Paper and Surface Chemistry – Part 1- Fiber Surface and Wet End Chemistry

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Abstract

Paper manufacturing and converting involves a multitude of surface chemical interactions. Beating, stock preparation, coating and converting processes are steps where surface phenomena play an important role for product consolidation and performance. Interactions between fibers and colloidal particles, polymers, minerals and, dyes are fundamental in papermaking and most of them are complex and not very well understood. Thus, many paper formulations are designed according to an empirical trial-and-error approach. This work is a critical literature review of some of the interactions present in papermaking, coating, and printing. In the first part, the current models for fiber surfaces and their interactions in the wet end are discussed. Limitations concerning the fiber surface definition and the available models based on direct observation, DLVO theory, and a combination of qualitative and quantitative approaches are highlighted. Complexity factors such as surface composition heterogeneity, contamination from manufacturing processes, and surface mobility are suggested to be considered. Surface interactions present in the wet end, with focus on reversible and irreversible flocculation as well as on the flocculation mechanisms concerning fibers, polymers and micro-particles are also discussed. The role of the fiber surface chemical composition on flocculation and flock size and the influence from the chemical medium in the paper machine is reviewed. Papermaking is suggested as being a fiber surface modification process once polymers and other chemicals are used to change the surface energy and chemical composition. Modification by formation of cellulose esters or attachment of aluminum abietate onto surface anionic groups is believed to occur during sizing. Modification which affects the fiber-fiber bond with the aim of improving the wet and dry strength properties is also discussed. Accessibility of anionic groups in pulp fibers to the chemicals during the short time scale of papermaking process as well as competition for the same charged sites are still not clear and its implications are reviewed. Comments are made on the limitations regarding the present process monitoring using measurements with no specificity. A combination of different sorption and chemical microscopy methods is suggested as a suitable approach to clarify surface interactions. Why does a paper formulation need such a number of additives? Where are they attached on the fiber? Questions of this nature are challenges not only in the scientific point of view, but also to market perspectives, demanding critical research work. Another idea presented in this review is the application of surface engineering to pulp fibers. Surface engineering is a concept traditionally applied to development of coating for metals and its main goal is the modification of material surfaces in order to achieve desired properties. This concept has a good potential for eucalyptus based pulp and paper, especially for improving strength and absorbing properties. The strategic application of surface chemistry in the pulp and paper industry can also be a useful tool, not only for

patents and product development, but also to improve troubleshooting and customer support.

Key words: *Papermaking, pulp fibre, surface chemistry, flocculation, surface engineering.*

1. An overview of paper machine and papermaking

Paper is believed to be invented in 105 B.C. by Ts'ai Lun, a member of the Chinese Empire. Since that time until 1798, when the first paper machine was built, all paper produced over the world was hand made. The first paper machine was invented in France by Nicholas Louis Robert and was improved in England by Bryan Donkin and John Gamble. The work of improvement was supported by Fourdrinier brothers and then the paper machine was named Fourdrinier.

A paper machine is usually divided in different sections, i.e., head box, forming, press, drying, surface treatment, and reel (Fig. 1). The wet end part of the machine is that composed by the head box, forming and press sections and it is named like that because it requires a high amount of water to operate. The part composed by press and reel is usually named dry. Other paper machine types than the Fourdrinier were developed using different forming section designs. Paper machines can have different size and width, being from laboratory pilot scale to large industrial installations. The production speed of a paper machine can vary from a few to thousands meters per minute.
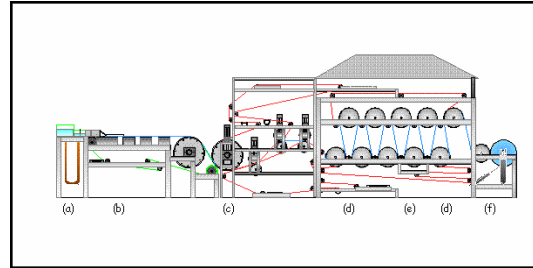
Figure 1. *Schematics of a Fourdrinier paper machine. (a) Head box; (b) Forming; (c) Press; (d) Drying; (e) Surface treatment (optional); (f) Reel (www.abo.fi/fak/ktf/pap, 2001).*

The production flow in a paper mill usually starts with pulp refining and subsequent addition of non-fibrous components such as fillers, starches, retention and sizing aids, optical brighteners and other, then dilution is made with water before or inside the head box. During this sequence there is a flocculation process where fibers, minerals, colloidal particles and dissolved substances are aggregated in macroscopic flocks. The flow goes from the head box to the forming section where a significant amount of water is removed from the flock before the sheet reaches the press, drying and reel. The surface treatment section can be on-line or off-line. Surface sizing, coating and calendaring are treatments often used.

