WET WEB STRENGTH DEVELOPMENT OF PAPER

by

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Winter 2007

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Master of Engineering

Your file Votre référence
ISBN: 978-0-494-32764-7
Our file Notre référence
ISBN: 978-0-494-32764-7

"Para minha querida e sempre amada mãe"
Martha Luzia Guimarães Melo

ABSTRACT

The adhesion of wet fibers is usually explained by the presence of capillary forces, which keep the swollen fibers together. These bonds are due to the free water present outside the wall of the swollen fibers. However, what happens when the free water is being removed and the tensile strength of the wet web continues to increase is not well understood. Tensile strength's measurements of refined fibers in presence of polyelectrolytes and mineral particles suggest that no enhancement of bonding occurs between the fibers when the free water is gone. The addition of microfibrils tends to enhance the wet web strength. This indicates strongly that fiber entanglement due to mechanical interactions may be the major interaction responsible for keeping the swollen fibers together in the transient region where neither capillary forces nor hydrogen bonding dominate.

The interactions between fibers, precipitated calcium carbonated (PCC) and retention aids, revealed that the wet web strength of PCC-filled handsheets is detrimental in the presence of flocculated PCC particles, while no detrimental effect is observed in the presence of stable PCC particles. Friction generated by the deposition of small and/or single particles on the fiber surface can explain their enhancement of strength, whereas bigger particles may prevent the entanglement of fibers. Finally, the addition of polyelectrolytes to swollen fibers reduces the wet web strength. The presence of an additional polymer layer results in an increased electrosteric repulsion between fibers, which decreases the friction between fibers. This reduction of friction makes the fibers slide more easily over each other, resulting in poor wet web strength.

RÉSUMÉ

On explique d'ordinaire la cohésion des fibres mouillés par la présence de forces capillaires qui maintiennent les fibres ensemble. Ces liens sont dus à la présence d'un excédant d'eau sur les surfaces extérieures des fibres gonflées. Cependant, on comprend mal comment la résistance de la feuille continue humide augmente lorsque cette eau résiduelle est enlevée. Des mesures de résistance à la traction de fibres raffinées en présence de poly-électrolytes et de minéraux indiquent qu'il n'y a pas d'amélioration des liaisons entre fibres quand il n'y a plus d'eau résiduelle. En revanche, l'ajout de micro-fibrilles tend à augmenter la résistance à la traction de la feuille continue humide. Cette observation suggère fortement que l'enchevêtrement mécanique des fibres est peut être le mécanisme principal par lequel la cohésion des fibres gonflées est maintenue dans la région transitoire où ni les forces capillaires ni les liaisons hydrogène ne dominent.

Les interactions entre les fibres, les agents de rétention et le carbonate de calcium précipité (PCC) révèlent que la résistance à la traction de la feuille continue humide diminue en présence de PCC floculé mais pas en présence de particules stables de PCC. Dans le premier cas, il est possible que la présence de gros agglomérats de PCC empêche l'enchevêtrement des fibres. Dans le second cas il est possible que la friction additionnelle générée par la présence de petits agglomérats ou de particules individuelles sur la surface des fibres soit la cause de l'augmentation de la résistance.

Enfin, l'ajout de poly-électrolytes aux fibres gonflées réduit la résistance à la traction de la feuille continue humide. Il semble que la présence d'une couche de polymère à la surface des fibres a pour effet d'augmenter leur répulsion électro-stérique, réduisant ainsi la friction entre elles. Cette diminution de friction permet aux fibres de glisser l'une sur l'autre plus facilement et résulte en une mauvaise résistance à la traction de la feuille continue humide.

ACKOWLEDGEMENTS

I would like to thank Dr. Theo van de Ven and Dr. Alince (deceased) for their continued guidance and encouragement, and for their dedication to the project. They have made me a better person and researcher, and I will be always grateful to them for their support and dedication.

Many thanks to Dr. Milan Maric for his encouragement, dedication and ensuring that the quality requirements of the Department of Chemical Engineering were respected.

Thanks to Domtar, namely Richard Gratton, Réjean Beaudoin and Harshad. Pande, for their dedication and enthusiasm with the project.

My special thanks to my colleagues at the Pulp and Paper Research Centre, and particularly to: Lojza, Agatha, Prasad, Laura, Thomas, Jimmy, Meng and Renata. Thanks also to my colleagues at Chemical Engineer Department: Santiago, Allen and Huang.

My sincere gratitude to Colleen, Louis and Mr. Rabello, for their help and invaluable contribution in many situations.

I also wish to thank my girlfriend Zofia, for helping me in many situations.

Finally, thanks to my brother, who believes in me above all circumstances. And my eternal thanks to my mother (in memoriam), and without whom, none of this would have been possible. *"Obrigado por tudo mãe!!!!!!!"*

CONTRIBUTIONS OF AUTHORS

The manuscript-based format was used for this thesis (Chapters 2, 3 and 4).

Chapter 2 "Wet web strength of paper at intermediate solids content"

Chapter 3 "Effects of PCC fillers on wet web strength of paper"

M. H. de Oliveira and T.G.M. van de Ven

These chapters were performed under the supervision of Dr. van de Ven who will be co-author of the papers. The author prepared the chapters and performed all experimental work and data analysis.

Part of the Chapter 2 was presented by the author at the Canadian Graduate Students Seminars PAPTAC 92nd Annual meeting in Montreal (Quebec, Canada) on February 9th, 2006. And part of Chapter 3 was presented by the author at the Canadian Graduate Students Seminars PAPTAC 93rd Annual meeting in Montreal (Quebec, Canada), February 8th, 2007.

Chapter 4 "The effect of polyelectrolytes on the wet-web strength of paper"

B. Alince (deceased), A. Vanerek, M.H. de Oliveira and T.G.M. van de Ven

The initial ideas for doing this work originated from Dr. Alince, who as result is listed as first co-author. All the experimental work, data analysis, graphs and original text were prepared by the author and A. Vanerek. Dr. van de Ven acted as co-supervisor.

The manuscript was published in the "Nordic Pulp and Paper Research Journal" Vol. 21 n. 5, 2006.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The strength of the wet web is an important property that controls the runnability (efficiency) of a paper machine. Although the design of the paper machine and the operating procedures are important for the efficiency of the process, the machine speed and the frequency of the wet end breaks are often related to the wet web strength.

The critical point in the papermaking process occurs between the press section and the dryer section, where the majority of breaks happen. These breaks generally occur, or are initiated at the "open draws", where the wet web is not supported by any wire or felt, and has to be transferred from one section to another, as shown in Fig. 1.1. In this process phase, the wet web contains around 35-50% solids content depending on the paper machine. In practice many breaks can occur per day, leading to a tremendous loss in paper production, as well as additional costs for cleaning and restarting the operation.

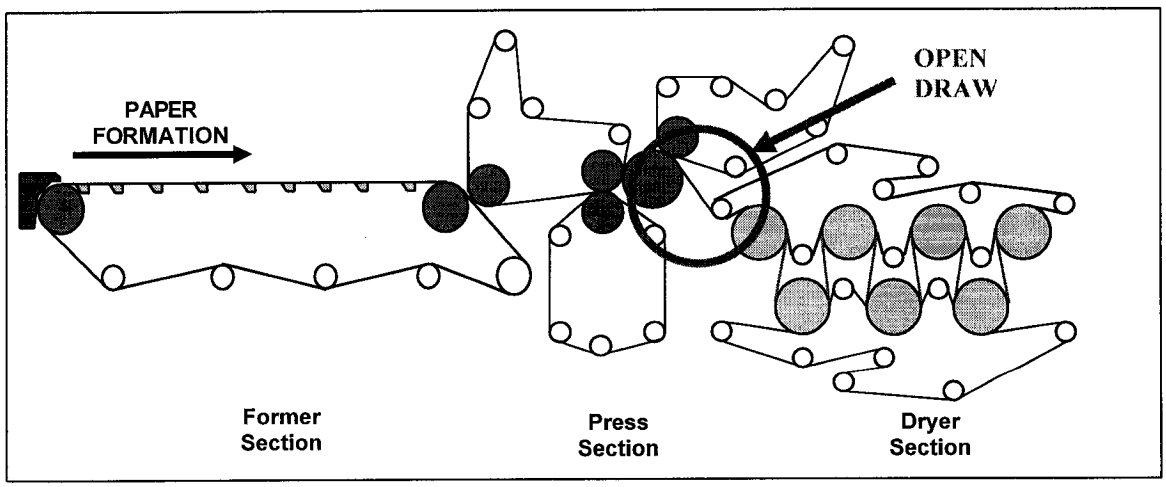

Fig. 1.1: "Fourdrinier" type paper machine with a typical "open draw".

Studies [1-4] have shown that wet webs with low solids content owe their strength to surface tension forces in the sheet, (or capillary forces) which keep fibers together. When water is removed fiber-water-air interfaces are created, where these forces of surface tension can act. Therefore, this concept may be applied to describe the wet web strength in the presence of free water, i.e. water which is not directly associated with swollen fibers. As the solids contents rise to levels where the free water is gone, above 30 – 50% depending on the sort of fibers, the tensile strength continues to increase. In the literature this phase is described as a transition between surface tension and interfiber bonding. The nature of these transitional "bonds" is not clear because hydrogen bonds can only be formed between fibers at very high solids content [5], when the paper is almost dry. Thus, the question remains: what keeps the fibers together in this transition phase where neither capillary forces nor hydrogen bonds play a major role?

It is important also to elucidate practical aspects of the papermaking production, such as, the colloidal interactions between cellulose fibers, fibrils, precipitated calcium carbonated (PCC), a very common filler encountered in fine paper, and polyelectrolytes, in order to improve the wet web strength under various conditions.

The so called "fillers" are mineral particles, added to the papermaking furnish as has been the practice for many years to improve properties or reduce costs [6]. The most used mineral particle for the production of fine paper or printing and writing paper is precipitated calcium carbonated (PCC). These mineral particles usually have a small particle size, negligible water solubility and a high degree of whiteness, so they can enhance the optical properties of the paper and provide better ink receptivity for printing. Finally, the replacement of cellulose fibers by mineral particles may cause a great

economic benefit since mineral particles are generally less expensive than the cellulose fibers.

1.2 Objectives

The topic of wet web strength development can be very broad and extensive. The present work will focus on two major points.

The first objective will be to elucidate the mechanism of wet web strength development in paper, using the fundamentals of colloid and polymer chemistry to explain the major interactions of fibers, fillers and polyelectrolytes while the paper web is still wet.

And the second one, more practical, will be to explore any possibilities of enhancing the bonding between swollen fibers. This enhancement can be achieved and verified by the addition of polyelectrolytes, insoluble particles, various kinds of cellulose fines and fibrils.

Another point to be considered in the second objective is the role of interactions between precipitated calcium carbonated (PCC), fibers and polyelectrolytes and their influence on the wet web strength. This issue is of an extreme importance for the pulp and paper industry, since it is known that the addition of PCC to the paper may reduce the cost of production and increase the quality of the fine paper produced [7].

1.3 Present Knowledge

The literature is restricted to only a few articles on research concerning the mechanism of wet web strength development.

The first study dealing with wet web strength was done by Campbell [1], who provided insight into the sequence of physical events during the paper production. His conclusions are still in accord with more recent works on this topic. He emphasized that the major factor contributing to the integrity of the wet web is surface tension. The surface tension (or capillary forces), as seen in Fig. 1.2, operates while there is free water between fibers. He visualized clearly the stage of compaction of the whole web induced by surface tension before the resistance of the fibrous networks breaks, followed by the opening of the surface tension envelope to allow entry of air. He then proposed also the next stage, wherein individual fibers in the wet web are still kept together by the surface tension forces of the remaining free water, and finally, when the fibers have been drawn into contact, and are held together by residual water menisci. In this way molecular attraction forces can play a role in the surface areas between fibers.

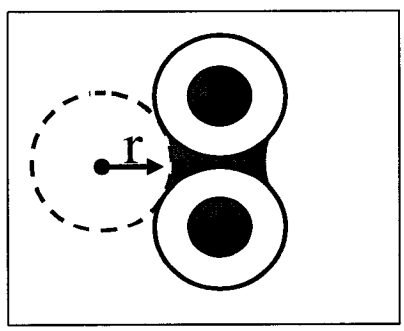

Fig. 1.2: Capillary forces between two adjacent fibers, where "r" represents the radius of curvature of the water meniscus.

Campbell also verified that the magnitude of the surface tension forces is independent of the dimensions of the fibers, but depends strongly on the deflection that could be produced by the fibers. In other words, the flexibility of the fibers can substantially increase the compaction of the wet web.

Based on this theory, that fibers are held together by surface tension of water, Page [11] developed the following equation for the quantitative determination of wet web strength:

$$T = \frac{\mu \cdot \gamma \cdot P \cdot L \cdot RBA}{C \cdot r} \qquad [1.1]$$

Here T is the tensile strength, μ is the coefficient of friction of wet fibers, γ is the surface tension of water, P is the perimeter of the average fiber cross-section, L is the fiber length, RBA is the relative bonded area in the sheet, C is the fiber coarseness, and r is the radius of the curvature due to the water meniscus.

This equation was derived by applying the concept called the "Campbell effect", which is based on the existence of a pressure difference across the curved surface given; according to this:

$$F = \frac{\gamma \cdot A}{r} \qquad [1.2]$$

Here F is the force holding two fibers together, γ is the surface tension of water, r is the radius of curvature of the water meniscus, and A is the area within the water

meniscus over which the surface tension forces act. It is important to note that as the r (radius of curvature) goes to zero, the surface tension forces do not increase to the infinity. In fact, the factor A/r goes to a constant value as r goes to zero, for parallel and crossed cylinders.

Other work was done by Stamm [9], who discussed the importance of surface tension in papermaking. He emphasized the balance between surface tension and structural restraint, and quantified the attractive force due to surface tension between fibers and fibrils. In his work, it was verified that fibers with smaller diameters result in menisci with larger capillary forces. These high internal tensions between fibers or fibrils far exceed the normally applied external compression force on the paper machine.

Table 1.1: Relation between diameter fibers and capillary pressure, Stamm [9].

Material	**Diameter (cm)**	**Pressure (kPa)**
Fibers	$2x10^{-3}$	600
Fibrils	$2x10^{-4}$	3,700
Microfibrils	$2x10^{-5}$	17,000

Lyne and Gallay [2,3] presented a series of studies dealing with the mechanism of the wet web strength and other properties during drying. In their work, they employed pressing between blotters and "air drying" in order to obtain the full range of solids content. They also observed that surface tension forces are predominant in wet web strength development in the early stages of drying. Some of their data indicated a fair demarcation of 50% solids content, at this stage they also observed a development of shrinkage tensions, shown below in Fig. 1.3. They also observed a critical water content of about 25% percent; above this solid content some kind of fiber-fiber adhesion appears to play a role.

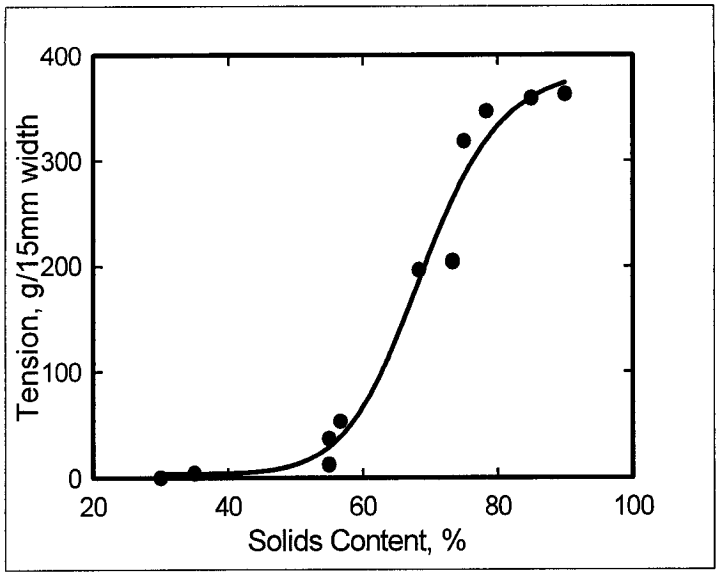

Fig. 1.3: Tension required to prevent shrinkage against solids of drying wet web, Lyne and Gallay [3].

Robertson [4], presented data on the development of tensile strength in drying wet webs accompanied by a parallel study of water retention. He noted an inflexion point around 50% solids as a possible transition point from surface tension consolidation to some other mode of interfiber adhesion. He divided the relation between tensile strength and solids content of wet web into several sections. Up to 15% solids, the web consolidates without air intrusion. At 15%, air intrusion starts and the removal of interfiber capillary water continues up to 30% solids. This is followed by removal of water associated with fibrils and the lumen, i.e. the hollow interior of the fiber, and at 50% solids content interfiber bonding starts to develop. In other words, Robertson described that the presence of free interfiber capillary water and the consolidation induced solely by surface tension ends around 30% solids content and molecular bonding between fiber surfaces starts above 50% solids. This means that the region of our interest,

i.e. 30-50% solids is transitional and neither capillary forces nor direct interfiber bonding dominates.

Rance [12] presented a study dealing mainly with the web compaction during drying, involving two distinct and successive phases. The first one is the compaction induced by surface tension, while the second one is the compaction induced by shrinkage of the fibrous components of the wet web during evaporation of bound water. These phases were designated "Inter-fiber web contraction" and "Intra-fiber web contraction" respectively. Baggerud [18] described a new technique for determining how paper is consolidated during drying as well.

Robertson [4] also worked on the development of various phenomena in wet webs. He also tested wet webs immersed in dioxane (a fluid with a very low surface tension) in Fig. 1.4, and it was observed that no strength between the fibers is developed below 50% solids content, indicating that surface tension forces are almost absent. But, as the solids content rises the wet web strength begins to develop at nearly the same solids content noted before, around 50% solids content. In this particular case, Robertson demonstrated that fibers can interact in the absence of surface tension forces, developing "mechanical interactions" between themselves. He also reported that the tensile strength is directly related to the flexibility of wet webs.

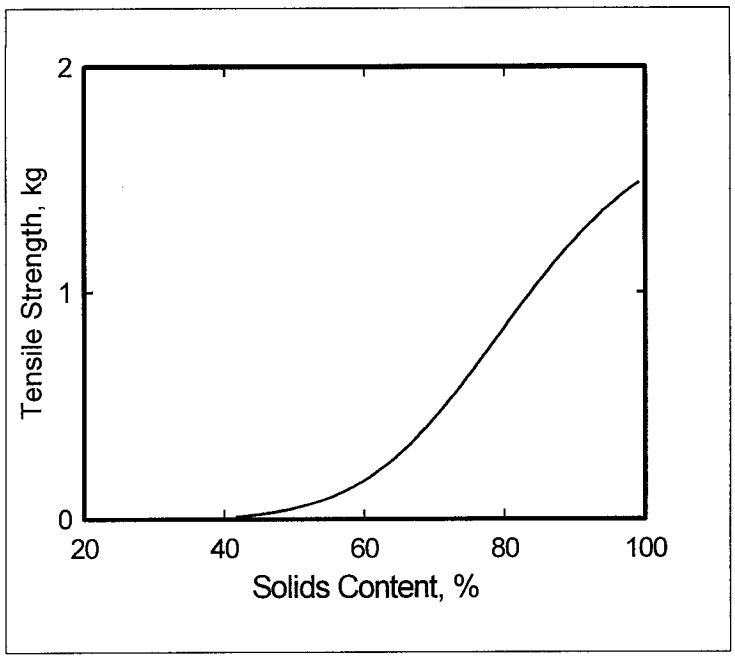

Fig. 1.4: Wet web strength immersed in Dioxane solution, adapted from Robertson [4].

Besides the fundamental studies dealing with the mechanism of wet web strength development, Nanko and Oshawa [10] presented an extensive microscopic observation of bonding between swollen fibers, which led them to conclude that at 50-55% solids content, all the water was removed from the fiber surface, corresponding to no more free water between fibers.

The rest of the published data dealing with wet web strength is of an empirical nature. It was shown [13-17] that beating increases the tensile strength of wet webs, that the contamination of the process water is detrimental and that introducing specific polyelectrolytes may result in wet web strength enhancement. However, pilot trials did not confirm the last claim. A number of water-soluble polymers, used as dry and wet strength agents, were also investigated without success. Indeed, their application is often detrimental to the wet web strength.

The conclusion from all the experimental observations, relating wet web strength to solids content, is that up to 30% solids content the capillary forces keep fibers together. The onset of direct interfiber bonding, believed to be via hydrogen bonds, is claimed to start above 50% solids. However, what happens in the critical region between 30% and 50% solids is not clear. It is difficult to envisage how to enhance the wet web coherence in this regime.

A schematic illustration of how the wet web strength varies as solids content increases and how this is related to the presence and the assumed location of water is shown in Fig. 1.5. The water associated with fiber wall is represented by dots.

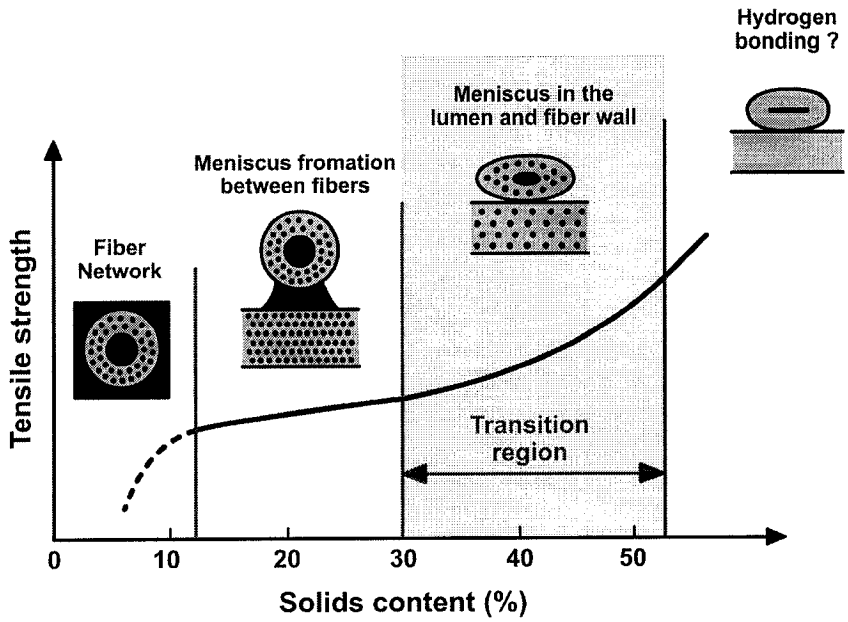

Fig. 1.5: Schematic representation showing the transition from surface tension forces to chemical bonding.

