint which initiates the failure, it depends on the load and the geometrical configuration of the joint. The other factor is the fracture toughness of the bond, which is the energy required to create the crack surface [71] it is equivalent to the bonding energy in the bonded surface.

The dependance of fiber-fiber joint failure on the peak stresses in the bonding region has profound implications on all types of single fiber-fiber joint strength testing methods [28, 29, 74, 83, 84, 85]. The strength of the joint is not only determined by the bonding area itself, but it also largely influenced by the shape of the fiber cross section, the configuration of the fibers and the load application [72]. In fact large differences in fiber-fiber joint strength for the same softwood pulp were found for different loading modes, predominantly mode 1 [28, 62], as well as predominantly mode 2 and mode 3 measurements [29]. The necessity to understand the actual load and the stresses in the fiber-fiber bonding region has led to a combined approach of physical testing of fiber-fiber joint strength and FEM modeling of the experiment [81, 86, 87]. Using this combined approach the resultant forces and moments [86, 87] in the bonding region can be calculated and the peak stresses [87] can be estimated. This type of analysis can be used to analyze the failure mechanism of fiber fiber bonds. The results of two of these studies [87, 88] both indicate that mode 1 failure (i.e. normal load) might be relevant for fiber-fiber joints. This is in sharp contrast to the common believe that shear forces are the main source of failure in fiber-fiber bonds.

5 CONCLUSIONS AND FUTURE CHALLENGES

The area in molecular contact between the fiber surfaces is the most important parameter for fiber-fiber bonding as it provides the surface where the individual molecular bonding mechanisms then can take place. Measuring it in actual pulp fiber-fiber bonds and quantifying its contribution for the overall bonding will be one of the most important challenges that need to be solved in order to obtain a quantitative understanding of fiber-fiber bonding. Interdiffusion essentially also

increases the area in molecular contact, it is yet unclear how large its contribution to fiber-fiber bonding is. From an experimental point of view nanoscale measurements of fiber surface mechanics (hardness, viscoelasticity, surface topography) need to be conducted for different kinds of pulp, also in the presence of wet end strength additives. This should lead to a better understanding of the bonding mechanisms of different pulp types and wet end chemicals.

Regarding the molecular bonding mechanisms it seems that both, Van der Waals forces as well as hydrogen bonding are playing a relevant role in fiber-fiber bonding. There is no conclusive evidence yet that one or the other is prevalent. Coulomb interactions definitely contribute directly to fiber-fiber bonding, carboxylic groups on and in the fiber additionally promote swelling and thus the molecular contact area.

The two non-molecular bonding mechanisms are mechanical interlocking and capillary bridges. It has been shown conclusively that mechanical interlocking of the fibrils on the fiber surface, which are, for example, created by refining, indeed contributes to fiber-fiber bonding. The existence of capillary bridges in dry paper is quite likely, however experimental results indicating a contribution to fiber-fiber bonding have not yet been worked out.

Finally, it will be very important to gain a deeper insight into the failure mechanisms in fiber-fiber bonds. Determination of the actual fracture toughness of different types of fiber-fiber bonds is a highly interesting, yet challenging research goal.

In terms of advancing fiber-fiber bonding the mechanism with probably the highest potential for significant improvements is Coulomb interaction, as it is a strong and far reaching interaction and the concentration of carboxylic groups on the natural fiber surfaces is limited. Clarification of the actual molecular contact area in fiber-fiber bonds will reveal if there is also potential for improvements. If the degree of molecular contact between fibers is low that would be a large and promising potential for strength improvements, if it turns out to be close to 100% further research there is not necessary. All other mechanisms can hardly be improved. They either depend on the number of available species (hydrogen bonds) or on the total number of atoms (Van der Waals bonds) within the area in molecular contact. Capillary bridges can only occur when there is no molecular contact between the surfaces – it is only an improvement if molecular bonding is not taking place. Considering mechanical interlocking an ideal fiber treatment would promote external fibrillation without shortening the fibers or reducing their strength.

Right now we are only at the beginning of understanding quantitatively how fiber-fiber bonding is actually working. Many key questions are still unresolved. It remains puzzling that something as simple as making a sheet of paper, which people have been doing for more than two thousand years now, turns out to

involve three molecular adhesion mechanisms, contact mechanics and fluidics on the nanoscale and gel-phase swelling/diffusion.

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Transcription of Discussion

FIBRE–FIBRE BOND FORMATION AND FAILURE: MECHANISMS AND ANALYTICAL TECHNIQUES

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Jose Iribarne WestRock

Okay. Alfred Nissan is turning over in his grave because paper is, according to him, and he had a lot of evidence, a hydrogen bonded dominant material. So why do we have so much evidence that hydrogen bonds have relevance and then you show that they do not. So how do you explain all the phenomena with water just by capillary forces?

Ulrich Hirn Graz University of Technology

No we are not explaining all the phenomena with capillary forces, this is just one of the bonding mechanisms. What is the evidence for hydrogen bonding you are referring to? What is the evidence that in your eyes Nissan is bringing? That you need water for bonding, is it that? That you need to put the fibres in water?

Jose Iribarne

I refer you to the book by Alfred Nissan [Nissan, A. (1977), “Lectures on Fibre Science in Paper”, *The Joint Textbook Committee of the Paper Industry*, TAPPI and CPPA 1977]. He has a very significant amount of work.

Discussion

Ulrich Hirn

Yes, I know, essentially he is relating all the paper mechanics, and all the mechanics of the bond to the hydrogen bond on the nano scale.

Jose Iribarne

In creep phenomena and a lot of other things.

