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The role of fiber entanglement in the strength of wet papers

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Abstract

Experiments show that the wet web strength of paper cannot be explained by capillary forces, which are found to be negligible above the fiber saturation point (FSP). Instead it is proposed that fibers entangled in a wet sheet cause an entanglement friction, which keeps the fibers in the sheet together. Various experiments were performed to investigate this entanglement friction. Adding cellulose microfibrils to a sheet was found to increase the wet web strength. Adding microfibrils on top of a wet sheet caused a tremendous increase in the friction between wet sheets, especially above the FSP, which is of a mechanical nature, because capillary forces are absent in this region. Also depositing fibers on top of wet sheets increased this mechanical friction. Replacing microfibrils with rigid glass fibers leads to weak sheets with little entanglements. Lowering the surface tension of water by a surface active agent inert to fibers leads to a reduced sheet friction, as predicted by theory, but the entanglement friction was reduced as well. A possible explanation is that surface tension affects the consolidation of the sheet, resulting in fewer or weaker entanglements for lower surface tensions. Finally it was found that van der Waals forces do not affect the entanglement friction or friction between wet sheets.

Introduction

It is generally believed that wet paper is held together by capillary forces Campbell, 1933, Rance, 1980, Page, 1993). It was recently shown (van de Ven, 2008), that the friction force between two wet sheets could be fairly well described by capillary forces acting between fibers, caused by liquid bridges in fiber crossings. This friction force was found to pass through a maximum, first increasing with the solids content of the paper, reaching a maximum at around 40% solids, and subsequently decreasing to zero at the fiber saturation point (FSP), when there is no more free water between the fibers. The maximum friction force per unit area between two wet sheets can be estimated as (van de Ven, 2008)

$$F_{fr} \approx \frac{\pi\lambda\mu\gamma\varphi^{*2}}{D} \approx 4.8\frac{kN}{m^2} \qquad [1]$$

Here λ is the dimensionless capillary force (estimated as about 1.5), μ is the friction coefficient for wet fibers sliding over each other (~ 0.44), γ the air-water surface tension, D the fiber diameter and φ^* the effective volume fraction of fibers, estimated as about 0.7 for solids contents for which the friction force is maximum. The solid fraction, c*, at which the friction is maximum occurs when the volume of the liquid bridges in fiber crossings is maximum and the only water in the sheet is in fiber crossings and in the fiber wall. It can be estimated from

$$c \approx \frac{1}{FSP + Q\alpha\varphi^* + 1} \qquad [2]$$

The first two terms in the denominator account for water in the fiber wall (FSP, g water/g fiber) and the water in liquid bridges at fiber crossings, α being the dimensionless volume of a liquid bridge and $Q = D\langle\sin\delta\rangle/8\pi d\rho_r$, d being the thickness of the fiber wall, δ the fiber crossing angle and ρ_r the density ratio of (dry) fiber and water (~ 1.5). For typical pulp fiber dimensions, Q ≈ 0.2. Eq.[2] applies at solids contents $c^* \leq c \leq c_{FSP}$, with α decreasing with solids content, $\alpha \sim 3$ at c* and reaching zero at the FSP.

Assuming the force required to break wet paper is $F_{br} = N_c F_c$, with N_c being the number of liquid bridges at fiber crossings that need to break for the sheet to rupture and F_c the friction force per bridge, estimated as $3\pi\mu\gamma D$, then the wet tensile strength at c* is (van de Ven, 2008)

$$T^* \approx \frac{3\pi\mu\gamma L\varphi^*}{(FSP+1)C} \qquad [3]$$

Here L is the fiber length and C the fiber coarseness (mass per unit length). This equation underestimates the wet tensile strength by at least one order of magnitude at c* (van de Ven, 2008), implying another mechanism is operating. At higher solids content the theory underestimates T even more. It was proposed that an entanglement friction was responsible for holding the fibers together. A similar suggestion was made in order to explain why cationic polyelectrolytes lower the wet web strength, by reducing the friction between wet fibers (Alince *et al.,* 2006).

