FUNDAMENTAL ASPECTS OF ADHESION BETWEEN CELLULOSIC SURFACES IN CONTACT – A REVIEW

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ABSTRACT

This paper presents a review on the adhesion between cellulose fibers. The function of water in the assembly of paper is examined. The contributions of friction, interfibrilar water structure, hydrogen bonds, van der Waal forces, as well as electrostatic linkages therein are discussed. The phenomena of adhesion between wet cellulose fibers in the consolidation of a fibrous web can be visualized as a sequence of events with water playing a key role throughout. Initially, the drainage of water brings the fibers together to form the wet web where the water-structuring effects of the hydrophilic cellulose surfaces can contribute to long-range interactions to form a virtual gel between fibers. Subsequently, with the departure of more water, the cellulose surfaces are drawn even closer so that chemical interfiber bonds ranging from van der Waals forces through hydrogen bonds, ionic to covalent, if appropriate functional groups are present can become activated. Finally, the most common additives utilized commercially for the enhancement of interfiber adhesion are summarized in terms of the accepted operating mechanisms.

INTRODUCTION

The adhesion between cellulose fibers is critical to the strength properties in paper and cardboard, both in the dry and wet states. In the past 50 years the formation of hydrogen bonds by hydroxyl groups on adjacent cellulose surfaces has been accepted as the main cause of unions between fibers (Nissan, 1962).

Recently, however, it is believed that more factors come into play, and that water could have a more important role than previously thought; even the preponderance of hydrogen bonds is still a subject of debate for some authors (McKenzie, 1984; Hubbe, 2006). The adhesion between cellulosic fibers is a complex phenomenon not yet fully understood. The main theories about the adhesion of cellulosic fibers that have been proposed to date include (Gardner, Oporto *et al.*, 2008):

1. Mechanical interlocking, caused by irregular surfaces.
2. Intermolecular diffusion caused by molecular chains interacting between the cellulosic surfaces.
3. Chemical interactions/attractions that can be attributed to acid-base interactions, hydrogen bonding, van der Waals and electrostatic forces.

So far, there is no single theory to explain the phenomenon of adhesion in a satisfactory manner, rather it may be seen as the sum of several mechanical, physical and chemical forces, which can operate simultaneously and influence each other. But ultimately, it is recognized that the union of cellulosic fibers is due to hydrogen bonds. However, a fundamental fact cannot be ignored: to form hydrogen bonds cellulose fiber surfaces are required to be in contact in the range of molecular distances. All distances reported in the literature vary from 0.15 to 0.35 nm (Pelton, 2004; Linhart, 2005; Gardner, Oporto *et al.*, 2008). These values are much smaller than the actual dimension of surface roughness of fibers, ranging from 10 to 10,000 nm. Thus, the roughness can drastically limit the molecular contact between adjacent surfaces (Hubbe, 2006). Even softwood pulp

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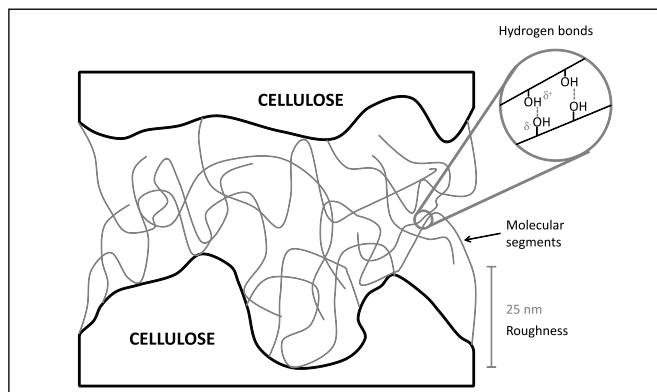
Figure 1. Schematic representation of two adjacent cellulosic fibers surfaces. Roughness and microfibril formation of hydrogen bonds between them are showed

fibers, unbeaten and fully bleached, have 25 nm roughness, and crevices and valleys (pores) of various sizes (Pelton, 2004) (**Figure 1**). It is therefore highly unlikely that a significant number of hydroxyl groups on opposite surfaces could form hydrogen bonds when the surfaces are brought closer only by pressing (McKenzie, 1984).

MOLECULAR DIFFUSION THEORY

One of the most relevant concepts that may lead to a plausible mechanism responsible for bringing together cellulosic surfaces to a distance favorable for interactions on a molecular level is the diffusion theory of Voiutskii (1963).

This theory suggests that the surfaces of cellulosic fibers in water behave like a swollen polymeric hydrogel, i.e. water-soluble polymers that cannot be dissolved because their chains are restrained. The adhesion between wood pulp fibers in water does not occur at this point, because their surfaces interact more favorably with water molecules than with each other, an effect known as "steric stabilization". The spontaneous formation of flocs observed is probably due to mechanical interlocking (Pelton, 2004).