Ulrich Hirn

Yes, he is just focusing on his perspective and he knows that hydrogen bonds are there, and from there he is developing this idea that there are all these bonds and hydrogen bonding could explain everything. But, I think if you consider that you always have Van der Waals forces at the same time, you can build up the same body of work starting from the idea that it is a mixture of Van der Waals and hydrogen bonding, so I don't really see the contradiction there.

Jose Iribarne

Okay. This will probably take much more time than the rest of the morning, but it is entirely possible that because of the swelling characteristics of the surfaces, they actually deform to maintain hydrogen bonds, so they don't break. They are still directional, but the surface has actually moved.

Robert Schennach Graz University of Technology

Yes, but still there is only a limited number of hydrogen bonds possible. They will always be outnumbered by Van der Waals forces, and people also find that in density functional theory (DFT) calculations for many other systems containing hydrogen bonds.

James De Witt Sappi N.A. Basepaper Technology

It's sort of a related question. If you take as the fully formed sheet that you have a dominance of Van der Waals bonds, why is it so readily debonded with water? Because the Van der Waals bonds would presumably evolve to being over extremely short distances where it would be difficult for water to even penetrate so, if the sheet is 60 or 70% held together by Van der Waals forces, why is it so easily disassembled with water?

Robert Schennach

Well, the same is true for hydrogen bonding.

James De Witt

Are you saying that van der Waals bonds are easily disrupted by water?

Robert Schennach

Cellulose crystals are held together by hydrogen bonding and do not disintegrate in water.

James De Witt

But paper does. The hydroxyls on the fibre surface in paper are more accessible than those within a crystal structure.

Robert Schennach

Yes, but when you bring water in between, you increase the distance and then you will lose both hydrogen bonds and Van der Waals bonds.

James De Witt

Before you increase the distance, you will have to break the bond.

Ulrich Hirn

Well, you also have instant swelling and you soften the surface a lot. When you wet the fibres, it is like re-wetting an adhesive layer, it gets very soft. You get a very low yield stress and already very small forces can separate the fibre surface. In our opinion, dissolving of the paper in water is not necessarily related to direct opening of the hydrogen bonds by the water.

James De Witt

To verify one or the other I think you need to consider the dynamics of rewetting and why the bond is broken.

Discussion

Ulrich Hirn

Yes.

Bill Sampson University of Manchester

I think consideration of how different bond types explain observed moisture dependencies is going to be something you have to work on over the next few years.

Tetsu Uesaka Mid Sweden University

First of all, I really enjoyed your talk. This is the first time I have listened to something different from the usual fibre-to-fibre bonding story. I must say it is a good provocative talk. You mentioned new information in the literature, for example, contact area vs. scale that is a scale-free structure, a self-similar structure. This means that if you go into the molecular level, there may be no contact area, because it will not be continuous obviously. You can see all these zigzag structures as you go down in scale. So, in that sense, we really have to change the concept of the bond structure completely. At the same time, the capillary bridges also exist. Water is not only coming from the actual drying process but also from the ambient humidity, and actually condenses. The issue is that this condensation point does not necessarily follow the old Kelvin's equation (for capillary condensation). The recent literature showed that equation is not valid. Experimentally it did show that even in a very large distance, very close to 1 micron, you see a water bridge formed under ambient conditions. Even if you heat it, you can't remove it. So, water bridges are very persistent. The size is far larger than the molecular distance. It is a huge structure between fibres. So, I think this is a very fantastic topic and also you have entered into this very interesting area for research. I have to congratulate both of you.

Ulrich Hirn

Thank you.

Bill Sampson

Have you looked at Hiroki Nanko's micrographs of stained fibrils? He pretty much dismisses mechanical interlocking of fibrils in his 1989 FRS paper. He describes all manner of things, but he says he can't see mechanical interlocking of fibrils.

Tetsu Uesaka

Maybe, I have a different paper than him.

Bill Sampson

Okay. That is my reading of his paper.

Artem Kulachenko KTH Royal Institute of Technology

Most of the research done on fibre bonds is performed through studying two crossing fibres joined under pressure outside the network. Even there, as you demonstrated, the variation between the bonds prepared of more or less identical fibres under controlled conditions was large in terms of bonded area. When you then consider a real paper sheet, you will have all kinds of variations there. Stress distribution in the bonds will be very much dependent on the geometry, fibre alignment, and the contact area, so I would not be generalizing conclusions about the dominance of normal forces or shear forces in the bond region because of this huge variability. My question is, whether there are any attempts to connect those model fibre bond systems to the real bonds that you have in the paper sheet?

Ulrich Hirn

The first thing I would like to say is that, of course, that a stand-alone fibre–fibre bond is a different system than the paper, but the key idea is that we have stress concentrations at the edges of bonds and that is what we also have in paper. The point we were trying to make is that you have to look at these stress concentrations and the crack growth procedure which is starting on the bond edges and moving on into the bonds from there. Paper is a highly porous material, so you have lots of cracks and lots of stress concentrations. That key mechanism is the same if the bond is in paper or if you have an individual stand-alone fibre–fibre bond. Of course, the direction of loading and the stresses, they are much more complex in paper than in a stand-alone fibre–fibre bond. Anyway, what I want to point out is that even when apparently there is a pure shear load situation, like a stand-alone fibre–fibre bond under in-plane load, in fact there is a high amount of normal stress and this stress is concentrated in the edges of the bond, however complex the geometry of the bond may be. Normal stresses really do play a very relevant role also and that is not the notion in the conventional image on the failure of fibre–fibre bonds.