1.4 References

1. **Campbell, W. B**. "The cellulose-water relationship in papermaking." Forest Service Bulletin 84. Dept. of the Interior, Canada, 1933.
2. **Lyne, L. M. and Gallay, W**. "Studies in the fundamentals of the wet web strength". Tappi 37 (12) 698 (1954).
3. **Lyne, L. M. and Gallay, W**. "The effect of drying and heating on the swelling of cellulose fibers and paper strength." Pulp Paper Mag. Can. 51 (10) 129 (1950).
4. **Robertson, A. A**. "Measurement and significance of the water retention properties of papermaking fibers." In Consolidation of the paper Web, F. Bolam, Ed; Vol. 1, p. 90. Tech. Sec. BPBMA, London, 1966.
5. **Pelton, R. and Zhang, J**. "The role of surface polymer compatibility in the formation of fiber/fiber bonds in paper". Nordic Pulp and Paper Research Journal vol.15 n. 5/2000.
6. **Zhao, Y., Hu, Z., Ragauskas, A. and Deng, Y**. "Improvement of paper properties using starch-modified precipitated calcium carbonate filler". Tappi Journal, Vol. 4, n.2 2004..
7. **Burgess, M. S., Phipps, J. S**. "Flocculation of PCC induced by polymer/microparticles systems: Floc characteristics". Nordic Pulp and Paper Research Journal vol.15 n. 5/2000.
8. **Robertson, A. A. and Mason, S. G**. "The role of fiber collapse in papermaking. In The formation and Structure of Paper. F. Bolam, Ed., Vol. 2, p.639. Tech Sec. BPBMA, London, 1962.
9. **Stamm, A. J**. "Wood and Cellulose Science.", p.523. The Ronald Press Company, New York, 1964.
10. **Nanko, H. and Oshawa, J**. "Mechanism of fiber bond formation." In Fundamentals of Paper Making." C. F. Baker, Ed.; Vol.2, p.783. Mechanical Engineering Publications, London. 1989.
11. **Page, D. H**. "A quantitative theory of strength of wet webs." Journal of Pulp and Paper Science: Vol. 19, n.4, July 1993.
12. **Rance, H. F**. "Effect of water removal on sheet properties." Tappi 37 (12) 640 (1954).
13. **Caufield, D. F**. "The effect of cellulose on the structure of water". In Fiber-Water Interactions in Paper Making, Vol.1, p.63, BPBIF, London, 1978.
14. **Rance, H. F**. "Consolidation of the paper web." In The raw materials and processing of papermaking. H. F. Rance, Ed., Vol.1, Chapter 5, Elsevier Sci. Pub. Comp., 1980.
15. **Seth, R. S., Barbe, M. C., Williams, J. C., and Page, D. H**. "The strength of wet webs: a new approach". Tappi Journal, Vol. 65, n. 3, March 1982.
16. **Gurnagul, N., Seth, R. S**. "Wet web strength of hardwood kraft pulps". Pulp & Paper Canada, 98:9 (1997), 44-48.
17. **Laleg, M., Pikulik, I**. "The effect of dissolved materials and fines on the efficiency of strength polymers". 1996 International Paper and Coating Chemistry Symposium, p.67-75.

18. **Baggerud, E., Stenstrom, S.** "Further insight in the web consolidation process: Part III. Modelling of paper shrinkage - A model for the web consolidation process in the paper dryer is developed and compared with experimental data for kraft pulps. The results for the new model were further compared with three previous models from the literature." Nordic Pulp and Paper Res. Journal, vol. 20, n.1, p. 54, 2005.

CHAPTER 2

WET WEB STRENGTH OF PAPER AT INTERMEDIATE SOLIDS CONTENT

2.1 Abstract

The common explanation for the assembly and coherency of swollen fibers in the press section of the papermaking process is that the capillary forces bring the fibers together. These forces act on the surface of the fibers and are mainly due to the free water present outside the fiber wall. What happens when the paper sheet moves from the press section to the dryer section of the paper machine, thus reducing the water content, is not well understood. The present work serves as basis for an investigation of the main interactions between swollen fibers when the free water is present and/or absent, and its influence on the wet web strength. Besides wet web strength determination, the shear tension of swollen fibers was measured as well to assess the effect of friction between fibers on wet web strength. The colloidal interactions were studied by screening out the electrostatic forces with the addition of salt, leaving only the attractive van der Waals forces acting between the fibers. The results show that van der Waals forces do not contribute to the wet web strength of paper at intermediate solids content. Mechanical interactions or fiber entanglements were proposed to explain the adhesion between wet fibers. Microfibrils, flexible and thin fibrils, were confirmed to enhance the wet web strength and to increase the shear tension. A likely explanation is that microfibrils form more entanglements within the fiber network.

2.2 Introduction

One of the most critical points in the papermaking process is when the wet paper is being transferred from the press section to the drying section. At this point the wet web is about 40-50% solids content, therefore very weak and prone to break. The gap between these two sections, where the wet web is not supported, is called the "open draw" and may be very long (several centimeters) for some old fashioned paper machines. This large distance may cause variations in the tensile strength of the wet web, provoking several paper breaks per day, resulting in a greater loss in production. One possibility to prevent such breaks is to increase the wet web strength at the 40-50% range of solids content.

In order to enhance the wet web strength, it is necessary to understand paper formation, where swollen fibers are drawn together, mainly by capillary forces. When the free water leaves between the fibers, few articles in the literature propose a mechanism for how the fibers are kept together, in the range of 30-50% and higher. It is known that hydrogen bonds may play a definitive role when the paper is nearly dry, in which case interfiber bonding can take place due to the collapsing of the fiber walls, bringing the fibers together in close contact (less than 1 nm [1]). For wet paper the distance between fibers is much larger than 1 nm, thus preventing interfiber bonding by hydrogen bonds.

The objective here is to describe the main interactions of swollen fibers in the wet web during paper formation, particularly to address the question of what keeps fibers together as the water leaves the system. In the range of 30-40% solids content it has been argued that capillary forces are the major interactions between swollen fibers [2-6]. But

as the solids content start to rise to 40-50%, the capillary forces start to become less important, and explaining what keep swollen fibers together at this point is the main objective of the present work. One proposition is to verify the effect of colloidal forces between swollen fibers, evaluating whether colloidal forces play a major role in wet web coherency. Mechanical interactions will also be analyzed, in order to evaluate their impact on the interfiber bonding. We will also try to verify if the wet web strength and shear tension (see procedure section 2.3.4) can be affected by only changing the surface tension of the solvent surrounding the fiber wall. This can be performed by simply adding Sulphonated Kraft Lignin (SKL) to the pulp suspension. From the Campbell effect [2], we would expect to have lower capillary forces between fibers when the surface tension is also lower, which would affect weak wet web strength on paper machines.

2.3 Materials and Methods

2.3.1 Pulp Fibers

Blotter papers, made of unbeaten softwood kraft fibers, were used for the experiments. They were placed in a cell where salt, Sulphonated Kraft Lignin (SKL), fibers and microfibril solutions were passed through them, as seen in Fig. 2.1. The blotter papers were treated with the specified solution suspension for posterior shear tension tests. For the wet web strength experiments, the blotter papers were reslushed and the separated fibers were then place in a container with continuous agitation as shown in Fig. 2.2. After that, salt, SKL or microfibril solutions were added to the fibers at various

concentrations. Finally, this furnish was used to make handsheets, following TAPPI procedure T 205 om-88 [7].

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. Microfibrils used in the experiments were made from pure cellulose fibers with special fibrillation, and they were supplied by the Japanese company Celish.

2.3.2 Salt and SKL Preparation

Sodium chloride (NaCl) used in these experiments was dissolved in deionized water at several concentrations. SKL was utilized in the form of free-flowing brown powder and dissolved at concentrations of 1 g/L in deionized water. The degree of sulfonation of SKL was 0.8 and the average molecular weight was 10,0 MDa, measured by the supplier CIBA Chemicals Inc.. 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.

2.3.3 Wet Web Strength Test

The samples were prepared by placing a plastic mesh over the metal screen of the Standard British Handsheet Machine along with a template mold, as seen in the Fig. 2.2. The template had a pattern to create eight paper strips 25 mm wide and 55 mm 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 the Tensile Tester TMI Lab Master Testing Machines Inc.

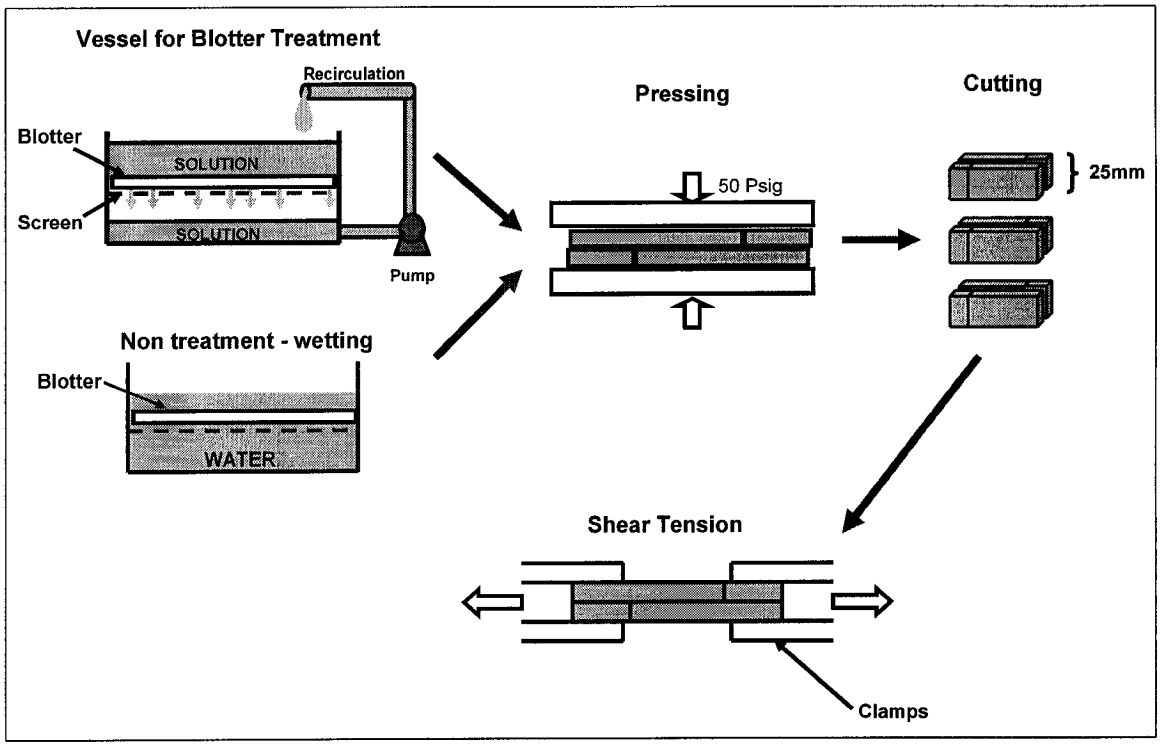

Fig. 2.1: Shear tension test procedure.

2.3.4 Shear Tension

The blotter sheets were soaked for 1 hour in deionized water and then placed into a custom-made cell (Fig. 2.1, top left). The cell had a rectangular compartment (~1.5 L volume) equipped with a screen. The main function of this apparatus was 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. A salt or SKL solution (1L) was introduced to the cell, and passed through the blotter continuously, being

recirculated by the peristaltic pump for 30 minutes. In the experiments involving treatment of microfibril solutions and reslushed fiber on the surface of the blotter paper, just one circulation was performed.

The treated blotter paper was then cut into strips of two different lengths (15 mm and 40 mm wide). They were placed together facing the treated side, as shown in Fig. 2.1. After, the strips were then placed between two Teflon plates and pressed at 350 kPa for 5.5 minutes in a "sandwich" format. After the press, the specimens were then cut into strips of 25 mm in width for the shear tension measurements. To obtain the shear tension of the samples we used again the Tensile Tester John Chatillon and Sons, NY.

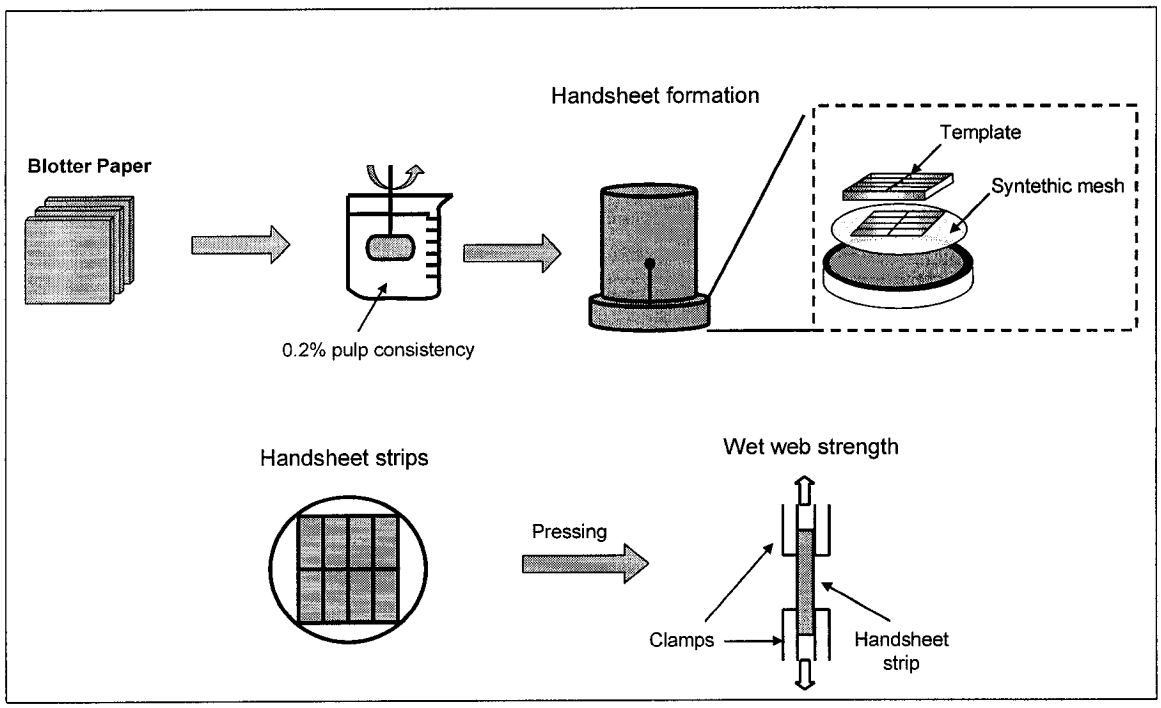

Fig 2.2: Wet web strength procedure, following TAPPI T-205 om-88 for handsheets preparation.

2.4 Tensile Strength and Shear Tension

The coherency of paper is mainly due to the cross linkage interactions between the fibers. It is unfeasible for completely parallel fibers to form a coherent sheet, even when the fibers have a large potential contact area between themselves, or are subject to large capillary forces. Those swollen fibers will eventually collapse and fall apart after the free water is gone. This explanation can be demonstrated by pressing together two blotter papers previously soaked in water. Their fibers can swell and deflect in response to the capillary forces generated. The results shown in Fig. 2.3 indicate the importance of the capillary forces for the adhesion of swollen fibers. The fibers in contact can be tested by two different ways: inside the fiber network (tensile strength); or by the pressing of two pre-formed blotter sheets (shear tension). It is evident that the shear tension between two blotters reaches a maximum at about 38% solids content, close to the actual values of the wet web strength (tensile strength). These results indicate that the major contribution for the adhesion between swollen fibers at 33-43% is due to capillary forces.

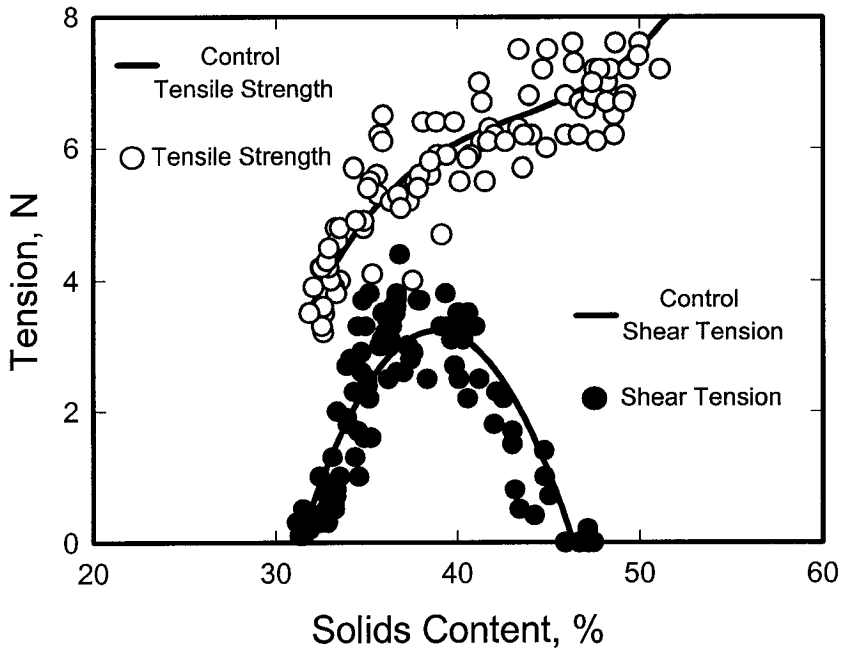

Fig. 2.3: Tensile strength of reslushed blotter and the shear tension required to separate two wetted blotters. Tap water was used in both cases. The lines refer to the statiscal averages of the experimental data, and will be treated as control for subsequent results.

2.4 Free Water

In the present context, "free water" means the water outside the swollen fibers, i.e. the water believed to be responsible for keeping the fibers together due to the capillary forces. The water associated with a swollen fiber, i.e. located in the fiber wall and in the lumen does not contribute to capillary forces. The question is how much of the total water in the wet web is free and how this changes with increasing water removal. A crude estimate, based on the assumption that one part of fiber can accommodate one part of water within its wall and two parts within its lumen, suggests that there is no free water

between fibers at around 25% solids content. By admitting that water from the lumen can replenish the lost free water outside fibers (for instance during pressing), the cut off will be at 50% solids, as shown schematically in Fig. 2.4.

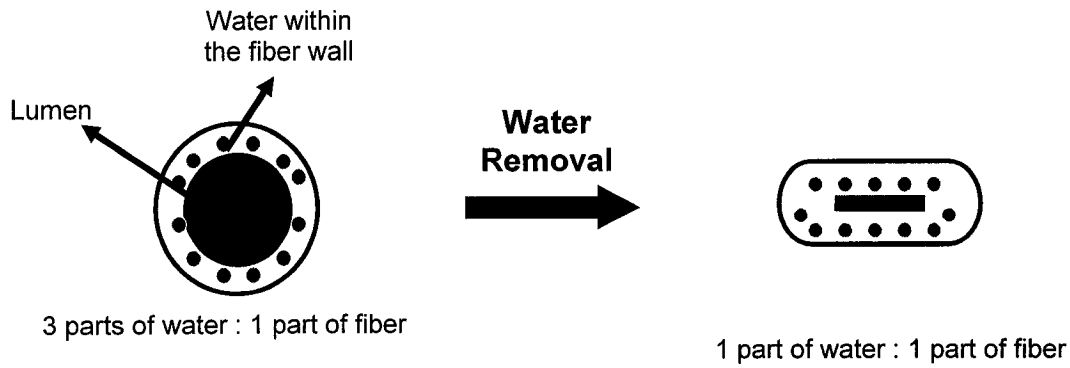

Fig. 2.4: Diagram showing the water inside the lumen and within the fiber wall. The gray color represents the water, while the white color the fiber wall.

One simple method to determine the amount of water associated with the fiber wall is by evaluating the water retention value (WRV), using centrifugation [8, 9]. This parameter indicates the solids content at which the free water is absent.

The key point in determining the WRV of swollen fibers is to establish exactly what relative centrifugal force, F_c, is the optimum. Excessively low values of F_c will fail to overcome completely the capillary forces between the interfiber voids, resulting in a WRV at low solids contents where not all the water associated with the fiber wall is removed. On the contrary, excessively high values of F_c will result in intrafiber water loss, or the water inside the lumen, giving a false estimate of the water retention value in

the fiber wall. Following the results found in the literature [10], F_c was used for our purposes and was closer as 1000 times the force of gravity (1000g). Basically, F_c, can be determined by two factors, the speed of rotation and the radius of the pad of fibers from which water is being extracted.

$$F_c = 0.0000284RN^2 \qquad [2.1]$$

This equation describes the centrifugal force, where R is the radius in inches and N is the rotational speed in revolutions per minute

The experiment was performed by placing reslushed blotter fibers inside the cell, as shown in Fig. 2.5. The pulp was supported by one 100-mesh screen which allowed the water to pass through, yet was able to retain any fibrils or fines in the final pad. The fiber mat was then weighed and the difference between initial and final solids content of fibers suspension gave the WRV. The experiment was performed using the International Centrifuge Size 2 Model K by International Equipment NeedHam HTS., Mass.

Table 2.1: Water Retention Value (WRV) results for reslushed fibers from blotter.

Sample	Weight in, g	Weight out, g	Solids Content, %	Water Retention Value (WRV), g H2O/g fiber
1	2.8	1.3	46.43%	1.15
2	2.89	1.31	45.33%	1.21
3	2.7	1.3	48.15%	1.08
4	2.69	1.32	49.07%	1.04

The results have shown that there is no more water outside the fiber wall above ~47% solids content as seen in Table 2.1. This agrees with the results previously presented, indicating that no swollen fibers can form any sort of capillary force

interactions when the free water is absent. In fact the results from Fig. 2.3 show exactly this behavior, where the shear tension between two wet blotters decreases to zero values at ~45-50% solids content. At this range of solids content until the paper is completely dried, there should be other forms of interfiber bonding in order to keep the fibers together, because from this point on, the adhesion between swollen fibers increases, as shown by the wet web strength results in the Fig. 2.3.

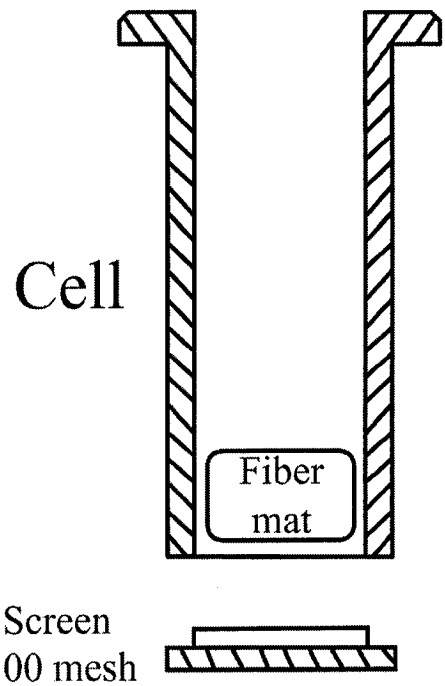

Fig. 2.5: Centrifuge cell assembly.