In accordance with the diffusion theory, it has been proposed that in papermaking the wet sheet is compressed by surface tension forces acting perpendicular to the plane of the sheet, so that water drains and fiber surfaces begin to approach (McKenzie, 1984); it also considers that the friction between fibrillar elements should play an important role in these early stages (de Oliveira, Maric *et al.*, 2008). However, despite these efforts the mechanisms of friction between cellulose surfaces remain largely unexplained; there have been attempts to relate friction with the adhesion phenomena, but research is limited by the effects of roughness and surface humidity, which usually are not taken into consideration (Feiler, Stiernstedt *et al.*, 2007).

In later stages of paper production, such as wet pressing and drying, the web continues to lose water until it reaches a content below which the hydrogel surfaces begin to adhere. According to Lyne and Gallay (1954), at this point (70%-80% moisture) the effects of surface tension of the sheet seem to pass through an inflection point, after which the bond between fibers seems to develop vigorously, as evidenced by a marked increase in sheet strength. This increase is due to the intermingling of mobile molecular segments on opposite surfaces (McKenzie, 1984; Pelton, 2004; Hubbe, 2006). If the process of removing water continues, it reaches the minimum distance required for short-range interactions to occur between cellulose chains, such as electrostatic attraction, polar interactions, hydrogen bonding and van der Waals forces.

^{1}H -NMR studies have shown that at 20% moisture content in paper the minimum separation between the microfibrils is four monolayers of water, which is reduced to only one when the moisture content falls to 10% (Topgaard and Söderman, 2001).

On the other hand, Pollack and coworkers have summarized previous observations on the phenomena of exclusion of many substances in areas adjacent to hydrophilic surfaces, including biological tissues, natural and artificial polymers, and proteins, among others. Although the nature of the exclusion zone is not well established and exists the notion that the organization of water can be extended to distances equivalent to two or three monolayers (Zheng and Pollack, 2003), recent studies using Nafion and UV/Vis spectroscopy have shown that water organization extends to distances of tens or hundreds of nanometers. The structured water (called the fourth state of water) could well be the direct bridge to interfibrillar linking (Pollack, Figueroa *et al.*, 2009).

Additional forces

Besides hydrogen bonds, van der Waals forces make an important contribution to the adhesion between cellulosic fibers. The attractive van der Waals forces exist between molecules of solids and result from the movement of electrons in atoms, creating temporary dipoles. There is a repulsive electrostatic double-layer force between charged surfaces in an aqueous medium, whose length is determined by the properties of the solvent in which, for example, the valence of the counterions has a dominant role. In addition, double-layer forces depend on the surface charge density and properties of the aqueous medium, typically pH. These surface forces affect the molecular adhesion between cellulosic fibers and, consequently, the ultimate strength of paper (Eriksson, 2006).

van der Waals forces decrease as a function of surface separation,

which has implications in many practical applications. For example, wood fibers that have been subjected to intensive pulping and bleaching exhibit low surface charge, so that the repulsive component is relatively small compared to the van der Waals forces. Thus, at a medium surface separation, enough to overcome the usual roughness inherent to natural fibers, the resulting interaction will be one of attraction (Notley, Pettersson *et al.*, 2004).

On the other hand, chemical pulps have carboxylic groups that impart negative charges to fibers. These groups have their origin in the residual hemicelluloses after pulping, as well as the direct oxidation of cellulose with some reagents, such as ozone, oxygen and hydrogen peroxide in bleaching stages. The acid groups can cause swelling of the fiber, which increases its plasticity and the ability to form bonds (Barzyk, Page *et al.*, 1997). However, they also cause electrostatic repulsion if the concentration of these groups is considerable (Torgnysdotter and Wågberg, 2004). During sheet consolidation, there is a balance between compressive capillary forces and the electrostatic repulsion between fibers. If the latter decreases, the fibers will be able to approach, which should lead to better bond formation between fibers in contact (Torgnysdotter and Wågberg, 2004).

POLYMERIC ADDITIVES FOR IMPROVING PAPER RESISTANCE

The main factors that influence paper strength are fiber strength, bond strength between fibers, the bonded area (usually expressed as energy per unit-bonded area) and fiber distribution. Fiber strength is rather depending on the species of wood, pulping and bleaching processes used in the production of fibers and the number of recycles a fiber has undergone. However, strength additives are designed to affect mainly bond strength and bonded area (Scott, 1996).

The natural presence or addition of hydrophilic polymers to cellulosic fibers improves adhesion between surfaces and produces chemical hydration of fibers, thereby improving bonding. The presence of hydrophobic substances inversely affects the bonding process (Davison, 1980).