To understand this entanglement friction in more detail, we performed wet web strength experiments on sheets containing cellulose microfibrils, which, due to their flexibility and slenderness, are prone to entangle, or containing glass fibers which are rigid. In addition we measured the friction forces between two wet sheets covered with microfibrils, which allows us to differentiate between capillary forces and entanglement friction.

Forces between fibers could conceivably affect the entanglement friction. Here we look, as an example, at the effects of van der Waals forces on wet web strength. Finally the capillary theory predicts that the friction between two wet sheets is proportional to γ (see Eq.[1]), whereas the entanglement friction is expected to be independent of γ. Therefore experiments were performed in which the surface tension of the water was lowered by the addition of a surface active agent that is inert to fibers.

Experimental

1. Materials

Pulp Fibers

Blotter papers, made of unbeaten softwood kraft fibers, were used for the experiments. The blotters were chosen because they are made of unbeaten fibers and thus fibrillation is minimal. The density is low and therefore the fibers located on the surfaces can swell and deflect. Furthermore there are no additives or surface treatments.

Cellulose microfibrils

Microfibrils used in the experiments were made from pure cellulose fibers. They were supplied by Celish (Japan). A TEM photograph is shown in Figure 1.

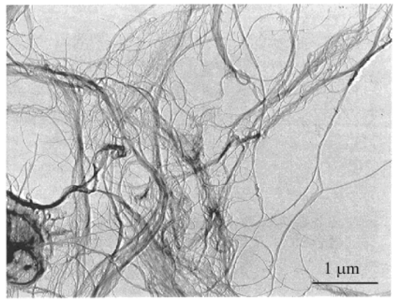

Fig.1: TEM photograph showing cellulose microfibrils ranging from a few up to about hundred nm in diameter.

Glass fibers

To evaluate entanglement friction, some experiments were performed with rigid glass fibers, about 300 µm long and 6 µm wide (CPG Inc, Lincoln Park, NY), which cannot entangle with themselves.

Salt and SKL

Sodium chloride (NaCl) was dissolved in deionized water at several concentrations. As surface active agent we used SKL (sulfonated kraft lignin, CIBA Chemicals Inc.), which was utilized in the form of free-flowing brown powder and dissolved at a concentration of 1 g/L in deionized water, to obtain a stock solution. The suspension was stirred with a magnetic stirrer for a period of 1 hour to ensure full dissolution. The pH of the sodium chloride was kept at 7, while the pH of the SKL stock was kept at 8, the natural pH of the SKL solids. From previous experiments (van de Ven and Alince, 1996) it was concluded that SKL does not adsorb on fibers.

2. Methods

Friction force between two wet sheets

For sheet friction experiments, the papers were placed in a cell where microfibril dispersions, fiber suspensions, salt or sulfonated kraft lignin (SKL) solutions, were passed through them, or applied on top, as seen in Figure 2.

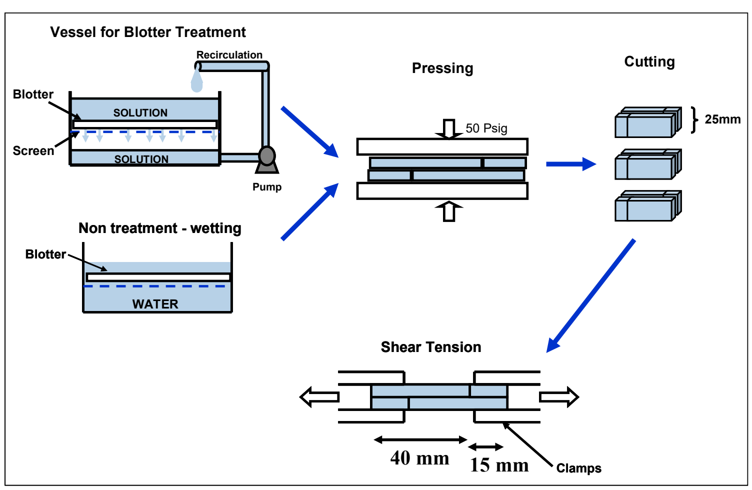

Fig.2. Sample preparation for friction force (shear tension) experiments.