2.6 Surface Tension Effects

The capillary forces responsible for keeping the fibers together, also known as "Campbell Effect", is based on the existence of a pressure difference across a curved surface given, for two parallel fibers, by the equation:

$$\Delta P = \gamma_{l,g} / r \qquad [2.2]$$

Where the γ is the surface tension and r is the radius of curvature.

From the equation above, it can be seen that the capillary forces increase or decrease by varying the surface tension of the liquid or the radius of curvature. Fibers are drawn together by the capillary forces and with water removal the radius of curvature decreases and the adhesion between fibers increases. Since the swollen fibers have the ability to deform as the water leaves the system then the fibers shrink (collapse) and change from a tube-like into a flat ribbon-like configuration, thus increasing tremendously the interfiber adhesion.

If the free water is absent, the fibers cannot develop interfiber bonding through capillary forces. One can assume that by modifying the surface tension of the liquid, wetting the swollen fibers, may have an impact on the wet web strength. Using commercial surfactants, such as Sulphonated Kraft Lignin (SKL), we can decrease the surface tension of the water, and evaluate if the wet web strength and shear tension of swollen fibers can be altered as well. The Fig. 2.6 shows the variation of surface tension by the addition of SKL. It is important to mention that SKL does not adsorb on fibers [11], thus not forming any kind of interactions between the swollen fibers. The experiments were performed using tap and distilled water. We decided to choose tap water and a SKL concentration of 250 mg/L, in order to evaluate a lower surface tension and its impact on the wet web strength and shear tension.

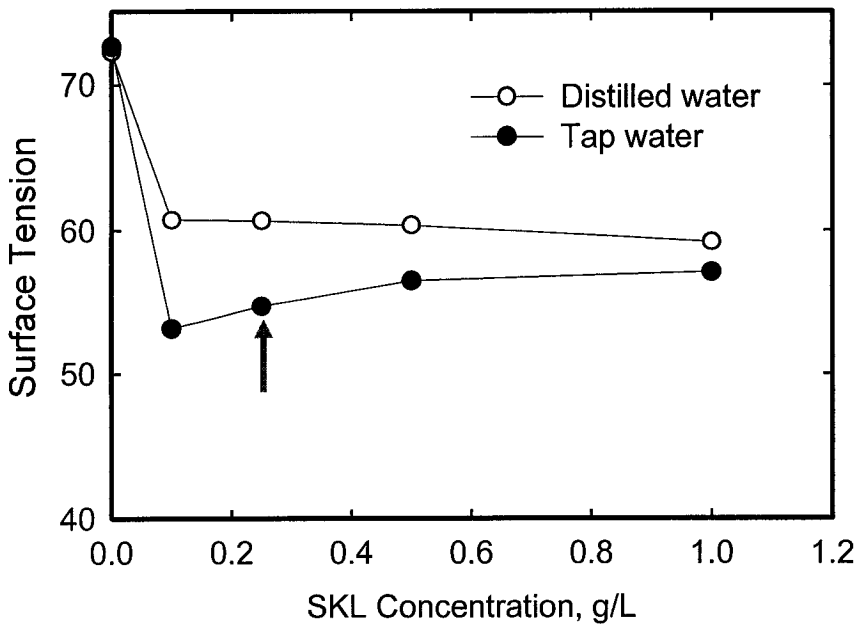

Fig. 2.6: SKL effect on the water surface tension, using tap and distillated water. The arrow indicates the chosen concentration (0.25g/L) for subsequent results.

The idea that the capillary forces are the major component for keeping fibers together at the range of 30-45% solids content is confirmed by the results shown in Fig. 2.7. Capillary forces are mainly the result of the surface tension of the solvent used and the radius of curvature. Using a suspending media with lower surface tension (0.25 g/L SKL), the wet web strength and shear tension are lower when compared to the case where the suspending media is only tap water. This strongly indicates that at this range of solids content, the adhesion can be influenced by the surface tension of the liquid wetting the fibers. Theoretically, the interfiber bonding between swollen fibers should improve by increasing the surface tension of the suspending media wetting the fibers. However, it is

extremely difficult to increase the surface tension of liquids and consequently these experiments were not attempted.

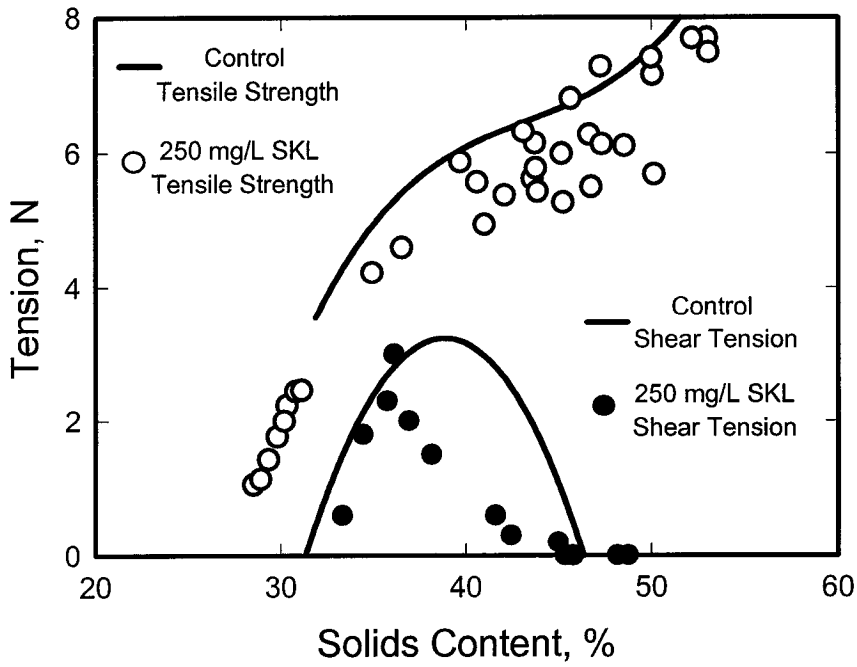

Fig. 2.7: Tensile strength of reslushed blotters and shear tension of two wetted blotters using 250mg/L SKL in tap water. Controls refer to tensile strength of reslushed blotters and shear tension required to separate two wetted blotters, using tap water. (The experimental points of the controls were omitted for clarity).

2.7 Effect of Salt

The strength of the assembly of the swollen fibers can be explained by interfiber bonding due the capillary forces, while the free water is present. During the water removal, especially after the water retention value, the interfiber bonds are not well understood. This range where the capillary force decrease and another kind of fiber-fiber

bond increases is called the "transition region". Many researchers believed that after the "transition region" the wet web coherency is governed mainly by the hydrogen bonds, which would indicate hydrogen bond formation between fibers from approximately 45% solids content until the paper is already dried. In fact, this explanation is not convincing, because there is an aqueous layer of wood polymers covering the surface of swollen fibers that prevent hydrogen bonds from being formed in this region of solids content [12]. According to [13] this layer can reach up to 100nm in thickness, thus preventing fiber-fiber surfaces to get into close contact (0.3 nm) where hydrogen bonds can be developed. Consequently, there is a region where neither the capillary forces nor hydrogen bonds are operative.

One possibility may arise from colloidal interactions between swollen fibers, particularly the van der Waals attractive forces. Using the classical DLVO theory of colloidal stability, it is possible to estimate the attraction between swollen fibers and their potential energy. Approximating the fibers as spheres to simplify the calculations, it is possible to calculate theoretically the potential energy as a function of the distance between cellulosic surfaces for different ionic strength.

$$V = V_R + V_A \qquad [2.3]$$

Here V_R is the potential energy of repulsion due to the electrostatic forces, and the V_A is the attraction potential energy due to the van der Waals forces. They can be expressed by following equations:

$$V_R = 2\pi\varepsilon a \psi_S^2 \exp(-\kappa H) \qquad [2.4]$$

Where ε is the permittivity ($6.9\text{x}10^{-10}$ $kg^{-1}m^{-3}s^4A^2$), a is the radius (70μm), ψ_s is the surface potential (20mV), κ^{-1} is the electric double layer (for 0.1mM NaCl the κ^{-1} is 30nm, for 1mM the κ^{-1} is 10nm, for 10mM the κ^{-1} is 3nm and for 100mM the κ^{-1} is 1nm) and H is the distance between the equivalent spheres representing the swollen thicken fibers. For these calculations, the electrolyte used was NaCl (sodium chloride) for simplicity. Equation 2.5 gives the attractive forces in terms of the Hamaker constant A ($1\text{x}10^{-20}$J).

$$V_A = -\frac{Aa}{12H} \qquad [2.5]$$

Calculating the total potential energy [2.3], using the equations [2.4] and [2.5] for different ionic strengths, we obtain the results shown in Fig. 2.8.

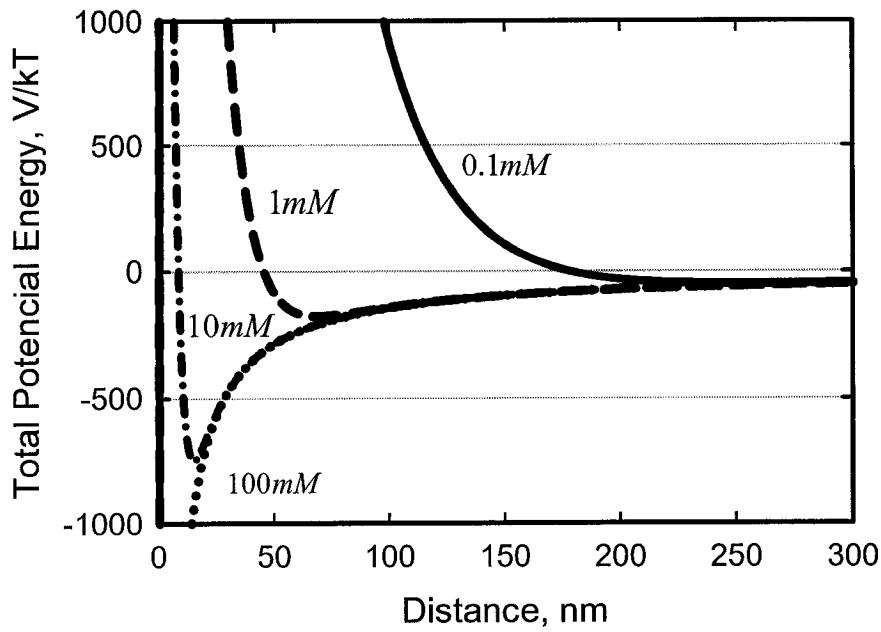

Fig. 2.8: Total potential energy V as a function of distance between cellulosic surfaces for different salt concentrations (sodium chloride). The total potential energy was calculated as the sum of energy of attraction V_A (due the van der Waals forces) and energy of repulsion V_R (due to electric double layer forces) between two fibers, approximated as spheres.

The positive values indicate repulsion, and the negative values indicate attraction between the fibers. It is apparent that by increasing the salt concentration, the attraction increases. In the presence of 100 mM NaCl, there are no repulsive forces and consequently only strong attractive forces apply between the cellulosic surfaces. This indicates that the adhesion between fibers should increase significantly in the presence of electrolytes, such as sodium chloride. Hence, as the adhesion between fibers increases due the colloidal interactions, the wet web strength and shear tension between swollen fibers may also improve in the presence of salt.

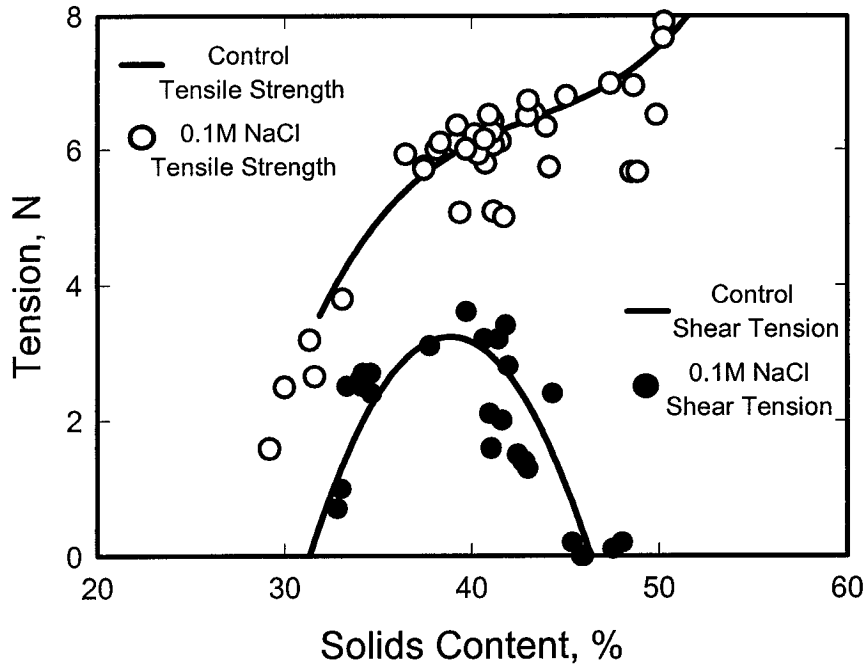

Fig. 2.9: Tensile strength of reslushed blotter and shear tension required to separate two blotters in presence of 0.1M NaCl. Controls refer to tensile strength of reslushed blotters and shear tension required to separate two wetted blotters using tap water. The experimental points of the controls were omitted for clarity.

The assumption that attractive van der Waals forces are a major factor in the adhesion of swollen fibers is not confirmed by the experiments however, as seen in Fig. 2.9. The addition of salt to the pulp suspension caused no substantial improvement in the wet web strength or shear tension. Theoretically, the addition of salt should decrease the electrical double layer thickness, screening out the repulsion forces, resulting in stronger van der Waals attractive forces. These results eliminate the possibility that colloidal interactions are responsible for keeping fibers together at this "transition region" (above ~ 45% solids content), where neither capillary forces nor hydrogen bonds are present.

2.8 Mechanical Entanglements

One may ask if the actual configuration of the fibers inside the wet web network may prevent the matrix to fall apart. Using an analogy, a bunch of flexible fibers inside the paper network may be more difficult to separate from each other than non flexible fibers. In this hypothetical example, the non flexible fibers will slide faster and easier over each other, while the flexible fibers will inherently form mechanical interactions between themselves or entanglements, preventing them from separation. The swollen fibers may follow the same path: the single fibers may form interfiber bonds by capillary forces, but they may also interact mechanically among themselves while the water leaves the system. These mechanical interactions are mostly due to the flexibility and length of the cellulosic fibers, characteristics that may contribute to the formation of mechanical entanglements which may be responsible for keeping the fibers together after the free water is gone (in the "transition region").

In order to evaluate the mechanical entanglements between swollen fibers, we applied individual fibers from a dilute suspension on top of blotter sheets, followed by the procedure shown in Fig. 2.1. Then, the blotters treated with additional free fibers were pressed together (with the treated sides facing each other). Afterwards, the specimens were tested for shear tension. The results in Fig. 2.10 indicate that the individual fibers on the top of blotter sheets completely prevent separation of the blotters. This is an argument implying that, mechanical interactions due to the entanglements of fibers and the friction caused by the addition of individual fibers on top of the blotters can be the explanation for keeping fibers together, in the absence of free water. All the experimental points reach

higher values than the capillary forces region, following the initial path of the control. But instead of decreasing the tension as the water leaves the system, the experimental points reach a plateau where the two blotters are kept together.

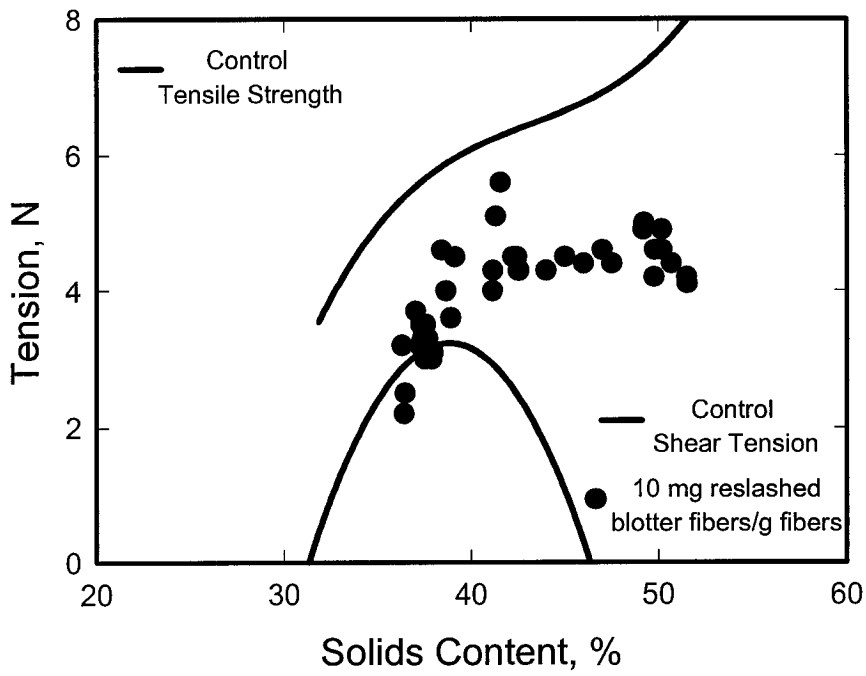

Fig 2.10: Shear tension required to separate two wetted blotters treated with reslushed blotter fibers applied to the top, the concentration was 10 mg of reslushed fibers per 1g of fibers. Controls refer to tensile strength of reslushed blotters and shear tension required to separate two wetted blotters, using tap water. (The experimental points of the controls were omitted for clarity).

Following the same path, the addition of more flexible and smaller fibers may increase the adhesion between swollen fibers even more. One attempt to reach this objective may be achieved using micro fibrillated cellulose, commercially known as microfibrils. The microfibrils used in this experiment are made from pure cellulose fibers that are highly refined by a special fibrillation technique. Fig 2.11 shows a TEM picture

with microfibrils surrounding the remaining swollen fibers, where the suspension is a well defined mixture of individual cellulose fibers and very thin and flexible microfibrils

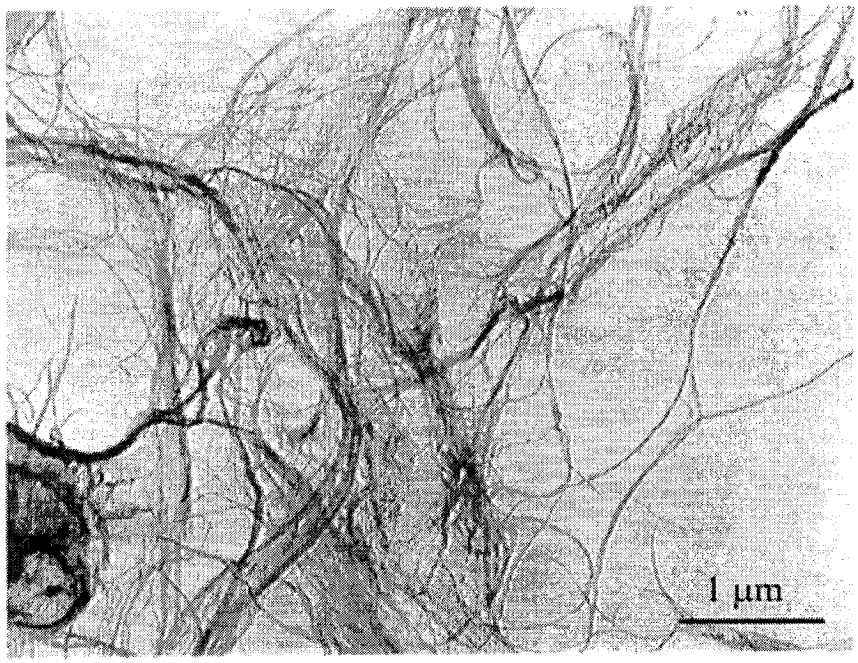

Fig.2.11: TEM photograph showing the extent of fibrillation of small fines with fibrils ranging from 5 nm (the microfibrils) up to several hundreds of nanometers.

We tested the addition of microfibrils within both the blotter fibers suspension and also on top of the pre formed blotter sheets. The results shown in Fig. 2.12 for the tensile strength and for the shear tension indicate clearly a much stronger improvement in the adhesion among swollen fibers. The addition of 3% of microfibrils over the total basis weight of the handsheet generates a higher wet web strength of ~20%, while the shear tension between the two blotter sheets reached impressive values, as high as their own wet web strength. In fact, some experimental values of the shear tension may indicate even stronger adhesion between fibers, since many specimens broke at the edge of the

tensile tester machine clamps, which indicates that the shear tension required to separate them was much higher.

All these arguments suggest that mechanical entanglements between swollen fibers play an important role for the development of the wet web strength during the paper formation. These mechanical bonds are mainly governed by how the fibers can interact physically with neighboring fibers, or how the fibers can entangle among themselves. With the addition of flexible and thin microfibrils, the wet web strength had a significant strength improvement and the shear tension reached values as high as its wet web tensile strength.

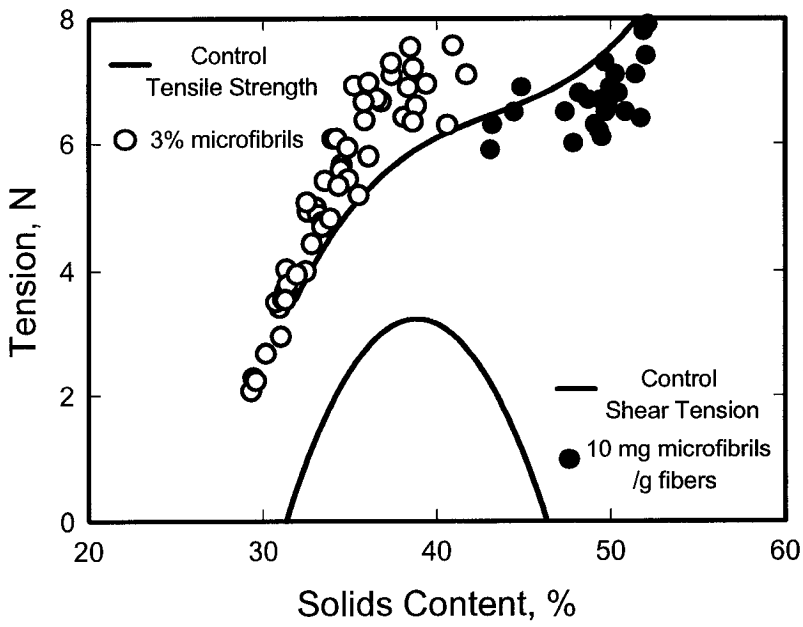

Fig. 2.12: Tensile strength of reslushed blotters with addition of 3% of microfibrils over the basis weight, and the shear force required to separate two wetted blotters treated with 10 mg of microfibrils per gram of blotter. Controls refer to tensile strength of reslushed blotters and shear tension required to separate two wetted blotters, using tap water. (The experimental points of the controls were omitted for clarity.)