2. Pulp fiber and definition of surface

Pulp fibers are cells extracted from plants. The extraction of pulp fibers from wood can be done using chemical, mechanical, thermo- and chemi-mechanical processes. Pulp is

2

composed by different types of cells which are dependent upon the wood used as raw material. The term "fiber" is related to libriform cells in hardwoods and tracheids in softwoods. Other cells are present in minor proportion and are not considered fibers, e. g., vessel elements in hardwoods and parenchyma cells in softwoods and hardwoods.

The thickness of the fiber cell wall can vary between 3-15 μm depending on the wood species. The cell wall is formed by the primary and secondary walls and the latter is divided in S1, S2 and S3 layers (Fig. 2). The primary wall is close to the middle lamella while the S3 layer is near the fiber lumen. Each layer is made of macrofibrils which are built from microfibrils. Cellulose macromolecules disposed on amorphous and crystalline regions build the microfibrils (Larsson et al, 1997). A monolayer of cellulose macromolecule has a thickness of 0.6 nm (Sugiyama et al, 1991).

Pulp fiber has a tubular shape with internal and external surfaces. The internal surface makes an interface with the lumen and the external surface makes an interface with the middle lamella (Kolseth and Ruvo, 1986). The fiber cell wall is porous and the pores also contribute to the internal surface. During chemical pulping and bleaching a large fraction of the primary cell wal is removed with lignin. Thus, the external surface of the bleached pulp fiber is believed to be the secondary fiber wall (Laine and Stenius, 1996; Treimanis, 1996). In case of mechanical, thermo- and chemi-mechanical pulps the external surface is mainly formed by fractions of middle lamella and primary cell wall.
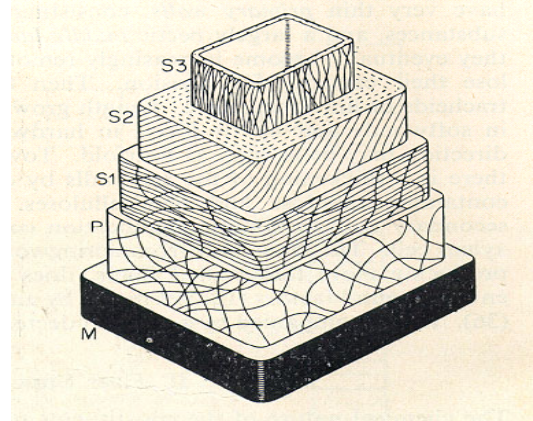

Figure 2. *Cell wall structure of a wood fiber. Middle lamella (M), primary cell wall (P), transition lamella (S1 layer), main layer of the secondary wall (S2 layer), tertiary wall or tertiary layer of secondary wall (S3 layer) (Rydholm, 1965).*

Research and studies on the characteristics and interactions of external fiber surfaces when present in aqueous and papermaking media have been performed based on models. Pelton (1993) did an interesting review and has classified the models for external surfaces as qualitative and quantitative ones. He has also proposed a combination between them to be more adequate. The current models are discussed in the next section.

2.1 Qualitative models for the fiber external surface

Qualitative models are based on direct observation of the pulp fibers and no physical or mathematical approach is applied. According to the qualitative models, fiber surfaces show roughness at nanometer scale. Experiments performed using Atomic Force Microscopy (AFM) has also indicated that lignin can be unevenly distributed on the unbleached fiber surfaces, with regions of exposed and covered fibrils (Lorenzoni, 1998). AFM image of a eucalyptus pulp