The blotter sheets were soaked for 1 hour in deionized water and then placed into a custom-made cell (Fig.2, top left). The cell had a rectangular compartment (~1.5 L volume) equipped with a screen. The main functions of this apparatus were to: (i) support the blotter paper on the top of the screen; (ii) allow solutions to pass through the blotter paper with the help of a peristaltic pump; and (iii) seal the edges of the blotter paper, forcing the solutions to pass uniformly through the blotter paper. In the experiments involving treatment of microfibrils and reslushed fibers on the surface of the blotter paper, just one circulation was performed. When salt or SKL solutions (1L) were introduced to the cell, they were passed through the blotter continuously, being recirculated by the peristaltic pump for 30 minutes.

The treated blotter paper was then cut into strips of two different lengths (15 mm and 40 mm wide, see Fig.2). They were placed together facing the treated side. Afterwards the strips were sandwiched between two Teflon plates and pressed at 350 kPa for 5.5 minutes. After pressing, the specimens were then cut into strips of 2.5 cm in width for measurements of the friction force, using a Tensile Tester (John Chatillon and Sons, NY).

Wet Web Strength Test

For the wet web strength experiments, the blotter papers were reslushed and the separated fibers were then placed in a container with continuous agitation as shown in Figure 3. After that, microfibril, salt or SKL solutions were added to the fibers at various concentrations. Finally, this furnish was used to make handsheets of 100 g/m^2, following TAPPI procedure T 205 om-88. The samples were prepared by placing a plastic mesh over the metal screen of a Standard British Handsheet Machine along with a special template mold, as seen in Fig.3. The template had a pattern to create eight paper strips 2.5 cm wide and 5.5 cm long. The strips were then placed between two Teflon sheets and pressed at 350 kPa for 5.5 minutes. After the press, the samples were gently transferred and tested using a Tensile Tester (TMI Lab Master Testing Machines Inc.).

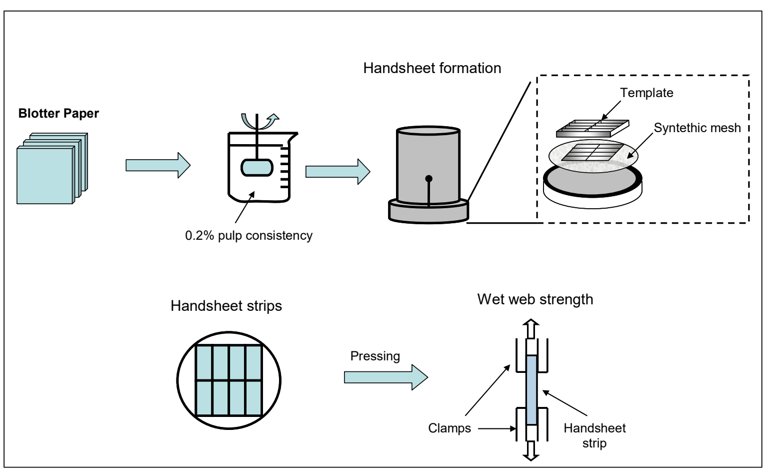

Fig.3. Wet web strength procedure, following TAPPI procedure T-205 om-88 for handsheet preparation. A special mesh produced 8 strips of paper, which avoided having to cut the weak wet handsheets.

Water retention values

The water retention value (WRV) is a measure of the fiber saturation point (FSP). It was determined by conventional centrifugation (Thode *et al*., 1960). The experiments were done using an International Centrifuge Size 2 Model K (International Equipment NeedHam HTS, Mass, USA). Four repeat measurements resulted in WRV = 1.1 $\pm$ 0.1 g water/g fiber [9].