Another experiment was performed in order to evaluate the wet web strength of three different components. Two distinct handsheets were made using rigid glass fibers, softwood kraft fibers and microfibrils. The first handsheet was composed of 50% glass fibers and 50% softwood kraft fibers, while in the second one the composition was 50% glass fiber and 50% microfibrils. The microfibrils are more flexible and thinner than the softwood fibers, and the glass fibers as shown in Fig. 2.13 are rigid and not flexible and impossible to entangle between themselves.

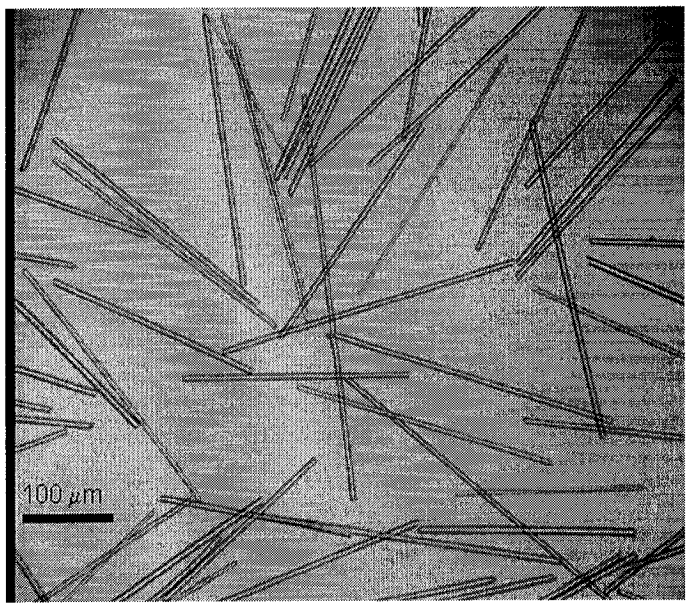

Fig. 2.13: Glass fibers using optical microscopy.

If mechanical entanglements play a fundamental role in the adhesion of swollen fibers, we would expect higher values of wet web strength for the mixture of microfibrils and glass fibers than the mixture glass fibers and softwood fibers, because microfibrils are more flexible and thinner being able for an optimum mechanical entanglement. In fact, these expected results are shown in the Fig. 2.14, where the microfibrils do increase

the wet web strength when compared to the mixture glass fibers and softwood fibers. Since the rigid glass fibers can only interact with surrounding fibers by capillary forces, we assume that the large difference in strength between the two graphs in Fig. 2.14 is due to the mechanical entanglements of the microfibrils when compared to the softwood fibers. Both have the ability to entangle between themselves and the rigid glass fibers, but if a more flexible and thinner fiber is used, the mechanical entanglements increase enormously, indicating that mechanical entanglements are of fundamental importance in the development of the adhesion between swollen fibers and consequently its wet web strength.

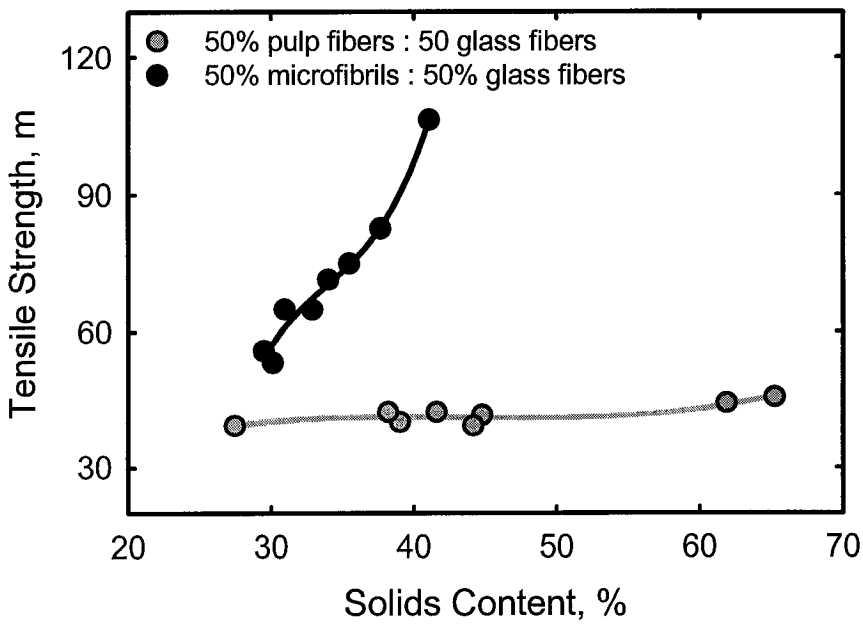

Fig. 2.14: Tensile strength of two different handsheets. First handsheet made of made of 50% glass rigid fibers and 50% of softwood kraft fibers, and the second made of 50% glass fibers and 50% microfibrils.

2.9 Conclusions

The adhesion among swollen fibers can be explained by capillary forces as long as there is still free water present outside the fiber wall. The capillary forces also play an important role in the range of 30-50% solids content, and it has been shown that the adhesion of swollen fibers in this range can be modified by simply varying the surface tension of the water wetting the fibers.

As the water leaves the fibers and capillary forces can no longer operate, many assumptions have been proposed to explain the coherency of the wet web. Above 45% solids, the interfiber bonding can be described neither by hydrogen bonds nor by attractive van der Waals forces. It is more likely that the assembly and coherency of fibers at this stage can be attributed to the mechanical interactions or entanglements of the fibers. These interactions may increase or decrease the fiber-fiber bonding depending mainly upon the flexibility, deformability, roughness, friction and length of the fibers. Microfibrils confirmed them to be a strong agent that improved the wet web strength and the shear tension of swollen fibers.

2.9 Acknowledgements

Thanks to the summer student Minh Tu that helped with some experiments presented here. Thanks also to Dr. Alince (in memoriam), for many stimulating discussions, and to Dr. Alois Vanerek. Financial support from Domtar and NSERC made this work possible.

2.10 References

1. **Pelton, R.** "A model of the external surface of wood pulp fibers." Nord. Pulp Pap. Res. J. 8(1), 113 (1993).
2. **Campbell, W. B.** "The cellulose-water relationship in papermaking." Forest Service Bulletin 84. Dept. of the Interior, Canada, 1933.
3. **Lyne, L. M. and Gallay, W.** "Studies in the fundamentals of the wet web strength". Tappi 37 (12) 698 (1954).
4. **Lyne, L. M. and Gallay, W.** "The effect of drying and heating on the swelling of cellulose fibers and paper strength." Pulp Paper Mag. Can. 51 (10) 129 (1950).
5. **Robertson, A. A.** "Measurement and significance of the water retention properties of papermaking fibers." In *Consolidation of the paper Web*, F. Bolam, Ed; Vol. 1, p. 90. Tech. Sec. BPBMA, London, 1966.
6. **Robertson, A. A.** and Mason, S. G. "The role of fiber collapse in papermaking. In The formation and Structure of Paper. F. Bolam, Ed., Vol. 2, p.639. Tech Sec. BPBMA, London, 1962.
7. Tappi procedure T 205 om-88. "Forming handsheets for physical tests of pulp.
8. **Thode, E. F., Bergomi, J. G. Jr.**, Unson, R. E. "The application of centrifugal Water-Retention test to pulp evaluation". Tappi Journal, vol. 43, n. 5, May 1960.
9. **Hubert, E., Mathes, A., and Weisbrod, K.** Kolloid Z. vol. 98, p.173, 1942.
10. **Rance, H. F.** "Effect of water removal on sheet properties." Tappi 37 (12) 640 (1954).
11. **van de Ven, T.G.M.** "Mechanisms of Fines and Filler Retention with PEO/Cofactor Dual Retention Aid Systems". J. Pulp paper Sci., 23(9), pp. 1447-1451, 1997.
12. **Pelton, R., Zhang, J., Wagberg, L. and Rundlof, M.** "The role of surface polymer compability in the formation of fiber/fiber bonds in paper." Nord. Pulp Pap. Res. J. 15 (5) 400 (2000).
13. **Neuman, R. D.** "Direct measurement of surface forces in papermaking and paper coating systems." Nord. Pulp Pap. Res. J. 8(1), 96 (1993).
14. **Robertson, A. A., Meindersma, E. and Mason, S. G.** "The measurement of fibre flexibility." Pulp Paper Mag. Can. 62 (1) T-3, (1961).
15. **Caufield, D. F.** "The effect of cellulose on the structure of water". In *Fiber-Water Interactions in Paper Making,* Vol.1, p.63, BPBIF, London, 1978.
16. **Rance, H. F.** "Consolidation of the paper web." In *The raw materials and processing of papermaking.* H. F. Rance, Ed., Vol.1, Chapter 5, Elsevier Sci. Pub. Comp., 1980.
17. **McKenzie, A. W.** "The structure and properties of paper. Part XXI. The diffusion theory of adhesion applied to interfiber bonding." Appita 37 (7) 580 (1984).
18. **Lepoutre, P.** "Adhesion in paper products." Svensk Papperstidn. 89 (1) 20 (1986).
19. **Seth, R. S., Barbe, M. C., Williams, J. C., and Page, D. H.** "The strength of wet webs: a new approach". Tappi Journal, Vol. 65, n. 3, March 1982.

20. **Gurnagul, N., Seth, R. S**. "Wet web strength of hardwood kraft pulps". Pulp & Paper Canada, 98:9 (1997), 44-48.
21. **Seth, R. S., Page, D. H., Barbe, M. C. and Jordan, B. D**. "The mechanism of the strength and extensibility of wet webs." Svensk Papperstidning, n.6, 1984, p. R36-R43.

CHAPTER 3

EFFECTS OF PCC FILLERS ON WET WEB STRENGTH OF PAPER

3.1 Abstract

This work evaluates the interactions of precipitated calcium carbonated (PCC) and cellulosic fibers induced by addition of retention aids, such as cationic polyacrylamide (c-PAM) and Polyethyleneimine (PEI). The wet web strength of handsheets formed with these compounds was measured and analyzed for various PCC and polymer concentrations. The particle size of PCC and the state of aggregation were varied as well. The flocculation resulting from the interactions of PCC and cationic polyelectrolyte in a dilute system was examined in real-time using a Focused Reflected Beam Measurement technique (FBRM). Both the flocculation of PCC by c-PAM and the stabilization of PCC by Polyethyleneimine (PEI) were studied. The results using PCC flocculated with c-PAM showed a detrimental impact to the wet web strength. On the other hand the stabilization of PCC with PEI prevented completely any wet web strength loss for solids contents varying from 30% to 40%. This may indicate that friction effects inside the network of the PCC-filled handsheets may play a fundamental role in determining the wet web strength. Also studied was the shear tension between treated blotters with stabilized PCC particles. The results showed also an enhancement of the tension, compared to the shear tension of blotters only. It was also found that the addition of microfibrils to the PCC-filled handsheets can increase the wet web strength, and the mechanical entanglements from the microfibrils is likely the main cause for this enhancement.

3.2 Introduction

The addition of mineral particles to a papermaking furnish as "fillers" is a common process practiced for many years in the production of printing and writing papers [1]. There are many positive aspects related to this process, but it is also important to quantify and understand the impact of fillers, such as precipitated calcium carbonated (PCC), to the wet web strength of paper. The replacement of fibers by these mineral particles (diameter size of 1-5 μm) decreases substantially the adhesion between cellulose fibers inside the sheet, reducing the wet web strength. But conversely, PCC enhances the optical properties of the sheet, for instance PCC increases the whiteness and opacity of the sheet [1]. Characteristics such as smoothness and ink receptivity are also better in a paper filled with PCC than in a non-filled paper [2]. There are also economical benefits when mineral particles are added to paper, because precipitated calcium carbonate is less expensive than cellulose fibers, and thus the replacement of fibers by PCC is a great opportunity to improve paper quality and reduce the cost of production [3].

The addition of PCC can reach high levels of up to 70-80% of the basis weight of the sheet, in laboratory handsheets. But at this higher PCC content, the paper will have a highly detrimental impact on quality standards, leading to a weak sheet, linting and two-sidedness [2]. In practice filler levels of 15-25% are common in the paper industry. To produce a highly concentrated filled paper in a real process, the sheet would have a low strength, causing a negative impact on its wet web strength, therefore leading to many breaks between the press and dryer section of the paper machine.

In the absence of "retention aids", not much adsorption of fillers on the cellulose fibers occurs; in fact simply adding mineral particles to a furnish is not sufficient to increase the PCC content of the sheet. The explanation for this is that the detachment rate of fillers from fibers is very large, due to the low bond strength caused by the roughness of cellulose fibers, which prevent close contact [4,5].

To increase PCC adsorption on the fiber surface, a "retention aid" system is used where charged polymers mostly via bridging interactions, retain the PCC particles on the fiber surface. These bridging interactions diminish the detachment rate of the fillers from cellulose fibers [6]. It is important to evaluate the right dosage of the retention aid, because at higher dosages steric repulsion between the cellulose fiber surface and mineral particles may occur [7-10]. At concentrations well above the full coverage of adsorbed polymers on the fibers, the rates of adsorption of PCC can significantly decrease due to steric repulsion, while at concentrations below the full coverage the rates of adsorption of PCC may reach its optimum value [11,12], as shown in Fig. 3.1.

It is important not only to measure the wet web strength of handsheets filled with PCC, but it is necessary to understand filler flocculation and the main interactions that occur among the fibers-polyelectrolytes-fillers. And for this, several experiments were performed using a Focused Beam Reflected Measurement (FBRM) that can measure the relative floc size of the system being analyzed [17]. There are many reports in the literature dealing with flocculation of fillers and charged polymers, but few of them have focused on the impact of PCC and its interactions with retention aids on wet web strength. In fact, the objective of this work is to evaluate the PCC effects on wet web

strength, and in addition to find alternatives to enhance the wet web strength of paper filled with mineral particles.

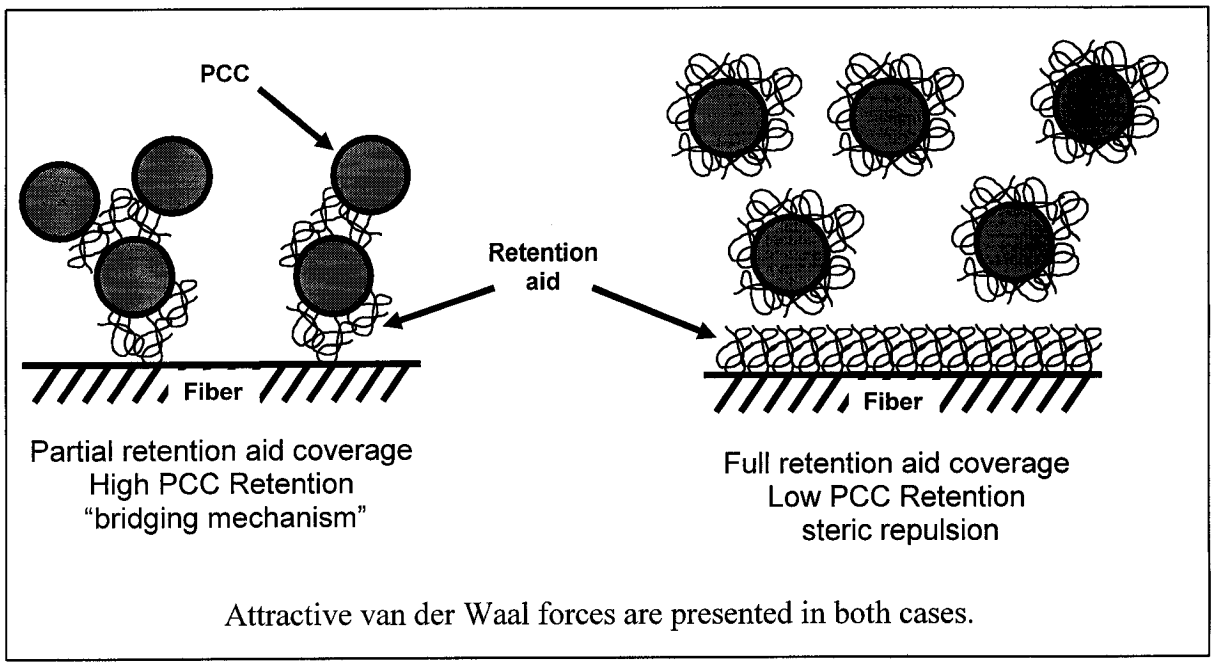

Fig. 3.1: Scheme showing the PCC aggregation and adsorption on fibers surfaces by "bridging mechanism" (partial retention aid coverage) and steric repulsion (full retention aid coverage).

In fact the flocculation rate is based on the "bridging mechanism" theory, where it is assumed that the flocculation rate, F, is proportional to the product of the particle collision frequency and the fraction of collisions that leads to bridging [4]. Thus, we have the following equations:

$$F = KE_{ij}N_0^2 \qquad [3.1]$$

$$F = KE_{ij}N_1N_2 \qquad [3.2]$$

Equation [3.1] represents homoflocculation and [3.2] represents heteroflocculation. Here, F is the flocculation rate, K is a constant, N is a number of particles and E_{ij} is the collision efficiency factor given by:

$$E_{ij} = 2\theta(1-\theta) \qquad [3.3]$$

$$E_{ij} = \theta_1(1-\theta_2)+\theta_2(1-\theta_1) \qquad [3.4]$$

Equation [3.3] represents homoflocculation and [3.4] represents heteroflocculation. The parameter θ is the fractional surface coverage of the retention aid.

In systems containing two different particle sizes, such as fiber (i) and filler (j), two types of interactions are involved to induce flocculation when a retention aid is used. The first is the interaction between anionic particles and the polymer segments, and the second interaction is between polymer segments and the surface sites free of adsorbed polymer. The present work will not focus on determining the collision efficiency factor between fibers and fillers, but it is fundamental in understanding the main interactions that may occur between fibers, fillers and charged polymers.

3.3 Materials and Methods

3.3.1 Pulp Fibers

Beaten softwood and hardwood kraft fibers were used through all experiments. They were supplied by Domtar Inc. with about 22% solids content, and always reslushed to form a 2% pulp consistency. Afterwards, the pulp suspension was stirred continuously

in a beaker, and then PCC was added to pulp suspension with posterior addition of c-PAM. Each material added to the pulp was kept in continuous agitation for 1 minute, as described in Fig. 3.2. Finally, the solution was used to make PCC filled handsheets, following TAPPI procedure T 205 om-88 [13]. The pulp stock was always prepared as a mixture of 80% beaten Hardwood and 20% beaten Softwood kraft fibers.

After the handsheets were tested for wet web strength, they were placed inside an oven for drying and evaluation of the solids content at the moment of testing. In the cases where fillers were added to the handsheets, the specimen was ashed for evaluation of the PCC content, following TAPPI procedure [14].

Microfibrils were also used in the experiments, in the same order of addition as described before. The microfibrils were made from pure cellulose fibers with special fibrillation, and they were supplied by the Japanese Company Celish.

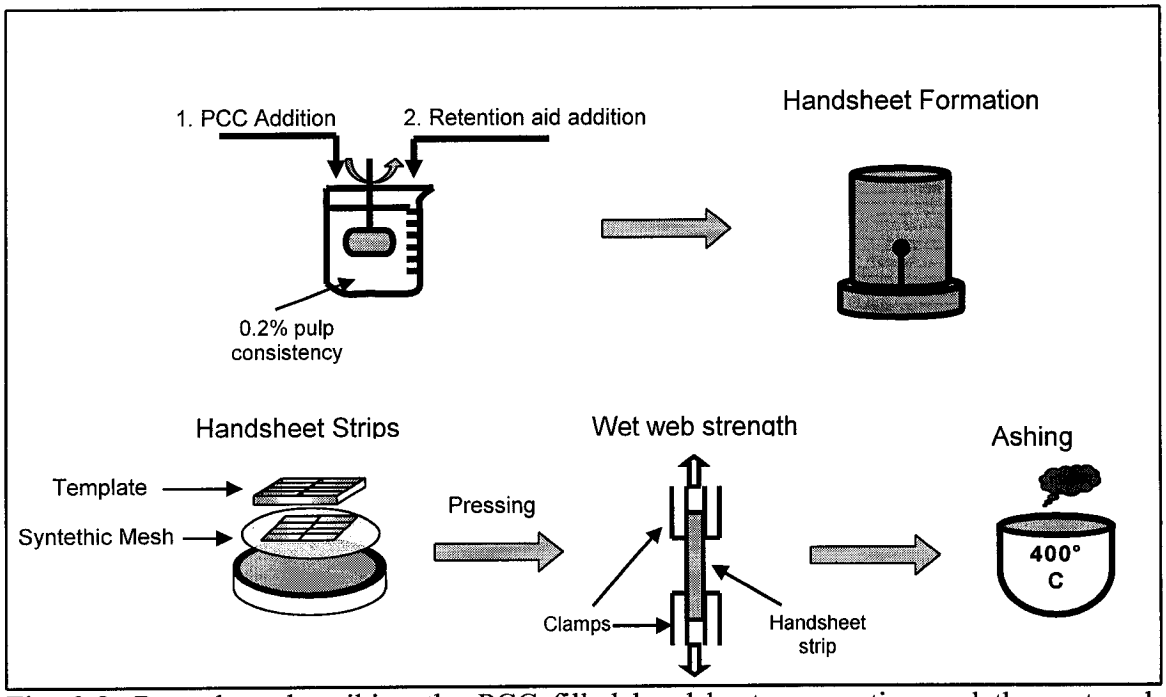

Fig. 3.2: Procedure describing the PCC filled handsheet preparation and the wet web strength tests.

3.3.2 Cationic Polyacrylamide (c-PAM) and Polyethyleneimine (PEI)

The retention aids used through all experiments were cationic polyacrylamide Percol 63 from CIBA Specialty Chemicals Canada Inc., and polyethyleneimine (PEI) from BASF. The average molecular weight of the c-PAM is 6 MDa and the degree of substitution is 40%. c-PAM and PEI were dissolved at concentrations of 1 g/L in deionized water, with continuous magnetic stirring to ensure full polymer dissolution. The pH of the c-PAM suspension was kept constant at pH=5 to prevent hydrolysis [15].

3.3.3 Precipitated Calcium Carbonated (PCC)

The filler used throughout all experiments was precipitated calcium carbonate (PCC) provided by Domtar Inc. The PCC utilized was scalenohedral positively charged because $CaCO_3$ is partially soluble in water and the Ca^{2+} ions preferentially adsorb to the

crystal surface, leading to positively charged particles [16]. Two distinct particle sizes (1.25 and 3.04 μm diameter) were used in the experiments to evaluate their impact on the wet web strength, as seen in Table 3.1. The PCC suspensions were diluted to 5 g/L, and the exact amount was then added to form the PCC filled handsheets. Fig.3.3 shows an example of the PCC particles used in these sets of experiments.