*refined in a PFI mill also showed stratification (Fig. 3).*
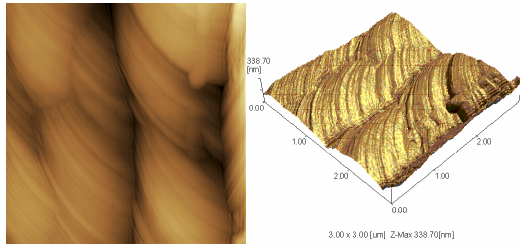
Figure 3. *AFM image of a kraft unbleached eucalyptus pulp, Kappa number 24, refined at 3000 revolutions PFI. Image presented in topographic mode, bi-dimensional (left) and tri-dimensional (right). Roughness and stratification observed at nanometer scale (Fardim, 1999).*

Limitations concerning formulation of models based on direct observation are mainly related to the susceptibility of the fiber to its external medium or changes on interfaces. When fibers are in contact with air or in high vacuum conditions such as used in Scanning Electron Microscopy (SEM), there is a reduction in the number of pores and deformations in comparison with the situation when fibers are in water, according to thermoporosimetry (Maloney and Paulapuro, 1999). Surface specific area is also drastically reduced when the pulp is dried (Herrington and Midmore, 1984a). This reduction can be irreversible and a phenomenon known as hornification may take place (Wise, 1998). Surface area can be defined in a simple way as the interfacial area between two different phases and if the pulp fiber is compared with a sponge, the surface area means the regions accessible to water or air and thus molecules or ions present in these components.

2.2 Quantitative model and DLVO colloidal stability theory

The quantitative model assumes that the fiber surfaces are flat and hold electrical charge in aqueous medium. The Deryagin-Landau-Verwey-Overbeek (DLVO) theory (Overbeek, 1970) is the fundament of the quantitative model and it based on estimation of energies of London-van der Waals (attraction) and double-layer overlapping (repulsion).

A sum of attractive (Va) and repulsive (Vr) potentials can be represented by a total energy interaction curve (Fig.4). According to this curve, particles at short and long distances have its attraction favored while particles situated at intermediary distances tend to face repulsion. Concentration of electrolytes can affect the maximum of the total energy interaction curve. High electrolyte concentration reduces the maximum potential and deposition is favored if particles have opposite surface charge. This deposition can be reversible, if it occurs at the point of secondary minimum in the curve or irreversible, if it occurs at the primary minimum (Fig. 4).
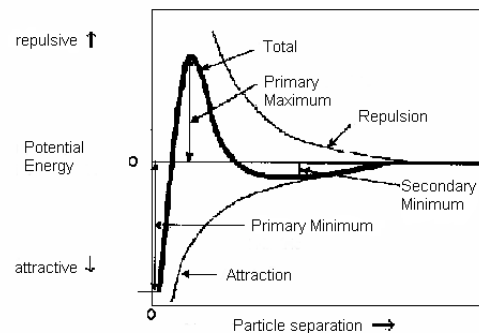

Figure 4. *Total interaction energy curve showing attractive London-van der Waals and electrostatic repulsive potentials (Pelton, 1993).*

The retention of colloidal particles by pulp fibers to build flocks is the base of papermaking. According to the DLVO theory, pulp fibers should have a high capacity of particle retention which could be observed in Britt Jar experiments. This prediction is also supported by the low Zeta potential values, within a range of -1.6 to -14 mV for kraft pulps (Herrington and Midmore, 1984b). However, low retention values were observed for TiO2 particles and pulp fibers, being up to 10 % and not improved by electrolyte addiction. This retention level is considered very low and it may indicate that the DLVO theory is not suitable to describe the fiber surfaces (Pelton, 1993).

2.3 Pelton´s Model

A combination between the quantitative and qualitative models was suggested by Pelton (1993) which consider a cover layer of hydrated polymer bearing terminal electrical charges on the surface in a similar way as it was previously proposed by Clark (1978). According to this model, the deposition of particles on the surface is inhibited by steric stabilization due to effect of a hydrated polymeric layer (Fig. 5). Adhesion between two surfaces can only be achieved if there is compression of polymeric cover layers, but this is not thermodynamically favored. Presence of electric charge on the surface layer can also enhance the water solubility and contribute to the steric stabilization. Surface roughness is another parameter which affects the adhesion between fiber surfaces and different particles due to irregular structure and absence of flat regions.
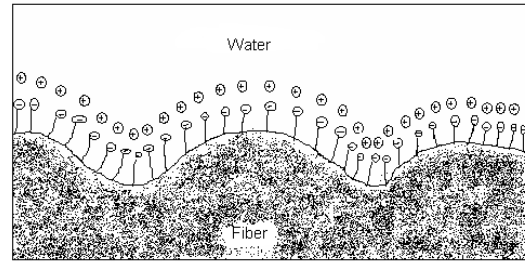
Figure 5. *Illustration of the Pelton's model (1993). Fiber surface is covered with a polymer bearing electrical charges and affecting adhesion of colloidal particles due to steric stabilization.*