Results and Discussion

Results for the wet web strength of handsheets made from fibers without any additives and the friction force between two untreated rewetted sheets (the controls) are shown in Figure 4. These results were discussed before (Alince *et al.* 1996, van de Ven, 2008). The friction between two rewetted sheets first increases with solids content, mainly because the wetting force increases as more fiber-water-air contact lines are formed by water removal. The force reaches a maximum when the water remaining between fibers is confined mainly in liquid bridges at fiber crossings. With further water removal the number of bridges remains the same, but the amount of water in each of them decreases. When all water between the fibers has left (at the FSP), the friction force becomes too small to measure. The maximum friction force is about 3N, which for paper strips of 2.5 x 2.5 cm, corresponds to a force equal to 4.8 kN/m^2, in fair agreement with the prediction of Eq.[1]. This shows that almost all friction is caused by capillary forces acting between two wet sheets.

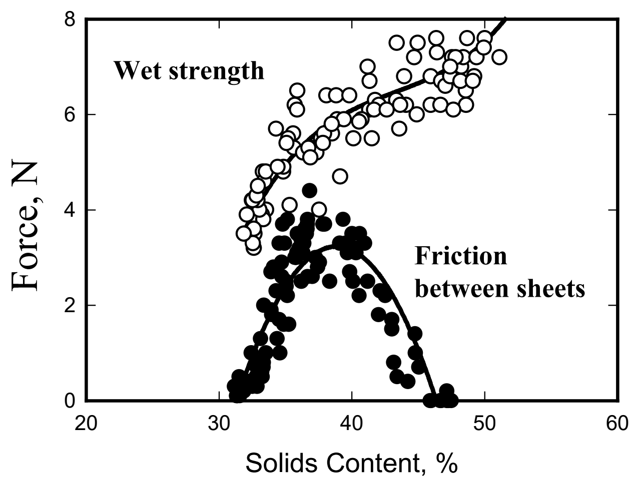

Fig.4. Strength of wet sheets and friction between rewetted sheets as a function of solids content (after Alince *et al*., 2006).

Not both sides of the sheets are equally smooth, as can simply be concluded by touching the sheets. The roughness depends on which side of the sheet was in contact with the screen during sheet making. Results for the friction force between wet sheets with either the smooth or the rougher sites touching each other are shown in Figure 5. It can be seen that the friction is larger when the rougher sites are in contact. For smooth surfaces, the fibers are more flattened, resulting in an increase in the effective diameter D and thus in a smaller friction force (cf. Eq.[1]). The flattening will also affect the value of λ, but apparently less so than the value of D. Also the fiber orientation affects the friction force. Figure 6 shows results for the friction force between wet sheets in which either the machine direction (MD) or cross direction (CD) is parallel with the applied force. The friction is larger for MD. The estimate of the friction force by Eq. [1] is based on arguments valid for axisymmetric wetting. The results suggest that the capillary force per crossing (λ) is not only acting normal to the fibers, but has a component in the plane of the sheet as well.

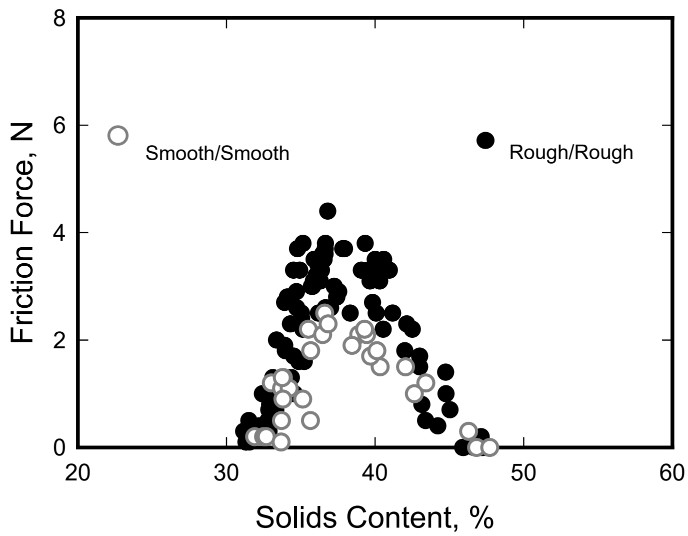

Fig.5. Friction force between two wet blotters with either the rough sites or smooth sites facing each other.