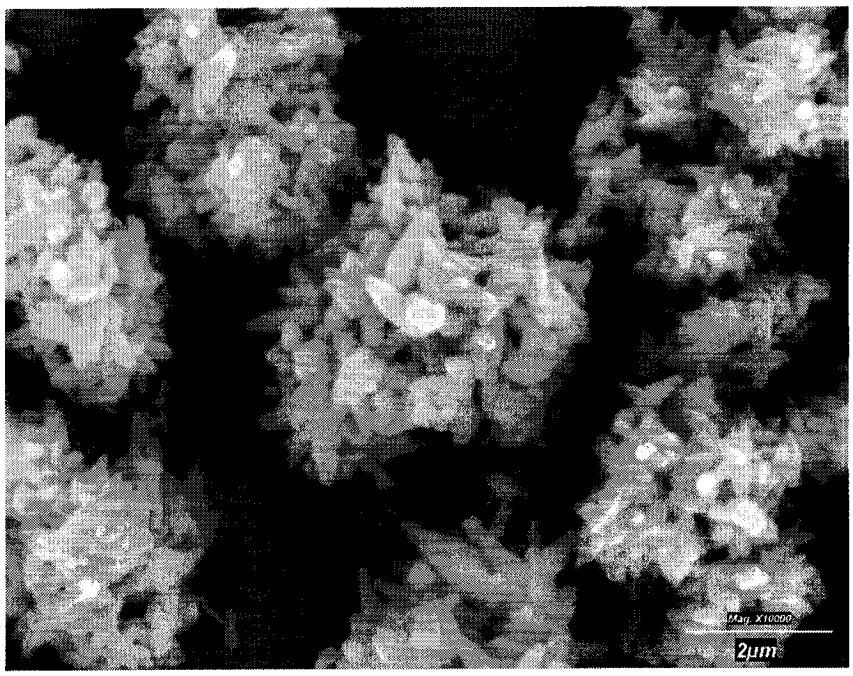

Fig. 3.3: Scanning Electronic Microscopy (SEM) picture of PCC particles (PCC 2).

Table 3.1: Comparison of the PCC particles used in experiments.

	Particle size (μm)	Specific surface area (m^2/g)
PCC 1	1.25	10.1
PCC 2	3.04	4.51

3.3.4 Focused Beam Reflectance Measurement (FBRM)

This set of experiments was performed with an FBRM-Lasentec analyzer. This equipment uses the Focused Beam Reflectance Measurement (FBRM) technique, which is composed of three parts: a probe which can be inserted directly in the process stream, the electronic measurement unit and a computer for data acquisition and analysis [17].

The suspensions to be analyzed and flocculated were placed into a beaker with continuous stirring. The suspension was kept at 200 RPM speed of stirring for two minutes and increased to 500 RPM to break down the flocs, and finally the speed was again decreased to 200 RPM to evaluate the re-flocculation process.

3.4 Wet Web Strength of PCC-Filled Handsheets

The addition of mineral particles, such as precipitated calcium carbonated (PCC), is known to reduce the dry and wet tensile strength of paper [18-20]. The replacement of fibers by fillers may reduce the interfiber bonding inside the sheet at 30-50% solids content. One can also argue that the adsorption of fillers on top of the fiber surface may increase the friction between fibers, which could lead to an increase in the wet web strength. This is not observed, since data found in the literature only show detrimental effects of the adhesion of fibers in the presence of fillers. In fact, since the fillers (PCC) are not stable, they will preferentially aggregate, forming big particles that will prevent interfiber bonding by mechanical interactions. Fig. 3.4 shows particles of PCC trapped inside dried handsheets.

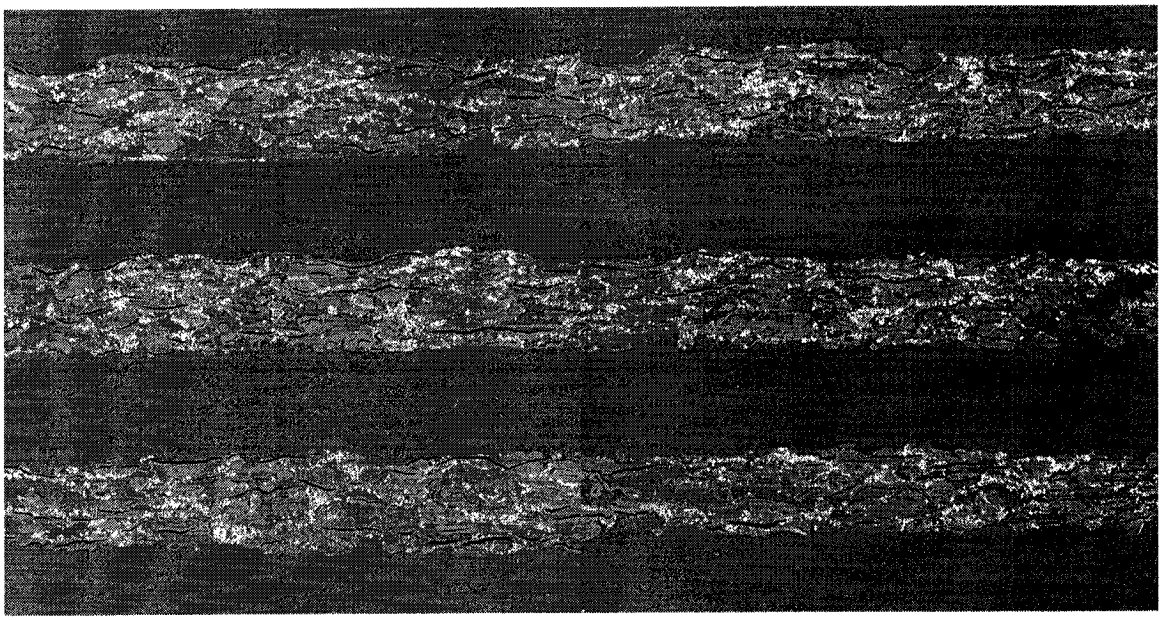

Fig. 3.4: Cross section of dry PCC-filled handsheets using c-PAM as retention aid. The white dots represent the aggregates of PCC inside the sheets.

The preferential flocculation of fillers happens because the PCC particles were already in the form of aggregates before adding them to the fibers, and after the c-PAM addition, the fillers tend to flocculate even more. Some of the c-PAM previously adsorbed on the fibers may also transfer to the fillers, helping in the formation of big aggregates of PCC, as seen in Fig. 3.4. This indicates a higher aggregation of PCC particles, than individual adsorption of PCC particles on fiber surface. While the handsheet is being formed, the PCC aggregates may adsorb on top of fibers or in the middle of the sheet, leading to weak spots inside the handsheets. These weak spots may be the first cause of failure when measuring the wet web strength of PCC-filled handsheets, thus explaining the negative impact when adding fillers to the paper.

3.4.1 Effect of Particle Size on Wet Web Strength of PCC-Filled Handsheets

The results shown in Fig. 3.5 give us a better perspective of the impact of PCC on paper. PCC reduces the wet web strength of pure fibers in the range of 30% to 50% solids content, indicating the detrimental effect of PCC particles (using c-PAM as retention aid). It is important to note that smaller fillers results in higher wet web strength when compared to bigger particles.

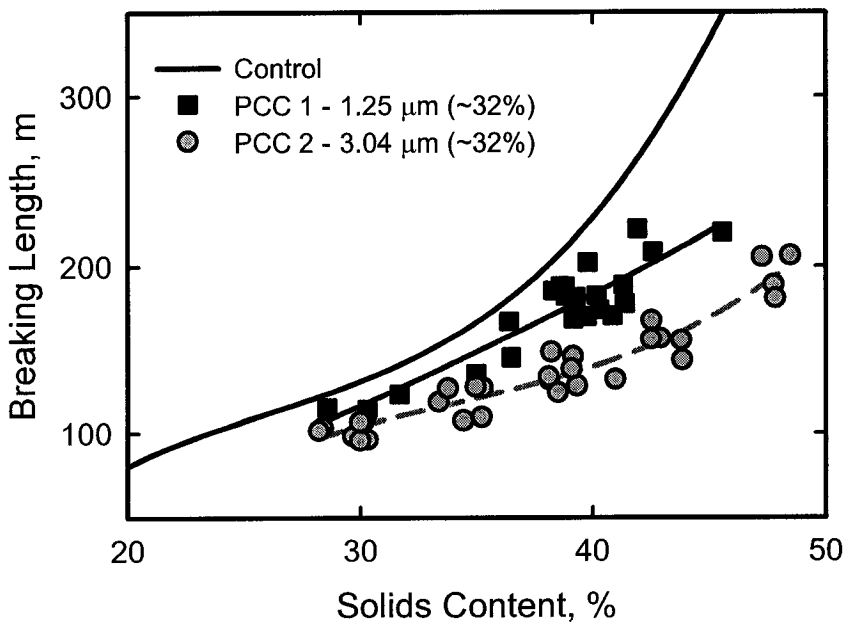

Fig. 3.5: Tensile strength of handsheets made of fibers and PCC. Control refers to the mixture of 80% Hardwood and 20% Softwood, and the PCC 1 & 2 refers to the handsheets filled with precipitated calcium carbonated. The numbers 1 and 2 represent the two different types of PCC used in the experiments, as indicated in the table 3.1 or 1.25 and 3.04 μm respectively. The percentage inside the brackets indicates the quantity of PCC retained inside the handsheet. (The experimental points of the control were omitted for clarity).

The first observation to be pointed out is that addition of PCC inside pulp fibers decreases the wet web strength as seen in Fig. 3.5. In all cases 0.3 mg of c-PAM per gram of solids was used in order to increase the retention of PCC onto fibers. This concentration is well below full coverage of PCC particles and fibers, in order to maximize bridging and minimize steric repulsion.

The comparison between handsheets filled with small particles (PCC 1) and big particles (PCC 2) indicates that small particles have less impact on the wet web strength. This explanation is consistent with the FBRM results, reported below. It is important to mention that bigger PCC particles will form bigger flocs in the presence of a retention aid (i.e. c-PAM), and as a consequence the mechanical entanglements formed by fibers at the wet stage (solids content~35-50%) will be decreased, reducing the wet web strength. This reduction in strength occurs because the fillers (already flocculated) will prevent interfiber contact, thus inhibiting fiber entanglement.

3.4.2 Retention Aid Influence in the PCC-Filled Handsheets

The retention of PCC particles on the sheet is mostly due to bridging interactions arising from the retention aids and the physical trapping of the mineral particles inside the handsheet. This experiment intends to demonstrate the retention of PCC inside the handsheet using various concentrations of c-PAM, and their respective wet web strength. Since for these experiments the effect of PCC particle size is not the main focus, only PCC 1 was used (particle size 1.25 μm). Fig. 3.6 shows the wet web strength of PCC-filled handsheets for various c-PAM dosages.

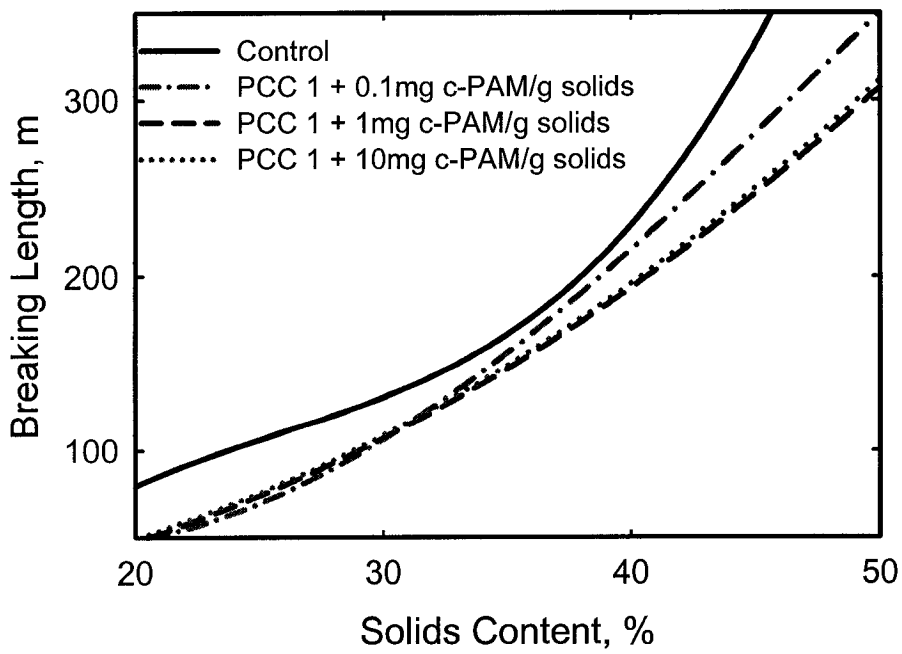

Fig. 3.6: Tensile strength of handsheets made of fibers and PCC. Control refers to the mixture of 80% Hardwood and 20% Softwood. The dashed, dotted and dotted-dashed lines refer to different concentration of retention aid. (The experimental points were omitted for clarity).

The results presented in Fig. 3.6 indicate that there is almost no effect in the wet web strength when the dosage of the retention aid is increased. The wet web strength of all PCC-filled handsheet is shifted down because of the addition of PCC particles, as discussed before. The only concentration of retention aid that seems to result in a greater wet web strength (above ~35% solids content) is 0.1 mg of c-PAM per g of solids. This concentration is less than full coverage of the fibers and fillers by the polymer, thus increasing the bridging between the fiber and the filler, as described in Fig. 3.1. The other concentrations of c-PAM were close to full coverage on fibers (1 mg c-PAM per g solids) and the close to full coverage of fillers and fillers (10 mg c-PAM per g solids). These concentrations seem to have a slightly negative impact to the wet web strength above

35% solids content. This detrimental impact to the wet web strength can be explained by the fact that the bridging interactions were also reduced at concentrations closely to full coverage.

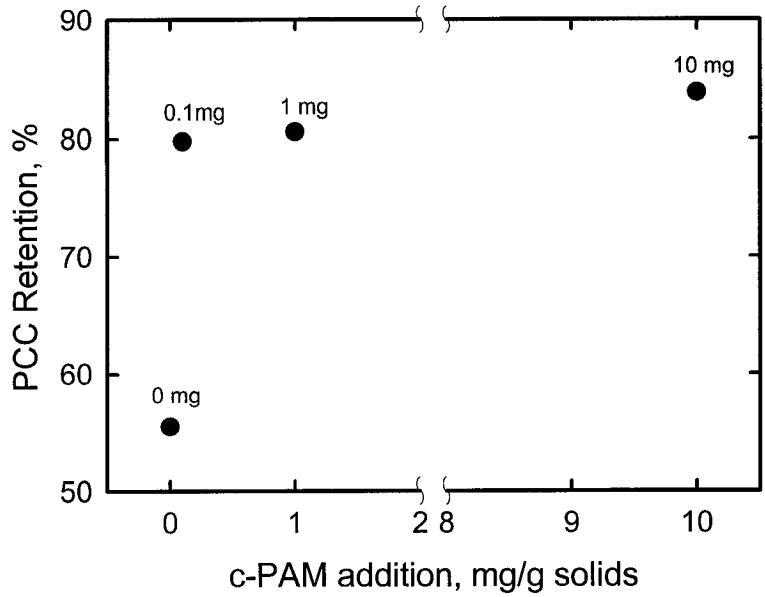

Fig 3.7: PCC retention by addition of c-PAM. The retention was obtained from the PCC-filled handsheets shown in Fig. 3.6.

Fig. 3.7 shows the effect of addition of c-PAM on the PCC retention. The retention of PCC particles in the handsheet is lower with no addition of c-PAM. In this case there is no bridging interaction, but still a very large amount of PCC is retained inside the handsheet, mostly due to physical entrapment inside the sheet. With the addition of c-PAM, the total PCC retention jumps significantly from nearly 55% to 80%. The total PCC retention is the percentage weight of the PCC obtained after handsheet

making. Increasing the concentration of the retention aid to full coverage (10 mg per gram of solids), results is relatively similar to partial coverage.

3.5 PCC Particle Analysis

To understand the main interactions between fillers, fibers and retention aid is the first obstacle to fully comprehend the wet web strength of PCC-filled handsheets. In order to evaluate the interactions between these components, the FBRM equipment will be used to measure the particles in the agitated suspension. The particle size measurement of this equipment ranges from 1 to 100 μm.

The FBRM probe can be inserted into a flowing medium of any concentration or viscosity. Then, a laser beam is projected through the sapphire window of the probe and highly focused just outside the window surface. This focused beam is then moved so it can follow a path around the circumference of the probe window. This focused beam moves at a high speed, so that the particle motion can be considered insignificant during a measurement.

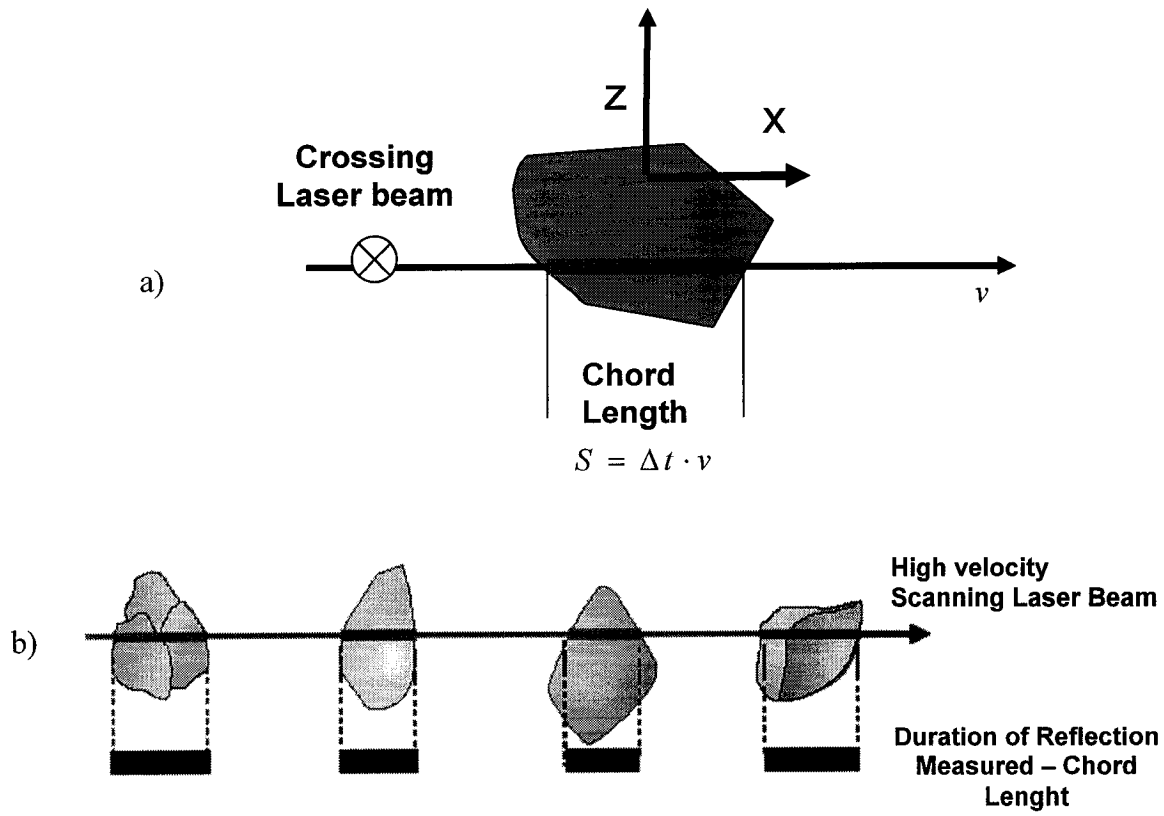

Fig. 3.8a: Chord Length (the laser beam direction is perpendicular to the paper) including coordinate system corresponding to the measurement.
Fig. 3.8b: Distance measured by Focused Beam Reflectance Measurement is chord length.

As particles pass by the window surface, the focused beam intersects the edge of a particle, as seen in Fig. 3.8. The particle then begins to backscatter laser light. The particle continues to backscatter the light until the focused beam reaches the particle's opposite edge. The backscatter is collected by the FBRM optics and converted into an electronic signal. A chord length distribution, Fig. 3.9, is a highly precise and sensitive means of tracking changes in both particle dimension and particle population. In addition, it is possible to analyze specific regions of the particle size distribution in a certain range.

Using this technique it was possible to compare the two types of PCC presented in Table 3.1 and already tested for its wet web strength as shown in Fig. 3.5. In the presence of c-PAM, the PCC particles tend to aggregate by polymer bridges. In fact the PCC particles were slightly aggregated, because the results shown in Fig. 3.9 indicate nearly 8 μm for PCC 1 and 15 μm for PCC 2, whereas the actual sizes of both particles are 1.25 and 3.04 μm respectively. The graph shown in Fig. 3.9 demonstrates three stages in the flocculation process. The first indicates the addition of a retention aid in order to form interactions mostly via polymer bridging, the second stage shows the breaking down of the flocs by increasing the stirring speed and the last stage is obtained by reducing the speed, leading to a re-flocculation process of the PCC particles. This last stage, is important because it simulates paper formation in the slice of the headbox (a device that delivers a uniform pulp suspension to the paper machine), where the pulp suspension is introduced to high shear forces (breaking down the flocs), and in fraction of a second the suspension re-flocculates again.

The results indicate that both types of PCC reach a floc size of nearly 75 μm in the presence of 0.5 mg of c-PAM per g of PCC particles. This may indicate a strong affinity between PCC and c-PAM, since nearly the same floc size was obtained in the re-flocculation process.

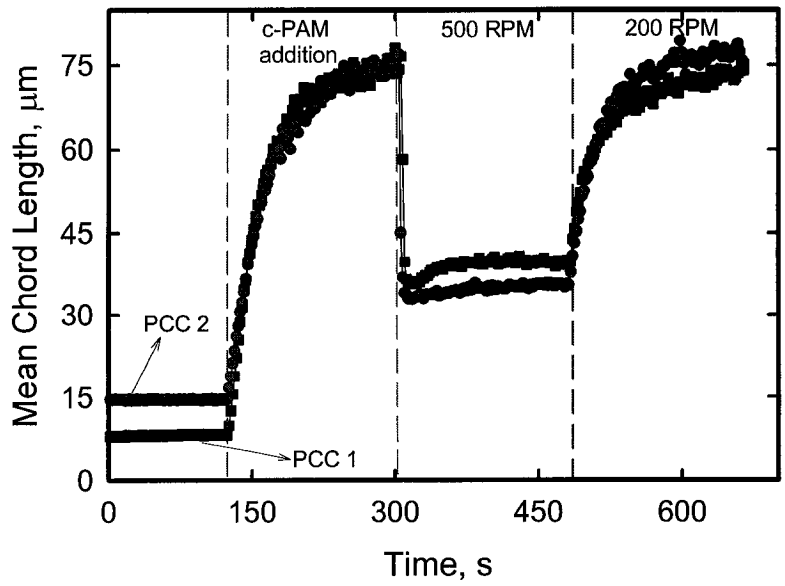

Fig. 3.9: Flocculation process using the PCC particles and c-PAM. The square shape points represent PCC 1 (1.25 μm) and the round shape points represent PCC 2 (3.04 μm)The PCC particles were diluted in deionized water in a concentration of 2.5g/L and the c-PAM dosage was 0.5 mg per gram of PCC .