2.4 The fiber surface complexity

The approach of a polymeric layer on the surface as it was proposed in the Pelton's model requires revision. Recent research using AFM (Okamoto and Meshitsuka, 1999; Simola et al, 2000), enzymatic hydrolysis and CZE (Sjöberg et al, 1999), MALDI-ToF-SIMS (Linqvist and Dahlman, 1998; Jacobs et al, 1999), contact angle (Fardim and Durán, 2000a), XPS (Laine et al, 1994; Westermark, 1999; Fardim and Durán, 2001) and ToF-SIMS (Fardim and Durán, 2000b; Fardim et al, 2001) has shown that the fiber surfaces have different components bearing different hydrophilic character and ionizable functional groups. These components can be fragments of lignin, hemicelluloses, cellulose and extractives located on the surface and originated during pulping and bleaching or simply deposited (Buchert et al, 1996). Contaminants which are present on closed circuits can also sorb onto the surface. Other parameter to be considered is the surface mobility or changes in the chemical composition of the surface monolayer according to the medium which makes interface with the fiber. Extractives which have hydrophobic character can migrate to internal regions and when the fiber is

5

dried they can return to the surface again. The complexity factors discussed here indicate that the fiber external surfaces have a heterogeneous character not considered in anyone of the current models.

3. Surface chemistry and paper machine wet end

The paper machine wet end is composed by stock preparation, head box, formation and press sections. The purpose of the press section is to remove the excess of water and the surface phenomena involved are limited to changes in surface tension during paper drying.

The formation of macroscopic flocks composed by polymers, colloidal particles, filler, and pulp fibers is the main goal of the wet end during paper production. Flocks must have enough strength to resist to the turbulent flow in the head box and also the shear forces in the forming wire. A multitude of surface phenomena are involved in the wet end and are direct related with desired paper characteristics.

3.1 Reversible and irreversible flocculation

Flocculation is an aggregation process where the particle identity is maintained and which can classified as reversible and irreversible. Reversible flocculation is believed to occur at inter-particle distances close to the secondary minimum on the DLVO total energy curve (Fig. 4) while irreversible flocculation may occur at the primary minimum. Reversible flocculation is also termed coagulation according some authors. Irreversible flocculation is a

spontaneous process if there is a reduction in the system total free energy.

Considering a system of colloidal particles separated firstly at infinite distance and then at H distance, makes possible to formulate a general equation for the total free energy (ΔG) involved in the flocculation process as following:

$\Delta G = \Delta G^{Atr}$ *(van der Waals)* $+ \Delta G^{Rep}$ *(short distance)* $+ \Delta G^{Rep}$ *(electrostatic)* $+ \Delta G^{Rep}$ *(steric)* $+ \Delta G$ *(other effects)*
[1.1]

All parameters on the Equation 1.1 take part on flocculation, but in case of irreversible flocculation there is a predominance of the parameter concerning the van de Waals attractive forces. When a particle approaches a flock there is a reduction in the translational movement of the aggregate system and also on its degree of freedom. Thus, the entropy (ΔS^{Agr}) *is reduced and the free energy increases according the Equation 1.2.*

$\Delta G^{Agr} = -T[\Delta S^{Agr}]$
[1.2]

Usually it is assumed that irreversible flocculation is dominated by free energy and the contribution form entropy is not significant (Everett, 1989). The energy barrier to reach the primary minimum at the DLVO total energy curve is overwhelmed in the irreversible flocculation resulting in a spontaneous process. This effect is obtained by addition of electrolytes which contribute to the compression of the Stern-Gouy electrical double layer and reduces the repulsion between particles (Mangelsdorf and White, 1998).

The addition of electrolytes is not enough for flocculation of pulp fibers and mineral particles in papermaking due to reasons already discussed in the section 2. The repulsive potential is then reduced by addition of polymers or polyelectrolytes which hold electric charges with different polarity as those present on the particle and fiber surfaces.