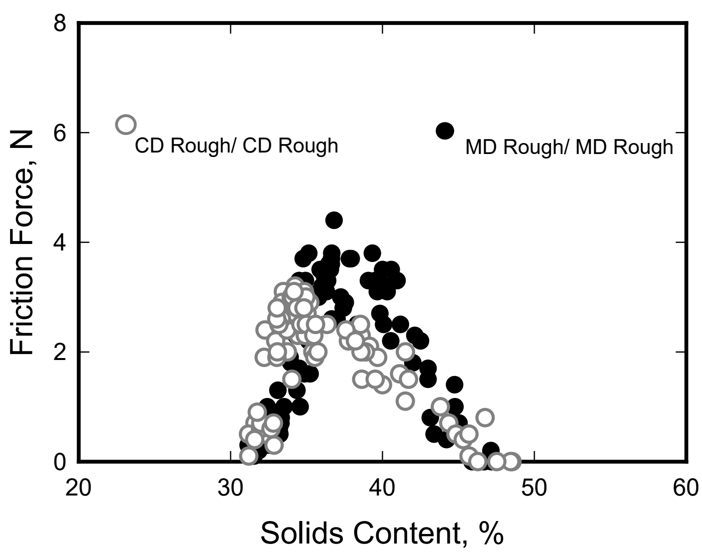

Fig.6. Friction force between two wet blotters with either the machine direction (MD) or cross direction (CD) parallel to applied force.

The wet web strength continues to increase with solids content, even in the region where the capillary forces go to zero (cf. Fig.4), implying an alternative mechanism for wet web strength development, likely to be an entanglement friction. To learn more about this entanglement friction is the main objective of this study.

The effects of entanglements can be judged by adding either long and flexible particles (such as microfibrillated cellulose, MFC), or long and rigid particles (such as glass rods). If the wet web strength were solely due to capillary forces, one would expect, according to Eq.[1], an increase in wet web strength for MFC and a comparable wet web strength for glass rods, since L/C is much larger for MFC than for pulp fibers, whereas for glass rods and pulp fibers L/C is comparable (~3 m^2/g). If entanglement friction is responsible for wet web strength, flexible microfibrils should increase the wet web strength of paper, whereas rigid glass rods should decrease the strength.

In Figure 7 the results for the wet strength and sheet friction are presented for sheets treated with cellulose microfibrils.

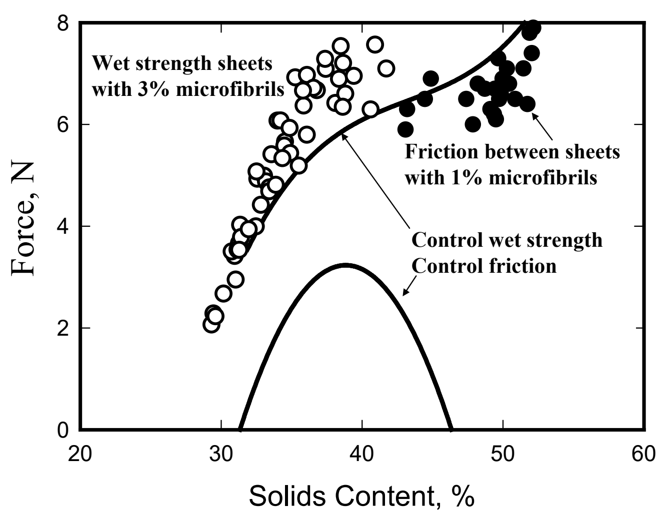

Fig.7. Wet strength of sheets containing cellulose microfibrils and friction force between two sheets treated with microfibrils. The lines are controls in the absence of microfibrils (cf. Fig.4).