Analyzing the re-flocculation process, it can be seen that PCC 2 reaches a larger floc size, about 78 μm against 72 μm for PCC 1. The formation of larger flocs by PCC 2 may be the cause of the low wet web strength values shown in Fig. 3.5. The large flocs can prevent interfiber bonding, therefore the mechanical entanglements demonstrated in Chapter 2 may be less effective, preventing the fibers from entangling with each other and thus reducing the wet web strength. The size distribution (during the re-flocculation stage), shown in Fig. 3.10, also indicates that in the range of 1-70 μm, the PCC 1 has formed more aggregates than the PCC 2. This can be another argument that the PCC 1 in the presence of c-PAM can form smaller aggregates than the PCC 2. As seen in Fig. 3.5,

the smaller particles have a higher wet web strength values than larger particles, mostly due to the higher friction provoked by the smaller particles inside the handsheet network.

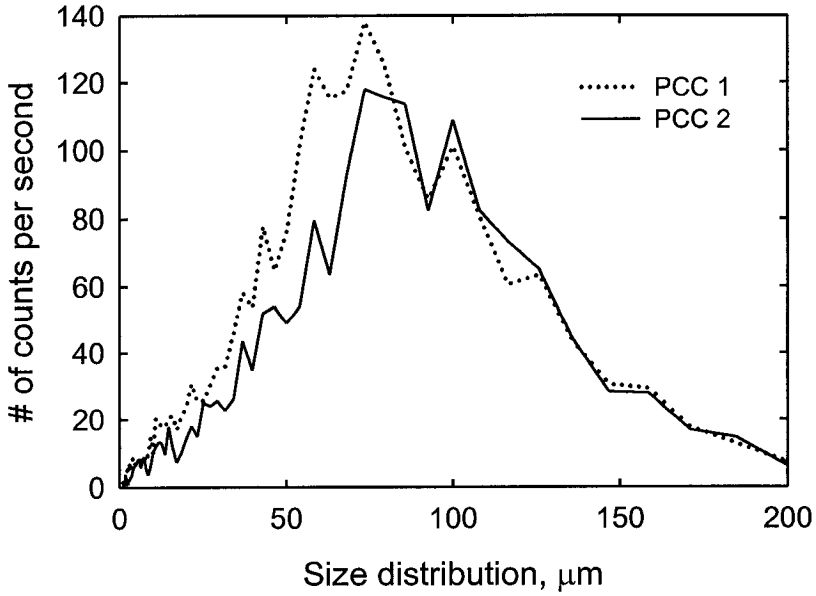

Fig. 3.10: Size distribution of PCC 1 (1.25 μm) and the PCC 2 (3.04 μm), using the FBRM equipment. The size distribution was taken in re-flocculation stage.

3.6 PCC Stabilization

In order to evaluate if PCC particles can increase the friction between fibers inside PCC-filled handsheet, possibly increasing the wet web strength, we need to stabilize the PCC particles. The stabilization of PCC will lead to adsorption of single particles on fibers, therefore increasing the friction between sliding adjacent fibers. In the following experiments the filler used was PCC 2, in order to also allow comparison with the wet web strength results as well.

Polyethyleneimine (PEI) is a common polymer which can be used to stabilize fillers [21]. The adsorption of PEI on the surface of PCC will increase the positive charge

of PCC, leading to a stable suspension. The PEI dosage in this experiment was 10 mg per gram of PCC or approximately 2mg of PEI per m^2 of PCC, indicating a full coverage of polymer over the filler surface.

As seen in Fig. 3.11, the addition of PEI does decrease the mean chord length of the PCC suspension, due to a stabilization of the PCC particles. After PEI was added, the shear was increased (500 RPM), which re-disperses the particles in the suspension, thus reducing the actual size measured by the FBRM. Finally, the particles were again subjected to a shear of 200 RPM, resulting in particles smaller than the initial size when the PEI was added. This smaller particle size indicates a better distribution of PEI over the PCC particles, resulting in a better stabilization of the suspension.

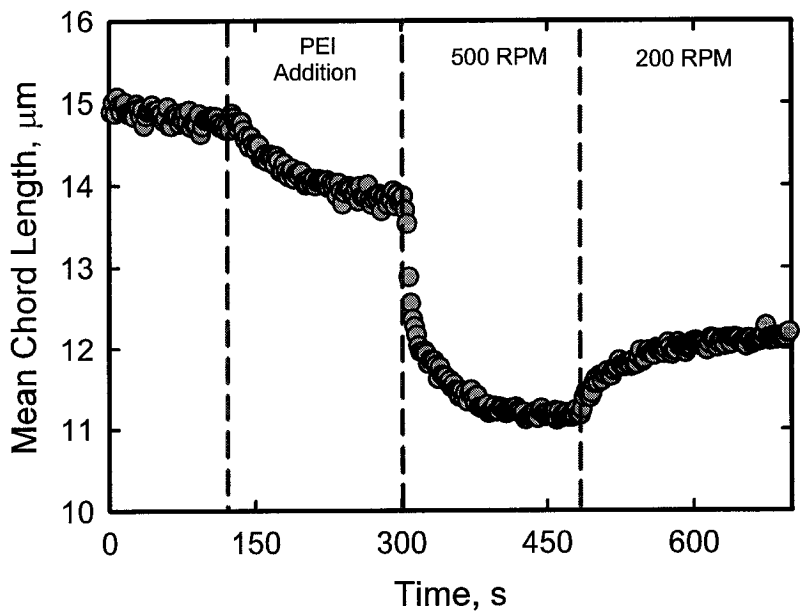

Fig. 3.11: PCC Stabilization process using PCC 2 particles (3.04 µm) and PEI. The PCC 2 particles were diluted in deionized water in a concentration of 2.5g/L and the PEI dosage was 5 mg per gram of PCC.

After analyzing the PCC particle interactions with PEI, the wet web strength experiments of PCC-filled handsheets were evaluated in order to analyze the impact of stable PCC particles inside a handsheet. The wet web strength in this case is of extreme importance, because it can predict if friction of small particles deposited on the surface of swollen fibers can play a role. It was observed that the addition of large flocs (c-PAM and PCC) inside the PCC-filled handsheets decreases the wet web strength in all cases. However it is uncertain if stable PCC particles are introduced inside the handsheet. The addition of large flocs inside the handsheet may prevent flexible swollen fibers to form entanglements, but the addition of stable PCC particles may increase the friction between adjacent fibers, without impacting the entanglements of swollen fibers.

As can be seen from Fig. 3.12, stable PCC particles do not decrease the wet web strength to the same extent as flocculated PCC particles do. In fact, in the range of 30-40% of solids content, the wet web strength of PCC-filled handsheet, using stable PCC particles, has the same strength as the non-filled handsheets. The wet web strength of stable PCC particles starts to slightly deviate from the control curve (pulp fibers only) after 40% solids content, indicating that another kind of interaction between fillers-fibers-retention aid is happening in order to prevent the negative impact of addition of PCC particles inside the handsheet.

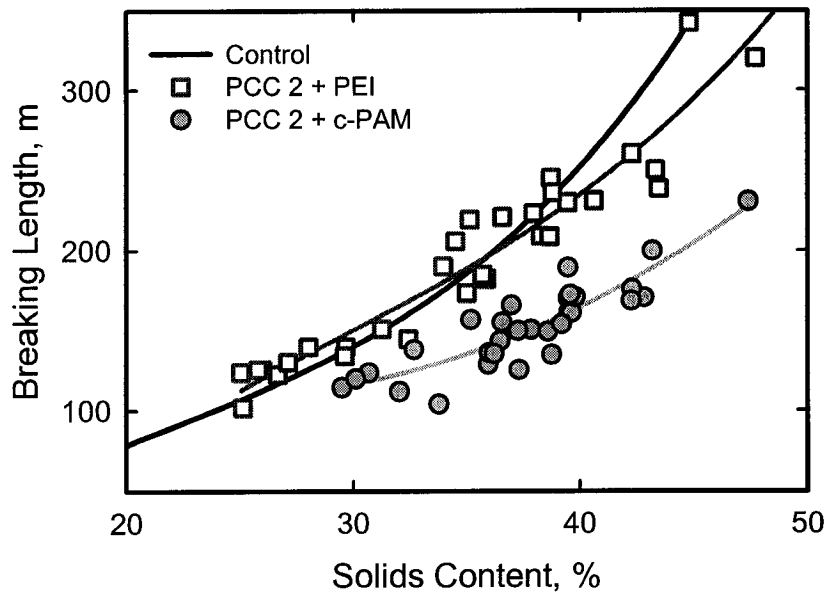

Fig. 3.12: Tensile strength of PCC-filled handsheet. The Control, described as the black line, refers to the mixture of 80% Hardwood and 20% Softwood only. The square points refer to addition of PEI and PCC 2 (3.04μm), and the gray round points refer to addition of c-PAM and PCC 2 inside the handsheets. The retention of PCC in both cases was approximately 22% of the basis weight and the concentrations of the retention aids added to the handsheets were 0.5 mg of c-PAM and 5mg of PEI per gram of solids.

The explanation that stable PCC particles do not decrease the wet web strength may be related to the friction caused by the deposition of single PCC particles on the surface of swollen fibers. The particles may prevent fibers to slide easily between themselves, thus increasing entanglements and hence the wet web strength, as shown in Fig. 3.12. But if the particles are too big or already flocculated by polyelectrolyte (c-PAM), the large flocs may prevent the entanglement of fibers leading to a decrease in wet web strength. In fact, this was observed in our experiments. The interaction between PCC

2 (3.04μm diameter) and c-PAM produced large flocs of approximately 80 μm diameter, as shown in Fig. 3.9. Similar flocs were formed during the handsheet making, resulting in a detrimental impact on wet web strength, as seen in Fig. 3.11.

The friction effect is a strong argument to explain why handsheets filled with stable PCC particles do not impact negatively the wet web strength. Fig. 3.13 shows the shear tension between two wetted blotters treated with stable PCC particles (using PEI), and the results clearly demonstrate that small individual particles applied on the surface of swollen fibers can increase adhesion by friction. When two wetted blotter are pressed together, there is adhesion between them when there is enough free water surrounding the fibers to generate capillary forces. When the free water is gone the adhesion of the blotters approaches zero. The same is not observed when the blotters are treated with stable PCC. When these blotters are pressed together the shear tension does not go to zero, even if all the free water surrounding the fibers is gone. This provides another argument that friction caused by deposition of small individual particles may increase the adhesion between fibers. The free water is absent around 50% solids content for the blotter paper, as shown in Chapter 2.

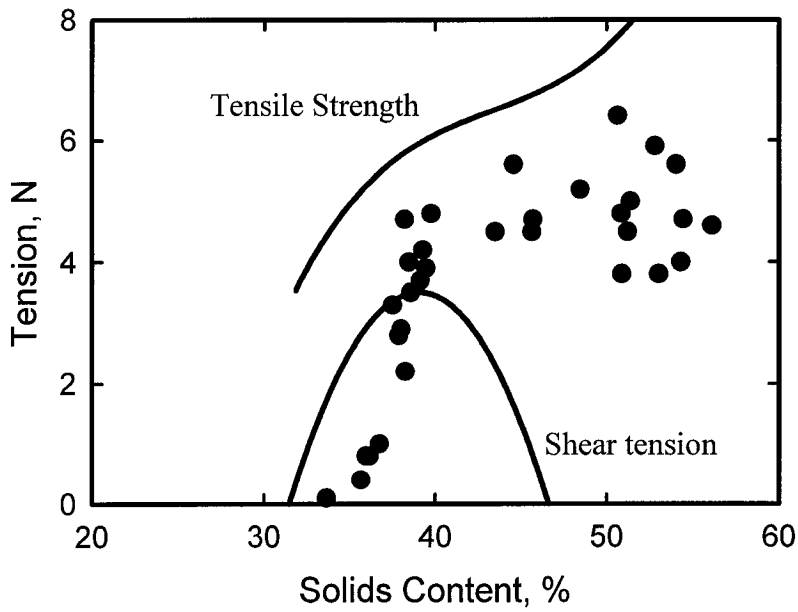

Fig 3.13: Shear tension required to separate two wetted blotters treated with PCC 2 and PEI. PCC 2 (3.04μm) was mixed with PEI before applying on top of the blotter paper. The concentration of PCC was 0.05 g per gram of blotter fiber and the concentration of PEI was 5 mg per gram of PCC 2. The PEI-PCC suspension was passed trough the blotter paper only once and the retention of PCC was approximately 6.5%. Controls refer to tensile strength of reslushed blotters and shear tension required to separate two wetted blotters, using tap water. (The experimental points of the controls were omitted for clarity.)

3.7 Impact of Microfibrils in PCC-Filled Handsheets

Microfibrils are flexible and very thin fibers. They can increase the wet web strength of paper mostly because of their facility to form mechanical entanglements inside the network of fibers, as described in chapter 2. The addition of microfibrils inside handsheets filled with PCC may also increase the wet web strength, minimizing the

negative impact of PCC addition. The microfibrils may entangle the fillers together with fibers, hence increasing the wet web strength.

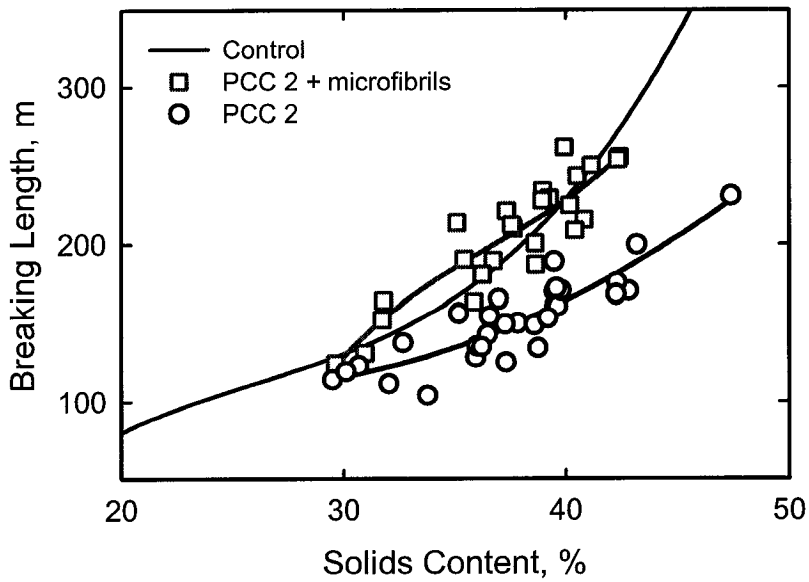

Fig. 3.14: Tensile strength of handsheets made of fibers, PCC, retention aid and microfibrils. Control refers to the mixture of 80% Hardwood and 20% Softwood. The square points refer to handsheets containing PCC 2, c-PAM and microfibrils, while the round points refer to handsheets using only PCC 2 and retention aid. The retention of PCC inside the handsheets was 22% of the total basis weight, the amount of retention aid used was 0.5 mg of c-PAM per gram of filler-fiber and the amount of microfibrils added was 5% of the total basis weight. (The experimental points of the control were omitted for clarity).

It can be seen that the microfibrils can prevent the reduction of wet web strength caused by the addition of flocculated PCC particles completely, as shown in Fig. 3.14. We have shown that addition of flocculated PCC particles with c-PAM (~80 μm diameter) does decrease the wet web strength at all conditions. But this negative impact may be eliminated by the addition of a small quantity of microfibrils inside the PCC-filled handsheet. The results seen in Fig. 3.14 show the wet web strength of handsheets

filled with PCC and microfibrils as high as the wet web strength of non-filled handsheets. The addition of microfibrils increases nearly 40% the wet web strength compared to the PCC-filled handsheet without microfibrils.

3.8 Conclusions

We conclude that the addition of precipitated calcium carbonate (PCC) to a sheet is not always detrimental to the wet web strength, as was supposed. The addition of stabilized PCC (using PEI as stabilizer) to a handsheet does not cause any negative impact to the wet web strength (in the range of 30-40%solids content), for additions of nearly 20% of PCC to the handsheet. The shear tension of two wetted blotters treated with stable PCC particles can generate higher tension than for wetted blotters alone. All these experiments can be explained by friction effects, created by the adsorption of mineral particles on the fiber surface, which can increase the tension required to separate two adjacent fibers sliding along each other. On the other hand, the addition of large PCC flocs (using c-PAM as flocculant) decreases the wet web strength. These large flocs (approximately 80 μm) may not enhance the friction between two adjacent fibers; in fact these flocs may prevent interfiber bonding due their size.

Another observation is that smaller PCC particles may perform better in the wet web strength than bigger particles. The small mineral particles can form smaller aggregates in the re flocculation stage leading to the formation of smaller flocs within the handsheet, giving a lower probability of wet web rupture.

The amount of retention aid added to the fiber-filler system is not the main driving force for the retention of PCC inside the sheet. The various concentration of c-PAM used in the experiments did not appear to make a large difference to the wet web strength, likely because in all cases it was sufficient to flocculate PCC.

Finally the addition of microfibrils to PCC-filled handsheets leads to a large enhancement in the wet web strength. As discussed in Chapter 2, the microfibrils are very flexible and thin, and consequently they may form more mechanical entanglements between the fillers and fibers, thus increasing the wet web strength.

3.9 Acknowledgements

The research was performed in collaboration with DOMTAR, namely R. Gratton, R. Beaudoin and H. Pande. Thanks also to Dr. Alois Vanerek.

3.10 References

1. **Scott, W. E.** "Principles of wet end chemistry". Tappi Press. 1996.
2. **Burgess, M. S., Phipps, J. S. and Xiao, H.** "Flocculation of PCC induced by polymer/microparticle systems: Floc characteristics". Nordic Pulp and Paper Res. J. 15(5), pp.572-578, 2000.
3. **Baker, C. and Nazir, B.** "Practical ways forward to achieving higher filler content papers". Use of minerals in papermaking, Pira International, Surrey, U.K., 1998, pp. 83-92.
4. **Cho, B-U. and Garnier, G.** "Filler retention with CPAM/bentonite retention system – Effect of collision efficiency". Nordic Pulp and Paper Res. J. 16(3), pp.188-194, 2001.
5. **Gruber, E. and Müller, P.** "Investigations of the flocculation behavior of microparticle retention systems". Tappi Journal, 3(12), pp.17-22, 2004.
6. **Cong, R., Smith-Palmer, T. and Pelton, R.** "A model colloid for flocculant testing". Journal of Pulp and Paper Science, 27(11), pp. 379-384, 2001.

7. **Alince, B.** "Polyethylenimine adsorption on cellulose". Cellul. Chem. Technol. 8(6), pp. 573, 1974.
8. **van de Ven, T. G. M.** "A model for the adsorption of polyelectrolytes on pulp fibers: Relation between fiber structure and polyelectrolyte properties", Nordic Pulp and Paper Res. J. **15**(5), pp.494-501, 2001.
9. **J. Petlicki and T.G.M. van de Ven.** "Adsorption of polyethylenimine onto cellulose fibers," Colloids and Surfaces **83**, pp.9-23, 1994.
10. **T. Lindstrom and C. Soremark.** "Adsorption of Cationic Polyacrylamides on Cellulose", Journal of Colloid and Interface Science, 55(2), pp. 305-311, 1976.
11. **Solberg, D. and Wågberg, L.** "On the mechanism of cationic-polyacrylamide-induced flocculation and re-dispersion of a pulp fiber dispersion". Nordic Pulp and Paper Res. J., Vol. 18 (1), pp. 51-55, 2003.
12. **Pèlach, M. A., Blanco, M. A., Roux, J-C, Vilaseca, F. and Mutjé**, P. "Study of the adsorption of polyethylenimine on cellulosic fibres in an aqueous suspension". Appita journal, Vol. 54, n. 5, pp. 460-465, 2001.
13. Tappi procedure T 205 om-88. "Forming handsheets for physical tests of pulp".
14. Tappi procedure T 245 om-98. "Silicates and silica in pulp (wet ash method)".
15. **Aksberg, R. and Wågberg, L.** "Hydrolisys of cationic Polyacrylamides". Journal of Applied Polymer Science, Vol. 38, pp. 297-304, 1989.
16. **Vanerek, A., Alince, B. and van de Ven, T. G. M.** "Colloidal behavior of ground and precipitated calcium carbonate fillers: effects of cationic polyelectrolytes and water quality", Journal of Pulp and Paper Science, 26(4), pp. 135-139, 2000.
17. **Blanco, A., Fuente, E., Negro, C., Monte, M.C. and Tijero, T.** "Focused Beam reflectant measurement as a tool to measure flocculation". Tappi Journal, Vol. 1, n. 10, December 2002.
18. **Zhao, Y. Hu, Z., Ragauskas, A. and Deng Y.** "Improvement of paper properties using starch-modified precipitated calcium carbonate filler". Tappi Journal, Vol. 4, n. 2, February 2005.
19. **Biermann, C. J.** "Handbook of Pulping and Papermaking". Second Edition, Academic Press, pp.194-197., 1996.
20. **Hagemeyer, R. W.** "Calcium Carbonate". Pigments for Paper, Tappi Press, 1984.
21. **Vanerek, A., Alince, B., and van de Ven, T.G.M.** "Colloidal Behavior of Ground and Precipitated Calcium Carbonate Fillers: Effect of Cationic Polyelectrolytes and Water Quality". J. Pulp Paper Sci. 26(4), pp. 135-139, 2000.
22. **Beazley, K. M., Dennison, S. R. and Taylor, J. H.** "The influence of Mineral Fillers on Paper Strength: Its Mechanism and Practical Means of Modification", pp. 218-238, Preprints Empire State Paper Research Associates, Inc. European Meeting: Maastricht, The Netherlands, 1979.