3.2 Retention aids and flocculation mechanisms

Polymers or polyelectrolytes used to improve flocculation in papermaking are usually termed retention aids. Cationic starch used in stock preparation is also believed to contribute to retention as well as on dry strength. Drainage and retention are important parameters in the paper production and requires that the flock formed has not only strength, but also that the water on its structure needs to be easily removed.

Retention is also affected by mechanical interlacing of flocks in the formation wire. High-molar mass polymers used as retention aids can increase the colloidal attraction forces and induce flocculation by different mechanisms, i.e., bridging, network, depletion, and bridging combined with micro-particles.

Bridging flocculation involves adsorption of terminal and intermediary regions of the polymeric chain on the particle surface forming an aggregate fixed by the polymeric chain (Fig. 6). High polymer concentrations can hinder the bridge formation between particles due to the tendency to cover their surfaces. It is believed that the optimum polymer concentration to achieve flocculation by this mechanism is half of the

amount needed to cover the entire particle surface (Lindström, 1989).
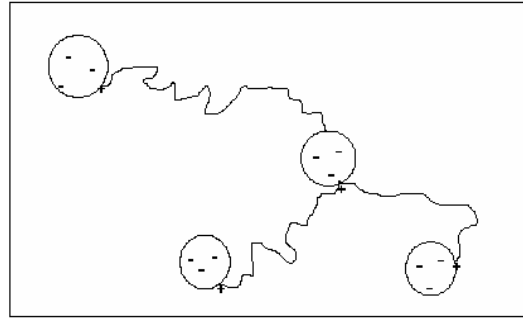
Figure 6. *Bridging flocculation mechanism. Different segments of the polymeric chain bind the particles and an aggregate is formed.*

Network flocculation can happen if the polymer concentration is very low, being adsorbed on the surface of a few particles and thus transform then onto small electric dipoles with extremes of opposite charges. Under this condition, particles are oriented in a way that mutual electrostatic attraction is achieved (Fig. 7).
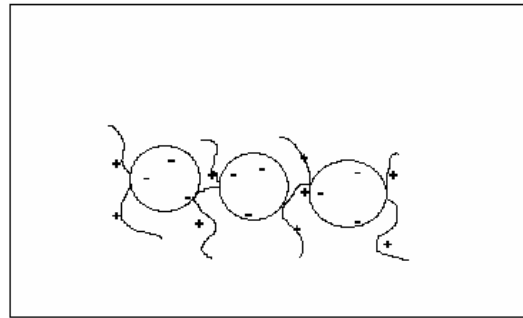
Figure 7. *Network flocculation mechanism. Polymers used in low concentrations are adsorbed onto the particle surfaces forming electric dipoles and generating inter-particle attraction.*
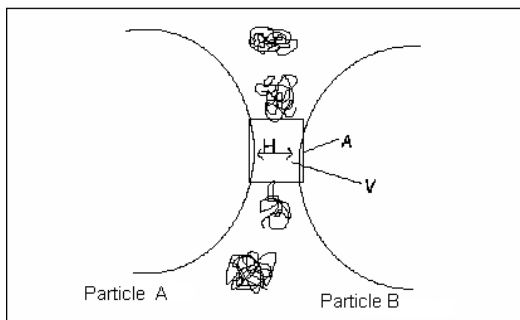
Flocculation by depletion mechanism occurs if a weakly or no adsorbed polymer is present when two particles approach each other. The polymer is excluded from an inter-particle region of a volume V, area A and separation H, causing a negative adsorption

7

according to the Equation 1.3, where c is the polymer concentration (Everett, 1989). When the particle separation H decreases, the negative adsorption increases resulting in an attractive force (Fig.8).

$$\Gamma = -cV$$
[1.3]

Micro-particle systems using either silicates or bentonite combined with high molar mass polymers are used in flocculation by bridging-micro-particle mechanism. The bridging is similar as described previously, but in this case the system highly flocculated after polymer addition is submitted to shear and the macro-flocks are broken into micro-flocks. At this point, micro-particles are added and the macro-flock is rebuilt, however, it has higher resistance to turbulence and shear than an ordinary macro-flock formed only using polymer. It is believed that the micro-particles interact via electrical charge attraction with the polymer segments attached to the particles and reflocculation is caused by bridging between polymer chains connected to the micro-particles (Swerin et al, 1995).