Fig.7 shows that microfibrils increase the strength of wet sheets. At 40% solids, the rupture force has increased from 6 N to about 7 N. A likely explanation is that the microfibrils cause more entanglements, that lead to a stronger wet sheet. It can be seen that the difference in wet strength for sheets containing microfibrils compared to the control, increases with solids content. This implies that the effects of entanglement friction become more pronounced upon dewatering. Microfibrils deposited on top of rewetted sheets increase the friction force between the sheets tremendously (solid black dots in Fog.7). Contrary to untreated sheets, for which the friction approaches zero at the FSP, the friction continues to go up with solids content for sheets treated with microfibrils. Sometimes the friction was so large that the sheets ruptured instead of sliding past each other. It is likely that microfibrils lying on top of one wet sheet can entangle with the microfibrils on the second sheet, thus leading to very large friction forces.

Figure 8 shows the effect of glass fibers on wet web strength. For comparison results for sheets made of glass fibers and cellulose microfibrils are shown as well. It can be seen that introducing glass rods into paper reduces the wet web strength, since breaking lengths without glass rods are considerable higher (e.g. at c = 0.4, T = 80 m for control without glass rods). Since this reduction cannot be ascribed to a reduction in the capillary forces, it clearly must be due to a reduction in entanglements. More flexible cellulose microfibrils are able to produce a strong sheet when mixed with glass rods.

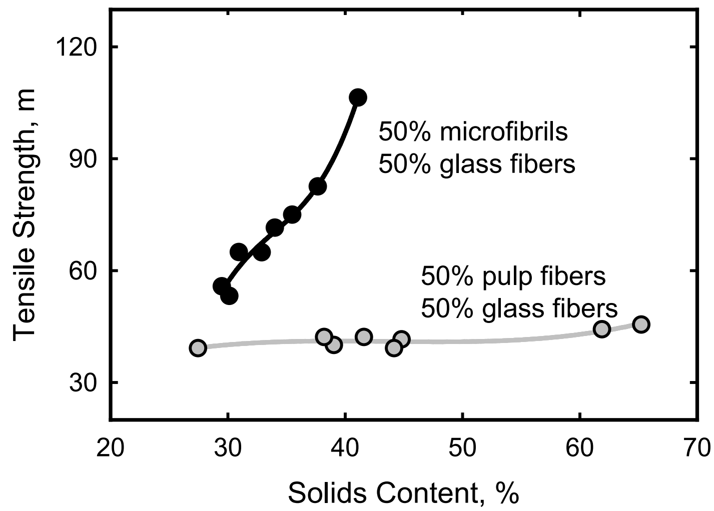

Fig.8. Wet tensile strength of sheets (expressed as breaking length for comparison) made from mixtures of microfibrils and glass fibers or pulp fibers and glass fibers.

The observation that flexible fibrils increase the wet web strength and rigid ones reduce it, implies that entanglement forces are more important than capillary forces. It is well-known that beating, a process producing fibrillated fibers (i.e. microfibrils protruding from the fiber surface), increases wet web strength. It is usually thought that this is due to an increase in the contact area between fibers. However, we can conclude from our study that the most important property of the fibrils is their flexibility, allowing them to entangle with other ones.

Another interesting question is whether we can modify the friction force by changing the configuration of fibers on the surface of wet sheets. We applied individual fibers from a dilute suspension on top of rewetted blotter sheets, followed by the procedure shown in Fig. 2. Next the blotters treated with additional free fibers were pressed together (with the treated sides facing each other). After drying to a certain solids content, the specimens were tested for sheet friction. The results in Figure 9 indicate that the individual fibers on the top of blotter sheets completely prevent the decrease in friction above c*. The only difference between this case and the control is the way the fibers are located on the surface of the sheet. It is possible that when fibers are deposited on a preformed wet sheet, some fibers penetrate the wet sheet to a certain depth and stick out from the paper, more or less randomly in all directions. When two wet sheets are pressed together, these fibers can penetrate the second sheet, thus forming some entanglements. These entanglements are absent when a wet sheet is pressed against a solid surface. It can be seen that in this case there must be mechanical friction above the FSP, because capillary forces are zero. This explains in part why multilayer sheets can be formed on a paper machine: each layer is rough, similar as the fiber-treated blotter papers, with fibers sticking out in all directions.