CHAPTER 4

THE EFFECT OF POLYELECTROLYTES ON THE WET-WEB STRENGTH OF PAPER

4.1 Abstract

In a wet web of paper at low solids content, the fibers are kept together by capillary forces due to the presence of free water between the fibers. The gradual removal of water results in deformation and collapse of the fibers and the strength of the wet web increases. But the swollen fibers cannot establish sufficiently close contact for interfiber molecular bonding to take place because of a layer of solvated hemicelluloses covering the fiber surfaces acting as a steric barrier. An introduction of cationic polyelectrolytes is often detrimental to the wet web strength because the steric and electrostatic repulsion between fibers is enhanced, when the fibers are fully coated. Experimental data on fibers coated by cationic polyacrylamide reported here, confirm this. Consequently, the distance to which fibers are drawn together increases, the interfiber friction decreases and it becomes easier for them to slide over each other. For polyelectrolyte dosages below full coverage, fiber flocculation occurs resulting in weak spots in the wet sheet.

4.2 Introduction

In the process of papermaking, the strength of the wet web is of critical importance when the web is transferred without a support from the presses into the dryer section. Insufficient adhesion among fibers may result in a costly break. In wet sheets with low strength, the swollen fibers slide over each other too easily. The obvious suggestion for preventing breaks in a given furnish would be to increase interfiber adhesion by means of water soluble polymers which adsorb on the fibers. The rational behind this idea is that a long-chain polymer may form a bridge between fibers, thus making it more difficult to slide. Suitable candidates could be cationic starches and polyacrylamide which are commonly used to enhance the tensile strength of dry or rewetted paper. However, fiber flocculation might also weaken the sheet, because of weak spots between the fiber flocs. For higher polyelectrolyte dosages the fibers become completely covered and polymers no longer induce bridging.

The expectation that upon forming a sheet, the existing interfiber bridges would improve the strength of the wet web has not been fulfilled. On the contrary, experience shows that often their presence is detrimental to wet-web strength. Their performance as a strength agent is realized only after drying.

So far, there is no product available that is specifically designed to enhance wet-web strength. In the literature, several compounds have been claimed to be effective (Laleg, Pikulik 1993a), but mill trials did not confirm this.

The intention here is to bring some insight into the process of wet-web strength development, and particularly to deal with the negative effect of polyelectrolytes.

4.3 Adhesion between swollen fibers

4.3.1 Capillary forces

Paper exists because of the tendency of fibers to stick together. But the interfiber forces for dry fibers and wet fibers are different. In the presence of water at low solids content, there are two kinds of water in the assembly of fibers: part of the water is associated with the swollen fibers and part is free outside of the fibers. The free water is responsible for keeping fibers together due to capillary forces. This concept was introduced by Campbell (1933). It is based on the fact that a pressure within a liquid that has a curved surface is different from that above the liquid (with a flat interface). If the surface is concave the pressure in the liquid is lower and is a function of radius of curvature. When two solid surfaces are connected by a capillary bridge of liquid, the pressure difference ΔP over the curved liquid can be calculated from the general form of the Laplace equation:

$$\Delta P = \gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \qquad [4.1]$$

Where γ is the surface tension of the liquid and R_1 and R_2 are the two principal radii of curvature, which depend on the precise geometry of the surfaces, the capillary bridge and the contact angle θ. For instance, for a meniscus in a narrow circular capillary of a radius r, $R_1 = R_2 = r/\cos\theta$. For two fibers connected by a capillary bridge with concave menisci, the pressure in the liquid is lower than the pressure outside, resulting in a capillary attraction between the two fibers. The capillary attraction forces can become very large:

e.g. for surfaces bridged by water with a capillary radius of 1 micron, the capillary pressure is in the order of 1 atm. For smaller radii the capillary pressures ΔP can reach much larger values. The capillary attraction will cause the fibers to get closer to each other and to deform and flatten. When water is removed by pressing or drying, the elastic forces arising from fiber deformation will be balanced by capillary attraction. In addition, when fibers are fully coated by hemicelluloses or adsorbed polymers, there are steric and electrosteric forces acting between the fibers. At any instant, there will be a pseudo-equilibrium state between the attractive capillary forces and the repulsive elastic and electrosteric forces.

4.3.2 Effects of roughness on capillary forces

In order to make an estimate of the attractive and repulsive forces operating between fibers at any instant, as discussed by Wågberg, Annergren (1997), we have to make an estimate of the capillary attraction between fibers. This is complicated by the fact that fibers are not smooth, but their surfaces are very rough with numerous small and large pore openings and with many microfibrils of various sizes protruding from their surface. This surface roughness is likely to significantly reduce the capillary attraction since the solid-liquid contact line could be pinned at positions for which the apparent contact angle is close to 90^{o}. This effect is illustrated in Fig. 4.1, where the capillary bridge is shown schematically (a) between smooth non-deformable fibers, (b) deformable smooth fibers, (c) rough non-deformable fibers and rough (d) deformable fibers.

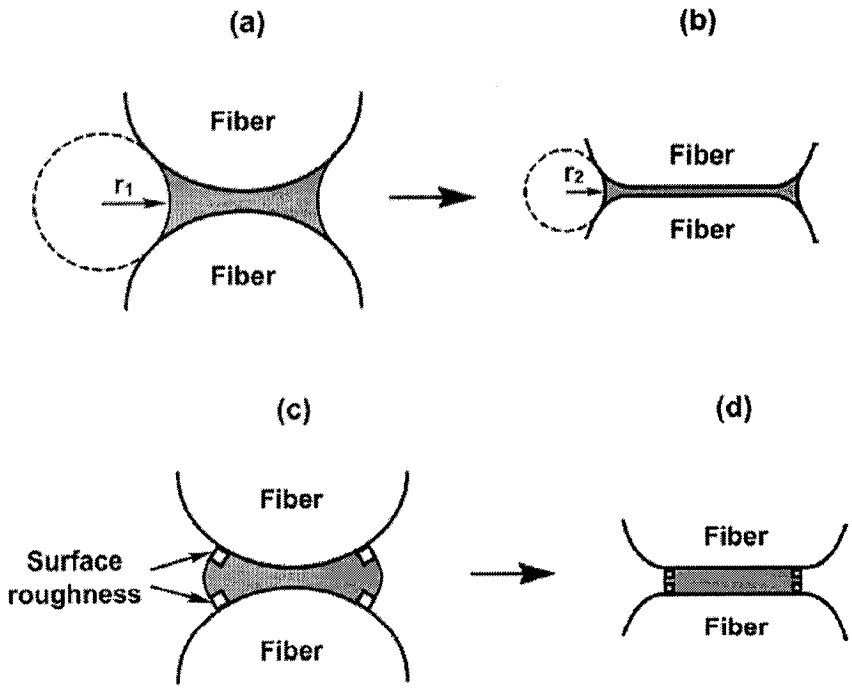

Fig. 4.1: In the presence of free water pulp fibers are kept together by capillary forces. The removal of water is accompanied by fiber deformation and collapse, thus increasing area of potential bonding. Four scenarios are shown schematically: (a) non-deformable smooth fibers; (b) deformable smooth fibers; (c) non-deformable rough fibers and (d) deformable rough fibers. In (c) and (d), only roughness at the contact line is shown, as a cross section of a microfibril lying on top of the fiber.

For smooth deformable fibers, the capillary attraction is larger than for non-deformable fibers, leading to even more deformation and flattening. For rough fibers, only roughness (for instance a microfibril lying on top of a fiber) at the contact line is shown. It is possible to have apparent contact angles close to 90°, with 0° contact angles with the fibril surface. An extreme case is shown in which the sign of the curvature is changed, leading to capillary repulsion (Fig. 4.1c). This would cause the contact line to

move inward, finding again locations with a concave meniscus and changing the repulsion into attraction. For deformable rough surfaces, the apparent contact angle could conceivably be close to 90°, thus leading to small capillary forces. This argument shows that surface roughness can reduce the capillary forces by orders of magnitude. Instead of drawing the fibers together, the contact line could adjust itself to find the minimum capillary force for a given roughness. This effect is similar to the pinning of a contact line at the top of a capillary. For very narrow capillaries with a height less than the equilibrium capillary rise height, the meniscus is pinned at the top of a capillary, where the contact angle θ can take on the value corresponding to $2\gamma \cos\theta / r = \rho g h$, r being the radius of the capillary, h its height, ρ the density of the liquid and g the acceleration due to gravity.

4.3.3 Fiber deformability

Fiber deformability is equally important. The difference in the behavior of the rigid and the deformable fibers, adapted from (Lyne, Gallay 1954), is illustrated in Fig. 4.2. At the low solids content, the action of capillary forces results in a similar progress in both cases. With the free water gradually disappearing, the adhesion between rigid glass fibers is lost. However, in the case of pulp fibers the strength of a drying wet web keeps increasing. The explanation in the literature is that with the free water leaving, the ensuing deformation and collapse of fibers brings their surfaces into such a close contact that molecular bonding, most likely hydrogen bonds, may develop. The process is described as a transition from surface tension action to interfiber molecular bonding. But there is a problem. Since interfiber hydrogen bonds may form only between almost dry

fibers over a distance of about 0.3 nm, the question is: What keeps the swollen fibers together after the free water is gone? According to different authors this may be anywhere between 25-50 % solids content depending on the type of fiber. So what happens in the transition period, when the strength of wet web keeps increasing with increasing dryness, is not clear.

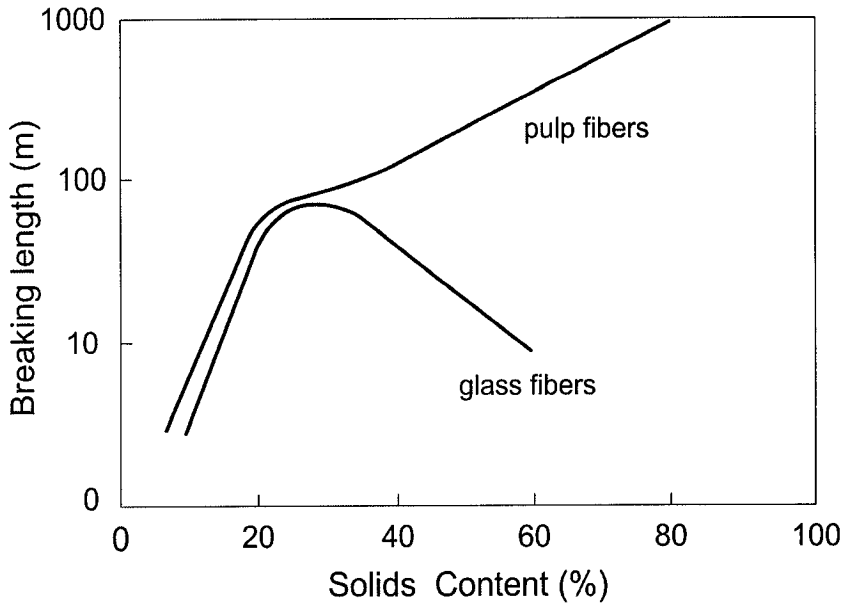

Fig. 4.2: The strength development as a function of solids content for web composed of either pulp fibers or glass fibers. Adapted from Lyne, L. M. and Gallay, W. (1954).

4.3.4 Electrosteric repulsion

Another factor to consider are the electrosteric forces operating between fibers fully coated by hemicelluloses or adsorbed polyelectrolytes. Observations of what happens between approaching cellulosic surfaces, both bare and covered by polymer have been reported by several authors. In a number of studies, the forces acting between cellulosic surfaces were measured as a function of distance using Atomic Force

Microscopy - AFM (Salmi et al. 2003), Surface Force Apparatus (Neuman et al. 1993; Holmberg et al. 1997; Osterberg 2000) and Colloidal Probe Microscopy (Zauscher, Klingenberg 2000a). Although the investigated cellulosic substrates were of a different nature than fibers (essentially films of regenerated cellulose), the observations are relevant. When measured in water, the cellulose surfaces repel each other. The repulsion increases with decreasing distance between the surfaces and could be both electrostatic due to charged surfaces and steric due to a solvated polymer layer covering the surface. The distance at which the repulsion becomes measurable increases when the cationic polymers are adsorbed on the cellulosic surfaces. How forces between fibers with adsorbed polyelectrolytes vary with distance is shown schematically in Fig. 4.3. From AFM measurements (Salmi et al. 2003), one observes forces close to 100 nN when two fibers coated by a polyelectrolyte are very close (the order of a few nm or less). Assuming an AFM tip area of 1 μm^2, this corresponds to 10^5 Pa (1 atm), which is comparable to a capillary force (between smooth fibers) with a capillary radius of about 1 μm.

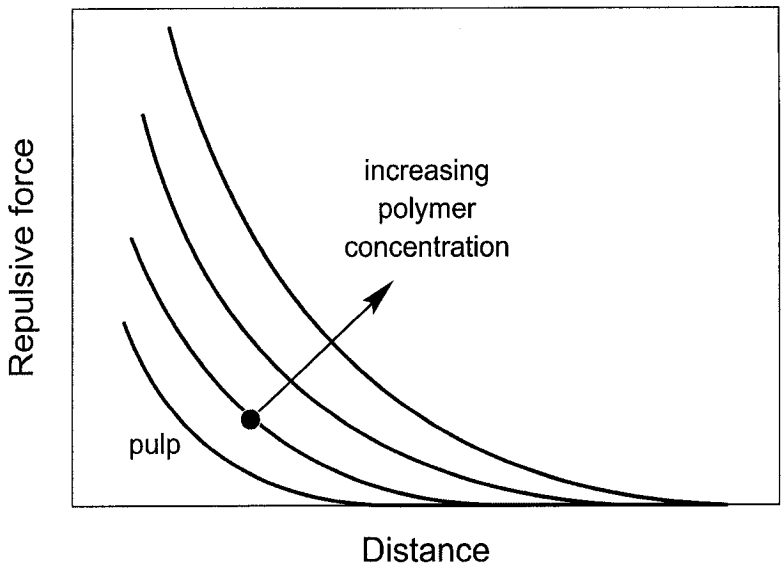

Fig. 4.3: The distance, at which the repulsion between approaching cellulose surfaces becomes noticeable, increases with the amount of cationic polyelectrolyte (schematic). The presence of the polymer results in enhanced steric and electrostatic repulsion which keep surfaces further apart.

4.3.5 Combination of forces acting on fibers

From these arguments, we can speculate what happens when fibers are brought together by capillary forces. For the capillary forces to become comparable to electrosteric forces, the pressure must be in the order of 1 atm or somewhat smaller. The elastic and capillary forces can adjust themselves by the extent of fiber deformation and pinning of the contact line at surface asperities. Thus, when fibers approach up to within, e.g. 10 nm, all forces (per unit area) are expected to be a fraction of an atm. This corresponds to very little water between the fibers, but nevertheless a large distance to establish molecular bonding between fibers. Figure 4.4 shows schematically two rough fibers covered by polyelectrolytes and bridged by a small capillary bridge. This more detailed description of water between fibers does not solve the problem of how bonds

form when fibers are still several nm or more apart. Instead, it compounds the problem because the capillary forces, weakened by surface roughness, do not bring fibers as close together as for smooth fibers, and thus, intermolecular bonding seems even less likely.

Two possibilities to resolve this dilemma can be considered. One is based on the assumption that with increasing dryness, the deformation and collapse of fibers becomes more effective. This would result in an increased overall friction due to mechanical means. The second possibility follows the same scenario i.e. increasing potential contact area among fibers upon drying, but accompanied by actual interfiber adhesion.

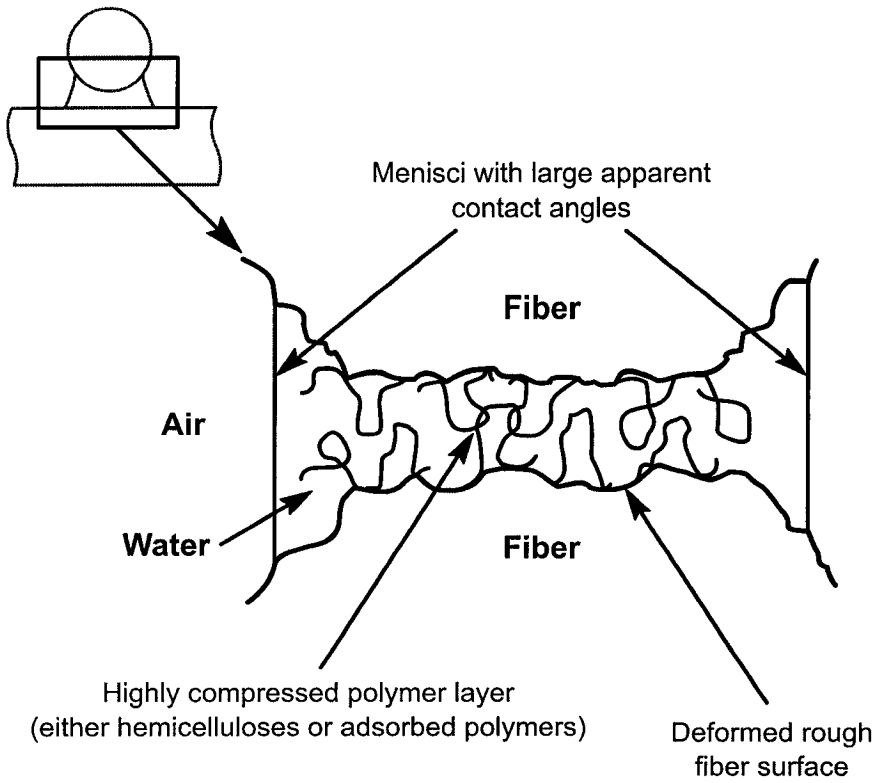

Fig. 4.4: Schematic representation of two rough fiber surfaces covered by polyelectrolyte, drawn together by capillary forces. Fibers are deformed by capillary forces and polymers in the gap are compressed, but the capillary forces are weakened by surface roughness.

4.3.6 Polymer interdiffusion

As suggested by McKenzie (1964) and convincingly discussed by Pelton (1993), it is appropriate to visualize the surface of fibers as being covered by an aqueous layer of solubilized cellulosic chains, hemicellulose and other wood polymers. The thickness of such a layer could reach 100 nm according to Neuman at al (1993). We ourselves estimated 35 nm, based on a reconciliation of pore sizes in fiber walls obtained from solute exclusion and polymer adsorption (Alince, van de Ven 1997). However, the negatively charged hemicellulose layer collapses upon adsorption of a cationic polyelectrolyte. The existence of such a gel-like layer on the fiber surface could contribute to a better understanding of wet-web strength development because it may play a dominant role in the transition period. As proposed by McKenzie and Pelton the capillary forces bring the gel covered surfaces into such close contact that the polymeric chains start to interpenetrate (interdiffuse). With the water leaving, the interpenetration increases until the collapsed fibers are "glued" together. It is, however, questionable whether enough polymer interpenetration can occur on the time scale of paper pressing. Eriksson at al. (2005) manifested the effects of polymer-chain interdiffusion on dry handsheets experimentally by building multilayers of weak polyelectrolytes onto fiber surfaces.

4.4 Materials and methods:

4.4.1 Pulp fibers:

Unbeaten, softwood, Kraft fibers forming blotting papers were used either as they were (i.e. blotting papers) where polymer solutions were passed through the blotting papers which were then cut into strips and tested for Shear Force, or the blotting paper was reslushed and such-obtained fibers were used in making of handsheets which were then tested for Wet-web Strength.

4.4.2 Cationic polyacrylamide (c-PAM):

Cationic polyacrylamides Percol 63, Percol 292 and Percol 368 from CIBA Specialty Chemicals Canada Inc. were utilized. These polymers vary in the molecular mass (Mw) and degree of substitution (DS) as shown in Table 4.1.

Table 4.1: Comparison of cationic polyacrylamides.

Polymer	Mw (MDa)	DS (%)
Percol 63	6	40
Percol 292	3	25
Percol 368	0.5	100

The polyelectrolytes were dissolved at concentrations of 1 g/L in deionized water, while stirring with a magnetic stirrer for a period of two hours to ensure full polymer dissolution. The pH of these stock solutions were kept at pH=5 to prevent polyelectrolyte hydrolysis.

4.4.3 Wet web strength test

The sample specimens were prepared by placing a plastic mesh over the metal screen of the Standard British Handsheet Machine along with a metal template mold. The template had a pattern with openings to create five paper strips 1.5 cm wide and 15 cm long. As the pulp suspension was introduced, stirred and drained (following the Standard CPPA Methods), due to the template openings, five even paper strips were "pre-cut" in the handsheet. The handsheets were pressed between two Teflon plates at 350 kPa for 5.5 minutes. After the press, the strips were retrieved and tested using Tensile Machine TMI LabMaster.

4.4.4 Shear force test

Whole, uncut blotting papers (20.5 × 20.5 cm) were soaked for two hour in deionized water and then transferred into a custom-made cell. In general, the cell was a rectangular reservoir (~1.5 L volume) equipped with a screen. The function of this equipment was to: (i) secure a blotting paper in place on the top of the screen; (ii) allow aqueous polymer solutions to pass through the blotters with the assistance of a peristaltic pump; and (iii) seal the edges of the blotter in such a way that a polymer solution was forced to go through the blotter, not around it. A polymer solution (1 L) was introduced to the cell and, as it passed through the swollen blotter, it was continuously recirculated by the peristaltic pump. After 30 minutes of treatment of the blotters with polyelectrolytes, the excess of polymer was washed by deionized water using the same technique. The polymer-treated blotting papers were then cut into strips (6 × 2.5 cm). Two paper strips were pressed against each other between two Teflon plates ensuring that

the total area of contact between those two paper strips was constant at 4 × 2.5 cm. The adhered specimens were then tested for shear force needed to separate them by using Tensile Tester John Chatillon and Sons, NY.

4.5 Results and Discussion

4.5.1 Fiber entanglement

Although parallel deformable fibers can develop a larger potential contact area than crossed fibers, they cannot form a coherent sheet. For paper to exist, the fibers must be entangled. Without entanglement the potential contact area among fibers, developed during drying, is not large enough to produce sufficient adhesion. This can be demonstrated by pressing together wet sheets and measuring the shear force required to separate them. In Fig. 4.5, an example is shown using blotting paper. The blotters were chosen because the fibers are unbeaten, without any additives and, because of low density, the fibers are relatively loose, and therefore, more deformable in response to capillary forces. The upper curve represents the tensile strength of wet sheets measured as a function of solids content. For the sake of clarity, the numerous experimental points (more than 80) are omitted. The results for the shear force indicates that as long as there is enough free water between two sheets, the shear force increases with increasing solids content. After reaching a maximum, the adhesion between the sheets decreases, becoming zero when no more free water is present between the fibers. The difference between the tensile strength and shear tension experiments shows that to form a coherent sheet the fibers must be entangled.