Figure 8. *Flocculation by depletion mechanism. A weakly or no adsorbed polymer is excluded from an inter-particle region.*

Research on flocculation dynamics is traditionally performed in experimental scale using turbidity and dynamic drainage or Britt jar measurements. However, more sophisticate techniques such as Scanning Tunneling Microscopy have been applied and information about flock size and resistance to shear forces may be obtained (Gerli and Clémencon, 1999).

3.3 Fiber surfaces and flocculation

Flock resistance is affected by different types of forces: normal forces between fibers, forces due fiber flexibility and elasticity, friction forces, and colloidal attractive forces. (Kerekes et al, 1985). There are different statements regarding which factor is predominant on flock formation and resistance. In one side there are hypotheses of domination of hydrodynamic effects (Beghello, 1998) while in another side there hypotheses that chemical effects and colloidal attraction dominate (Wågberg, 1987). There are also some common points between the different hypotheses. The common points are the effects of consistence, fiber length, fiber-fiber contact, turbulence and shear forces on flocculation. However, the main discordances are related to the effect of the medium, i.e., electrolyte concentration and pH.

Fiber surface composition is recognized as an important effect on flocculation by the different hypotheses. Both statements considered that the higher concentration of anionic groups on the surface makes the fiber more sensitive to paper machine medium and flocculation is reduced. Flock size is also affected by surface composition and small flocks are observed when

higher concentration of anionic groups is present on the surface (Beghello, 1998). The bleached pulp fiber with lowest total concentration of anionic groups is the pine ECF while the highest concentration is observed for eucalyptus ECF (Fardim et al, 2001). However, effects of formation of a surface layer gel on flocculation and particle retention for pulps with different amounts of anionic groups are presently been investigated.

3.4 Sizing, and dry and wet strength aids

Flocculation is not the unique phenomenon which involves surface interactions in the wet end (Isogai et al, 1997; Berg, 1993). During stock preparation or ahead of the head box, components are added to modify the fiber surface free energy. These addictives are compounds with hydrophobic character and holding terminal groups which can attach to the fiber surface via electrostatic interaction or chemical reaction. The latter can yield cellulose ester derivatives.

Modification of fiber surfaces with the purpose of reduce the water penetration into the paper structure is termed sizing. This process is classified as alkaline, neutral or acidic sizing, depending on the pH in the reaction medium (Tab.1). Additives used in sizing modify both surface free energy and surface chemical composition (Ozaki and Sawatari, 1997; Carlsson, 1996). A homogenous sizing aid distribution on the fiber is dependent upon the absence of restrictive effects and availability of superficial groups. Chemical interfering and morphological parameters such as excessive roughness are the main restrictive effects.

Chemical interference in sizing reactions using alkenyl succinic anhydride (ASA) can be attributed to dicarboxylic acids formed due to the ASA hydrolysis in water. Alkyl ketene dimmer (AKD) can also have hydrolysis in water at high temperatures and the formation of ketones interferes on the distribution of sizing aids on the fiber surface (Roberts, 1992).

Type of sizing	pH range	Components	Cellulose derivatives formed
Acidic	*3.5-5.5*	*Abietic acid derivatives and alum or aluminum polycloride*	*Alumium abitate attached on fiber anionic groups*
Neutral or Alkaline	*7.0-9.0*	*Alkyl ketene dimmer (AKD)* *Alkenyl succinic anhydride (ASA)*	*Cellulose ester*

Table 1. *Different sizing process in acidic, neutral and alkaline media (Roberts, 1992)*

Modification of fiber surfaces in papermaking is not limited to sizing, usually other additives such as dry and wet strength aids are employed and the interaction fiber-fiber is affected. The latter additives are believed to modify the fiber surface composition by insertion of functional groups which hinder the formation hydrogen bonds between fibers and water molecules with concomitant increase in fiber-fiber bonds. As a consequence the fibrous network has a higher strength in wet and dry media. Components usually applied for this purpose are anionic and cationic polyacrylamides, polyamines and polyamides. Imines, urea and melamine formaldehyde are also

employed specifically for wet strength purposes (Proverb, 1999).