The adhesion between such sheets is expected to be similar as that of the treated blotter papers in Fig.9.

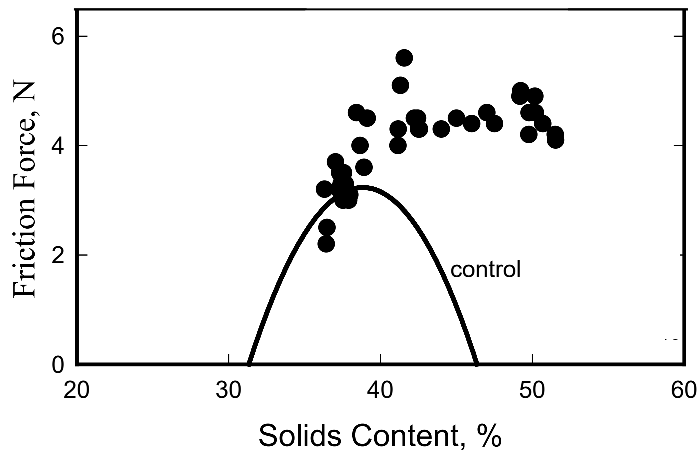

Fig.9. Friction force required to separate two wet blotters treated with reslushed blotter fibers applied on top. The concentration was 10 mg of reslushed fibers per 1 g of fibers.

One can assume that modifying the surface tension of the liquid that wets the swollen fibers may have an impact on the friction between two wet sheets, because this friction is determined by capillary forces (see Eq.[1]). The effect of surface tension on entanglement friction, and thus on wet web strength, is more difficult to predict, as we have as yet no quantitative theory for it. To see if the wet web strength and friction force can be altered by a decrease in the surface tension of the water, we used sulfonated kraft lignin (SKL), which lowers the surface tension of water; at a SKL concentration of 250 mg/L, the surface tension is 61 mN/m for distilled water and 54 mN/m for tap water, compared to 72 mN/m in the absence of SKL (de Oliveira, 2007). It is important to mention that SKL does not adsorb on fibers (van de Ven and Alince, 1996), thus it has no effect on the swollen fibers. We decided to choose tap water and a SKL concentration of 250 mg/L, in order to evaluate the effects of lowering the surface tension and to study its impact on the wet web strength and friction force. The results are shown in Figure 10. It can be seen from this figure that lowering the surface tension of water lowers the friction force between two wet sheets, as predicted by Eq.[1]. The FSP appears to be hardly affected, but the maximum friction appears at a lower solids content. According to Eq.[2], this implies a higher value of the liquid bridge volume α. A lower surface tension pulls the fibers less strongly together, because the capillary force, which is proportional to it, is lowered. If this explanation is correct, this implies that surface tension affects sheet consolidation. Also the wet web strength is lowered by the lowering of the surface tension of water, even above the FSP, where capillary forces are absent. At first sight this might seem surprising, because the wet web strength cannot be explained by capillary forces, which as we have seen underestimate the wet web strength by an order of magnitude at c* and even more so above. A likely explanation is that the surface tension affects the consolidation of the fiber network. This occurs at lower solids contents where capillary forces can bring fibers together. It is possible that higher surface tensions lock in more entanglements at consolidation than lower surface tensions. These entanglements are preserved during dewatering. Thus it is possible that the lowering of the wet web strength by surface tension is due to fewer or weaker entanglements being formed, rather than a lowering of capillary forces.