4.5.2 Wet web strength in the presence of polyelectrolyte

The idea of increasing the primary wet web strength by introducing cationic polyelectrolytes appears to be plausible by considering the fact that polymers increase the tensile strength of dry and rewetted paper. Their action could be visualized by either forming interfiber bridges or by increasing the concentration of polymeric components in the aqueous layer covering the fiber surface. In the first case, the adhesion between the fibers should be enhanced by additional interfiber bonds; in the second, case by more effective interpenetration of polymeric chains. The polyelectrolytes are known to flocculate fibers suspended in water, thus indicating adsorption and potential bridge formation. The extent of flocculation is, however, a function of polymer addition. It has been shown (Solberg, Wägberg 2003) that with modified cationic polyacrylamide (cPAM) of high molar mass (10 MDa), the maximum flocculation takes place at about half coverage of the fiber surface by a polymer. This is the optimum situation for bridge formation. With an increasing coverage the surface becomes further coated with polymer, and consequently, the opportunity for bridging decreases. At full coverage, the fibers in suspension remain dispersed due to electrosteric repulsion, but at the same time the opportunity for more effective interpenetration increases when fibers are brought together by capillary forces.

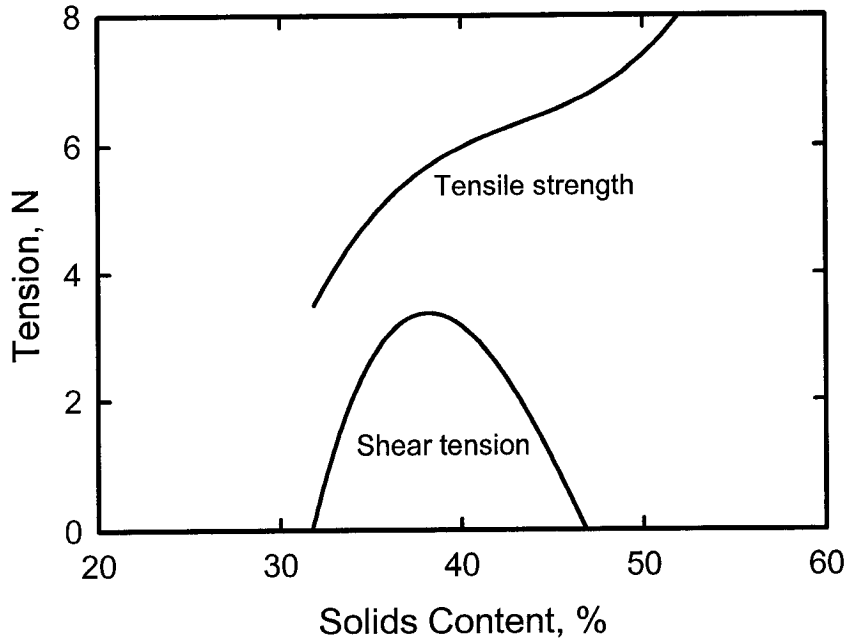

Fig.4.5: The comparison of the force to break wet blotters and the shear force required to separate wet blotters (pressed together at low solids). Experimental points are omitted for clarity.

The reality is that some polyelectrolytes adsorbed on fibers do not affect the wet-web strength, and those which are effective in enhancing the tensile in the dry sheet are actually detrimental to the wet web. It has been reported that increasing the addition of cationic starch results in a decrease in wet-web strength (Laleg, Pikulik 1993b). Figure 4.6 shows the effect of cationic polyacrylamide (Percol 63, CIBA) on wet web formed from unbeaten soft wood kraft pulp. The addition of 1 mg/g fiber is most detrimental apparently due to the fact that at this addition the fiber flocculation is at a maximum, resulting in a non-uniform distribution of fibers. The detrimental effect also increases with the molar mass of c-PAM as shown in Fig. 4.7, except for low molar mass for which there is no or a small positive effect. This could be due to a complex formation between

hemicelluloses and c-PAM. For low molar mass c-PAM, the thickness of the adsorption layer could be less than that of hemicelluloses alone.

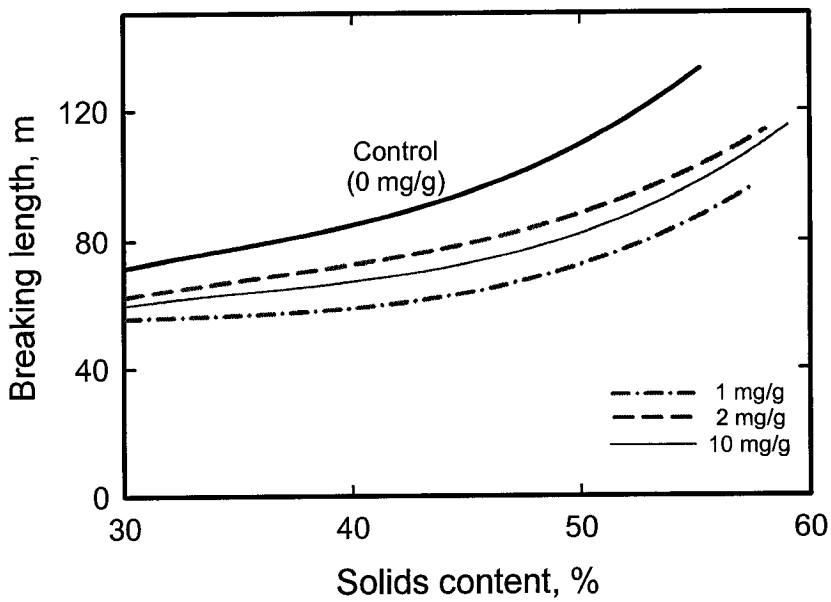

Fig. 4.6: Strength of wet web as a function of solids content for unbeaten Kraft fibers untreated and treated with different amounts of cationic polyacrylamide (Percol 63). Experimental points are omitted for clarity.

The interpretation of the observations appears to be quite evident. In the assembly of entangled fibers, the distance to which the capillary forces can bring their surfaces together, increases due to the presence of the adsorbed polyelectrolytes. The fibers can also slide easier over each other resulting in decreased wet-web strength. It has been shown (Zauscher, Kilengenberg 200b) that the friction between swollen fibers decreases when covered by polyacrylamide (Percol 175, CIBA, UK). The decrease is directly related to the amount of adsorbed polyelectrolyte, indicating that the polymer acts as a lubricant. Only after most of the water is gone, the polymeric chains can start to interpenetrate, and thus, to increase the interfiber bonding. Therefore, the polyelectrolyte, effective as a dry strength agent, is detrimental to wet-web strength.

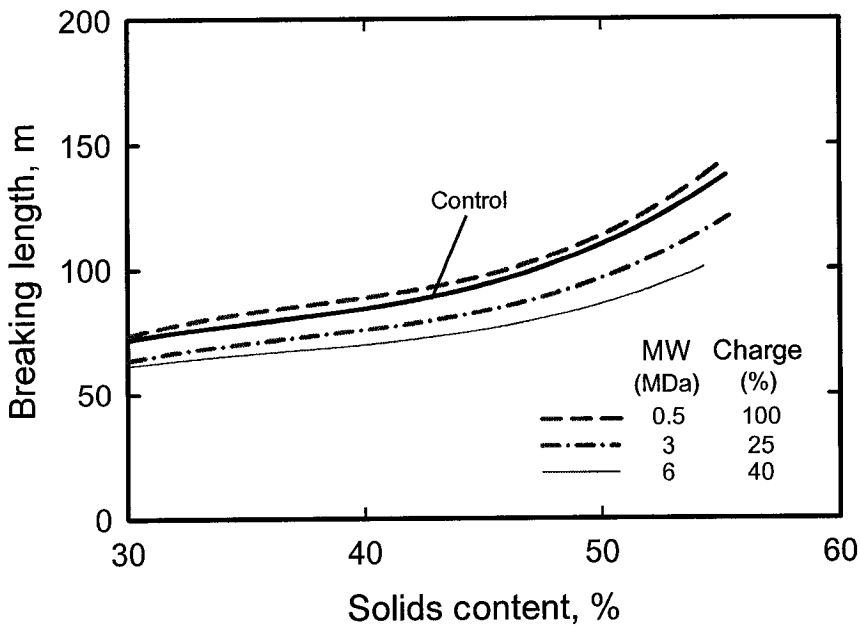

Fig. 4.7: Strength of wet webs as a function of solid content for unbeaten Kraft fibers treated with 10 mg of different cationic polyacrylamides per gram of fibers. Experimental points are omitted for clarity.

4.5.3 Shear force between two wet sheets

If it is true that decreased friction between polymer-coated fibers reduces the wet-web strength, one would expect a similar effect in the shear force between wet sheets pressed together. This was tested by fully coating wet blotters by c-PAM and pressing them together. The coating was done by circulating a cPAM solution through the wet blotters, held on a screen. The results of the shear force required for such sheets to slide over each other are shown in Fig. 4.8. It can be seen that cPAM weakens the shear tension at solids contents below the maximum and has little effect beyond the maximum. Thus overall, the shear tension is reduced, as expected. The behavior at solids contents beyond the maximum is related to the fiber saturation point (FSP), which is the amount of

water associated with the fiber wall. For a water content less than the FSP, no free water is present between the fibers and the friction between sheets is similar to that between dry sheets (i.e. very low). The adsorption of polymers on the external surface of the fibers does not have a large effect on the FSP, and one expects that very small shear tensions are reached at about the same solids content as for bare fibers, as observed. Thus, the shear tension experiments support the conclusion from wet web strength measurements that the reduction in wet-web strength with polyelectrolytes is due to reduced friction between fibers.

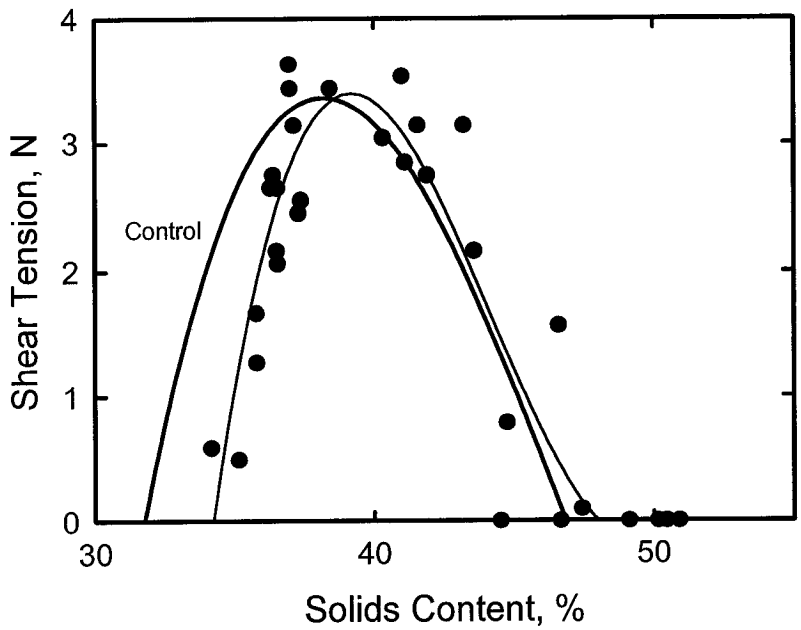

Fig. 4.8: Shear force required to separate wet blotters for non-treated fibers and fibers fully coated by c-PAM. For the sake of clarity, experimental points for untreated fibers are omitted.

The overall behavior also implies that the adhesion between fibers due to interdiffusion of polymeric chains in not significant in the region of solids content up to

60%. This would all leave the mechanical entanglement and the overall friction between fibers being responsible for the sheet coherency in the transition region between capillary attraction and molecular bonding.

4.6 Conclusions

The coherency of an assembly of entangled fibers is the result of two different phenomena occurring at low and high solids contents. In the presence of free water (at low solids content) the capillary forces keep fibers together. After drying (high solids content), it is believed that interfiber molecular bonding, most likely mainly by hydrogen bonds, are responsible. But what happens in the transition period, when the free water is gone, is not clear. The swollen fibers cannot develop close contact due to steric or electrosteric repulsion resulting from a layer of dissolved polymers covering the fiber surface. Two possibilities for the coherency of a wet sheet in the transition region are: (i) interdiffusion of polymeric chains that promotes interfiber adhesion; or simply (ii) a mechanical entanglement of fibers. However, an argument against the interpenetration of polymer chains (other than that interpenetration might be too slow on the time scale of paper pressing) is that the adsorption of cationic polyelectrolytes, which will increase the concentration of polymers on the fiber surface, is actually detrimental to the strength of the wet web. This can be explained by the observation that the presence of additional polymeric chains results in an increased steric and possibly electrosteric repulsion. Together with decreased friction, this makes it easier for the fibers to slide over each other, thus lowering the wet-web strength. For fibers only partly covered by polymer, the

wet-web strength is even lower, likely because of fiber flocculation causing non-uniformity in the sheet.

4.7 Acknowledgements

The research was performed in collaboration with DOMTAR, namely R. Gratton, R. Beaudoin and H. Pande. The financial support from DOMTAR and NSERC, Grant CRDPJ 272913-03 made this work possible.

4.8 References

1. **Alince, B. and van de Ven, T.G.M.** (1997): Porosity of swollen pulp fibers evaluated by polymer adsorption, 11th Fundamental Research Symp., Cambridge, UK, Sept. 1997, "The Fundamentals of Papermaking Materials," Vol.2, p. 771-788, Ed. C.F. Baker, Pira International, Surrey, UK.
2. **Campbell, W. B.** (1933): The cellulose-water relation in papermaking, Forest Service Bulletin 84. Dept. of Interior, Canada,
3. **Eriksson, M., Notley, M.N., and Wägberg, L.** (2005): The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibres, J. Colloid Interface Sci. 292, 38.
4. **Holmberg, M., Berg, J. and Claesson, P.** (1996): Direct measurement of forces between cellulose surfaces, International Paper and Coating Chemistry Symposium 1996, Ottawa, Canada pp. 77-81.
5. **Holmberg, M., Berg, J., Stemme, S., Ödberg, L., Rasmusson, J. and Claesson, P.** (1997): Surface force studies of Langmuir - Blodgett Cellulose Films, J. Colloid Interface Sci. 186, 369.
6. **Laleg, M. and Pikulik, I.I.** (1993a): Unconventional strength additives, Nordic Pulp Paper Res. J. 8(1), 41.
7. **Laleg, M. and Pikulik, I.I.** (1993b): Modified starches for increasing paper strength, J. Pulp Paper Sci. 19(6), 248.
8. **Lyne, L. M. and Gallay, W.** (1954): Studies in the fundamentals of wet web strength, Tappi 37(12), 698.
9. **McKenzie, A. W.** (1964): The structure and properties of paper, Part XXI. The diffusion theory of adhesion applied to interfiber bonding. Appita 37(7), 580.

10. **Neuman, R. D., Berg, J. M. and Claesson, P. M.** (1993): Direct measurement of surface forces, papermaking and paper coating systems, Nordic Pulp Paper Res. J. 8, 96.
11. **Osterberg, M.** (2000): The effect of cationic polyelectrolyte on the force between two cellulose surfaces. J. Colloid Interface Sci. 229, 620.
12. **Pelton, R.** (1993): A model of the external surface of wood pulp fibers, Nordic Pulp Paper Res. J. 8(1), 113.
13. **Salmi, J., Saarinen, T., Laine, J. and Stenius, P.** (2003): The effect of cationic polyelectrolytes on surface forces and structure of cellulose-polyelectrolyte interface, 5th International Paper and Coating Chemistry Symposium June, 2003, Montreal, Canada pp. 157.
14. **Solberg, D. and Wägberg, L.** (2003): On the mechanism of cationic-polyacrylamide-induced flocculation and re-dispersion of a pulp fiber dispersion, Nordic Pulp Paper Res. J. 18(1), 51.
15. **Wågberg, L. and Annergren, G.** (1997): Physico-chemical characterization of papermaking fibres, 11th Fundamental Research Symp., Cambridge, UK, Sept. 1997, "The Fundamentals of Papermaking Materials," Vol.1, p. 1-83, Ed. C.F. Baker, Pira International, Surrey, UK.
16. **Zauscher, S. and Klingenberg, D. J.** (2000a): Normal forces between cellulose surfaces measured with colloidal probe microscopy, J. Colloid Interface Sci. 229, 497.
17. **Zauscher, S. and Klingenberg, D. J.** (2000b): Surface and friction forces between cellulose surfaces measured with colloidal probe microscope, Nordic Pulp Paper Res. J. 15(5), 459.

CHAPTER 5

CONCLUSIONS

5.1 Overview

The assembly and coherency of swollen fibers inside a paper sheet are explained by the capillary forces produced between fibers, water and air. These forces are responsible for keeping the fibers together as long as there is enough free water wetting the fiber wall. From the point onward after the free water is gone, the interfiber bonding is believed to be sustained by hydrogen bonds created between the cellulose polymer chains. But hydrogen bonds may be developed only in a very close contact between fibers, i.e. when the fibers are collapsed and dried. This indicates that there exists a "transietion region" where neither capillary forces nor hydrogen bonds are predominant.

The results have shown that attractive van der Waals forces do not play a role in the adhesion of swollen fibers and that capillary forces are in fact the major interactions between swollen fibers in the range of 30-45% solids content. The importance of capillary forces for adhesion of swollen fibers was demonstrated by the shear tension between two wetted blotters pressed together. The results showed that as long as there is enough water wetting the fibers, the adhesion of the pressed blotters is almost as high as the tensile of wet blotter themselves. Another important observation concerns the role of water surface tension. By decreasing the water surface tension with Sulphonated Kraft Lignin (SKL), we obtained detrimental results for the wet web strength as well as for the shear tension, confirming our arguments that capillary forces are responsible for keeping fibers together at wet stages.

Beyond the region where capillary forces dominate, we propose that mechanical entanglements of fibers are the major interaction responsible for keeping fibers together.

In fact, the simple act of refining fibers enhances wet web strength. Similarly, the use of microfibrils for wet web strength and shear tension has proven to increase the adhesion between swollen fibers. The flexibility and size of the microfibrils indicates that they can entangle to a higher degree than fibers alone, therefore when they are applied together with fibers in the handsheet making or on top of blotter papers, they increase enormously the wet web strength and the shear tension, mostly due mechanical interactions. The difference between entanglements of fibers and microfibrils was also evaluated. Using glass fibers; handsheets made of glass fibers and microfibrils, we obtained results for the wet web strength three times higher then handsheets made of glass fibers and pulp fibers.

The interactions between Precipitated Calcium Carbonated (PCC) and swollen fibers were also evaluated using PCC-filled handsheets. The addition of stabilized PCC particles by Polyethyleneimine (PEI) has shown no detrimental effect to the wet web strength of PCC-filled handsheets (between 30-40% solids content). On the other hand, flocculated PCC particles by cationic polyacrylamide (c-PAM) caused a negative impact in all circumstances. This strongly indicates that friction, originating from deposition of single PCC particles or small aggregates on fiber surface, plays an important role in the wet web strength. In addition, the introduction of large PCC flocs (nearly 80 μm) inside the handsheets may prevent fiber-fiber entanglements, thus reducing the wet web strength.

Small PCC particles showed a better performance on wet web strength in all cases when compared to large PCC particles. In fact, the smaller fillers produced smaller flocs in the presence of retention aids (i.e. c-PAM), leading to less interference with fiber entanglements.

The retention aid dosage has shown to have little effect on the wet web strength of PCC-filled handsheets. Partial and full coverage of polymer has basically shown the same results, and no large differences were observed in the retention of PCC inside the handsheets by varying the retention aid dosage.

Also, the importance of polyelectrolytes to the adhesion of swollen fibers was evaluated. The adsorption of cationic polymer increases the concentration of polymers on the fiber surface, forming a polymer layer that is actually detrimental to the wet web strength. This polymer layer (formed by either hemicelluloses or adsorbed polymer) will generate a greater steric or electrosteric repulsion between the fibers, reducing the friction between fibers and therefore reducing the wet web strength.

5.2 Recommendations for future work

It is important to evaluate the importance of friction effects among swollen fibers. This will require additional experiments involving additions of insoluble colloidal particles and soluble polymers to the handsheets and/or blotters. Those experiments will detail the enhancement of the wet web strength by friction effects.

Another recommendation would be the optimization of the components: PCC and retention aid inside the handsheet. This may benefit the paper industry to optimize their process control of the wet web strength of papers filled with PCC.

APPENDIX

Tensile Strength

Tensile strength is the measurement of paper resistance (or wet web resistance) to stress produced by tension. It is defined at the maximum stress developed before the wet web breaks. A tensile tester machine TMI Lab Master Inc. was used in order to perform most of the experiments. This tensile has a very sensitive cell, in order to perceive any minimum difference in the measurement of the wet web strength. It has a maximum force of 2300 grams with a standard deviation of 0.5% of the reading. The testing speed may vary from 0.025 to 76 centimeters per minute [1], where the speed chosen for the experiments was nearly 2.5 centimeters per minute. The strips of the wet web were 1.9 cm wide and 6.5 cm long and they were placed vertically in the tensile tester supported by the clamps. A typical behavior of tensile strength graph is shown in Fig. 1.

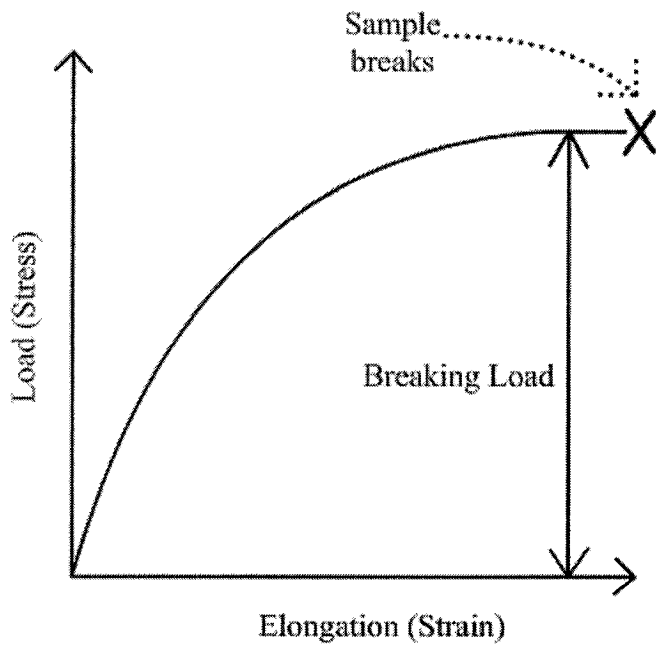

Fig. 1: Typical stress-strain behavior of wet webs.

Another way to measure the tensile strength is using the breaking length units, which describes how strong the material is regardless of its dimension. In fact the breaking length is the measurement of how long a hanging strip of any material (i.e. wet web) must be in order to break under its own weight. To find the breaking length of the wet web strip, we must measure the mass it takes to break it with known width and basis weight.

$$BL = \frac{m}{BW \cdot W} \qquad [1]$$

Here, BL is the breaking length (m), m is the mass to break the wet web (g), W is the width of paper (m) and BW is the basis weight (g/m2).

Reference

1. User Manual Tensile Tester TMI Lab Master Inc. Document no. IM/858000-0001 Rev.01.