4. Interactions in the paper machine, theory and reality

"I think that also we should be more careful in expressing too confidently our opinions about phenomena occurring in the papermaking processes…in most cases, we still have hypotheses only –which can be very helpful in our daily work, but at the same time it can be basically very uncertain and only render the mystery more mysterious" (Stén, 2000). In fact, concepts of interactions involving macromolecules are still limited not only for papermaking but also for polymer chemistry, bioactive substances, catalysis, lubrication and microelectronics. However, it is matter of time, budget and interest to clarify them in a scientific basis.

Paper machine has a universe of interactions and a great part of them are still unknown. A system containing fibers and a second component, i.e., filler, polyelectrolyte and starch can be studied in laboratory using a medium with a known ionic strength and a theoretical treatment considering the adsorption kinetics can be applied in spite of some limitations. However, in case of a paper machine the system is composed by fiber and a great number of additives in conditions where consistence and ionic strength can vary in a significant way. Another factor of complexity is the presence of organic and inorganic cations as paper chemicals and also in the paper machine white water. The existence of competition between the different cationic components to the anionic sites on the fiber is

practically unknown. Exchange between components with different affinity to anionic sites during the different stages of papermaking as well.

Other important factor in a paper machine is interaction time scale, i.e., at a few seconds. Laboratory experiments have shown that in spite of the flocculation occur in scales of less than a second, the diffusion of a polyelectrolyte through the cell wall can take up to 30 minutes in chemical pulps, being up to 120 minutes for mechanical pulps. This can be an indication that just a portion of anionic groups present in pulp are accessible to ion-exchange during papermaking.

Anionic group accessibility is dependent upon the medium which the fiber is inserted, its carboxyl group counter-ions and consequently degree of cell wall swelling (Sjöstrom, 1989). Probably, interactions concerning surface groups are favored due to the higher accessibility during the papermaking dynamics, but this can also increase the possibility of competition and or ion-exchange on the fiber anionic sites. The amount of surface anionic groups in ECF pulp fibers is about 20 % of the total anionic groups (Laine et al, 1996). This value is around 10 $\mu mol/g$ in the external surface layer of 10 nm depth. The distribution of these groups as well as its interactions with paperchemicals and in fiber-fiber bonds is still unknown.

Presently, the routine determinations of conductivity, turbidity and cationic demand in papermaking are limited parameters to interpret the phenomena here discussed, because they are unspecific parameters.

Determination of total organic carbon in the white water can give an indirect quantification of dissolved substances and colloidal particles, but it is also a parameter not specific. Application of chemical microscopy techniques (Hagenhoff, 2000, Brine, 1993) combined with adsorption methods (Wågberg and Ödberg, 1989) seems to be a suitable approach to evaluate which components are really attached onto the fibers.

5. Surface engineering, concept and strategies for eucalyptus pulp fiber

Surface engineering is the application of surface modification strategies to design new functional properties of a material. This field involves professionals of different areas, being usually applied to metal coating, but it was already suggested for pulp fibers (Tze and Gardner, 1999).

Papermaking is a fiber surface modification process according to several aspects discussed here, however; it is usually not recognized like that. The lack in this understanding has a consequence of opportunity losses regarding the development of new pulp and paper products. The knowledge of papermaking interactions in a molecular level is a great challenge with attractive perspectives not only for scientific interest but also for market purposes. Reduction of the number of raw materials used in paper formulations and a new level of competitiveness will be achieved with this knowledge.

Surface modification of eucalypt pulp fibers can be used to improve strength, printability and absorption properties

as well as to fulfill the needs of different types of paper. This strategy can add economic value to the products, make possible a positive distinction in international markets and generate patents. The effects of pulping and refining processes of eucalyptus pulp fibers on the surface chemical composition and its relation with physicochemical and absorption properties has been already reported (Fardim, 1999).

6. Conclusion

Concepts of surface chemistry are practically involved in all stages of papermaking. The papermachine wet end section has a multitude of surface interactions with the aim of formation of flocks with defined resistance to the hydrodynamic forces and shear present in process conditions. Fiber surface have experimental characteristics which are not in accordance to the current models proposed. Recent research has been showing that the fiber surfaces have a heterogeneous character and complexity factors not considered in current models. Knowledge about interactions between pulp fiber and paperchemicals are based on hypotheses and models limited to two or three components, requiring an approach more oriented to realistic situations. The concept of surface engineering usually applied for metal coating can also be applied to fiber surfaces with a good potential of technological improvement for eucalyptus pulp and paper.

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