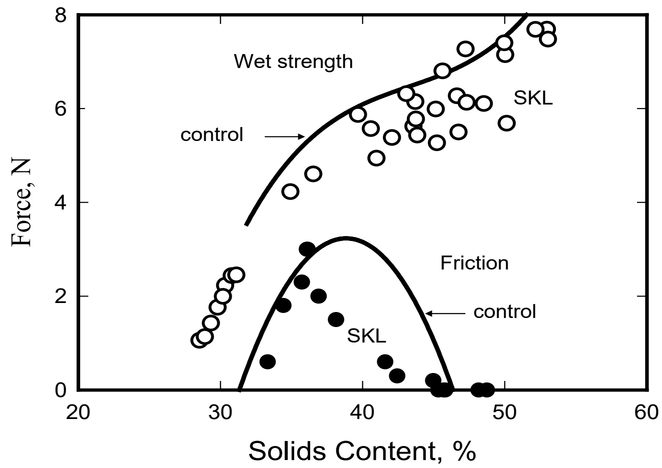

Fig.10. Wet strength and friction for sheets made with water containing SKL (γ = 54 mN/m). Open circles refer to wet web strength, solid dots to friction force between wet sheets. Solid curves are the controls in pure water (γ = 72 mN/m).

Finally we investigated whether colloidal forces could affect the wet strength or the friction force. Strong attractive forces could conceivably increase the friction and entanglement force. Pulp fibers are negatively charged and repel each other. This repulsion can be eliminated by adding an excess of salt which screens the electrostatic interactions. When the electrostatic repulsion forces are screened, the dominant force becomes the van der Waals attraction force. An analysis of these forces shows that a salt concentration of 0.1M NaCl is sufficient to screen the electrostatic forces between fibers (de Oliveira, 2007). Experiments were performed in aqueous 0.1M NaCl and both the wet web strength and the friction force were determined. It was found that 0.1M NaCl had no effect on the wet web strength, nor on the friction between sheets (de Oliveira, 2007). This proves that van der Waals forces are too weak to affect friction or entanglement. In retrospect this is not too surprising, because the capillary forces which bring the fibers together are larger than van der Waals forces. Capillary forces are of order $3\pi\mu\gamma D$, or about10 µN. Van der Waals forces are of order $AD/6h^2$, A being the Hamaker constant for fiber interactions in water (~ 10^{-20}J) and h the distance between the fibers at fiber crossings. It is generally believed that fibers do not come into true contact because of roughness and steric repulsive forces due to hemicelluloses on fiber surfaces. Taking h as low as 1 nm, leads to a van der Waals force of order 0.01 µN, which is three orders of magnitude lower than the capillary force.

Concluding remarks

It appears that capillary forces are negligible in wet paper above the fiber saturation point, because the friction between sheets, shown to be caused by capillary forces, is extremely small. In this regime the wet strength continues to increase with solids content, implying a force other than a capillary force is responsible for the wet strength. Similarly below the fiber saturation point, the wet strength is much larger than predictions based on capillary forces. These observations together imply that in the regime 30-50% solids content the main force for keeping the fibers together is another force, which we speculate is an entanglement friction. This hypothesis was tested by making sheets with different degrees of entanglements, using very thin and flexible cellulose microfibrils or rigid glass fibers. A very good correlation was found between the expected extent of entanglement and the strength of wet sheets. Moreover, it was demonstrated that a mechanical friction was present between wet sheets treated with microfibrils or pulp fibers, showing that when capillary friction is absent, mechanical friction can be induced between sheets. It is likely that this mechanical friction is similar to the entanglement friction in wet sheets. Somewhat surprisingly, the entanglement friction was found to depend on the surface tension of the water. A likely reason is that surface tension affects the consolidation of the sheet, an explanation consistent with the observation that the maximum friction between sheets occurs at a lower solids content when the surface tension is lowered. Finally it was shown that van der Waals forces have no effect on the entanglement friction or friction between wet sheets.

In addition we can conclude from our experiments that the adhesion between two rewetted sheets is very different from that between never-dried and never-pressed sheets. This is due to the smoothening of the surface of the sheet during pressing, which eliminates the formation of entanglements during rewetting. Never-pressed sheets are much rougher, leading to enhanced adhesion.

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