The following sections provide a brief discussion of the main strength additives used commercially, highlighting the main operating mechanisms to impart dry and wet resistance to paper.

Dry strength

Dry strength agents are generally water soluble polymers (or dispersible), which are incorporated into pulp and are able to adhere to the surface of fibers by hydrogen bonds or electrostatic interactions (Davison, 1980). Wood fibers have their own dry strength agent in the form of hemicelluloses. It is well known that if hemicelluloses are removed from fibers in pulping or by some other treatment, it is more difficult to develop a good bonding between them.

In general, a dry strength additive must meet at least three characteristics: high molecular weight (polymeric material), soluble or dispersible in water and substantive to fibers to ensure its retention.

Dry strength agents widely used by industry are starch and acrylamide based polymers. Others used in a smaller scale are some vegetable polysaccharides such as guar and xanthan gums (Wang and Jiang, 2006).

Starch is probably the dry strength additive most widely used commercially, accounting for approximately 95% of total such additives. Industry experience has shown that cationic substituents need to be incorporated into the structure of native starch in order to achieve the high retention levels required in paper manufacture (**Figure 2**). Thus, starches have been modified
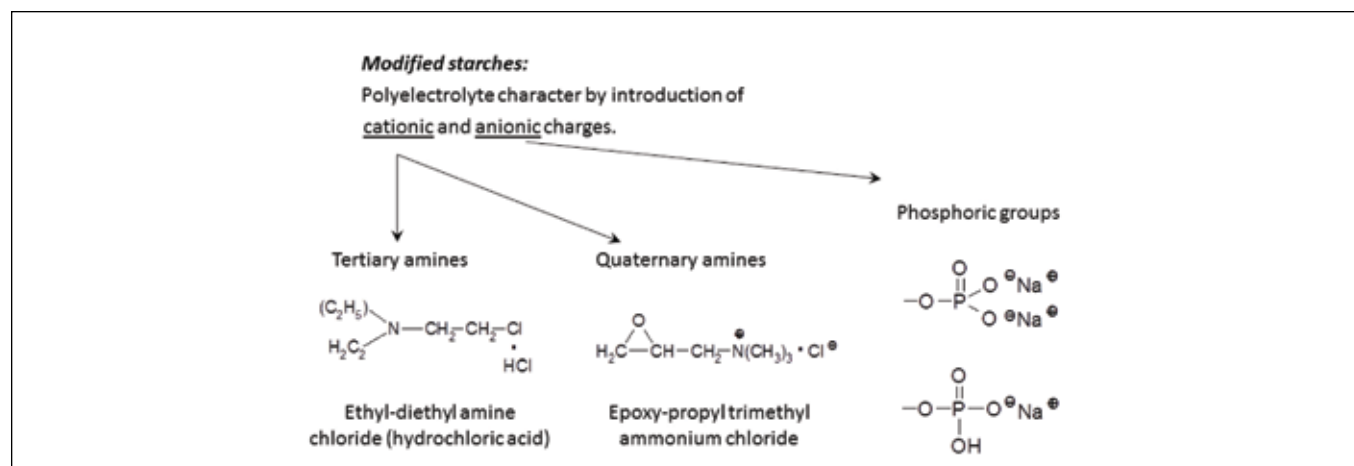

Figure 2. Starch derivatives most used as dry strength agents

to introduce tertiary (2-chloro ethyl diethylamine) and quaternary (e.g. 3-chloro-2-chloride hydroxypropyl trimethylammonium) amines (Scott, 1996). The product is a cationic starch (CS) with a high degree of dispersion and high retention on the fibers.

It has been suggested that CS imparts resistance mainly by increasing both the number of fiber-fiber joints and the specific strength of the bond. The combination of good retention and efficiency can achieve the desired results in dry strength with dosages of 0.5%-1%. Amphoteric starches constitute a different kind of modified starches, which are especially useful when the use of CS may generate too many cationic charges in the pulp. To produce the amphoteric character, a second reaction is needed after cationization, which can be etherification in alkaline medium to incorporate carboxyl or sulfate groups or esterification to incorporate phosphate groups. The latter are commonly used as additives for paper.

Polyacrylamide resins constitute the largest part of the world consumption of synthetic strength resins; the average consumption is 300 g of polymer per ton of paper (Holik, 2006). The first polyacrylamide resins used were anionic and required cationic substances, such as alum, for retention on pulp. Today, polyacrylamide copolymers are used with a wide variety of cationic groups, such as dimethyldiallylammonium chloride, viny benzyl trimethylammonium chloride or 3-acrylamido-3-methyl butyl trimethylammonium chloride (**Figure 3**). The molecular weight of these polymers varies from 100,000 to 500,000 Daltons, a range low enough to avoid flocculation by bridging between particles, and high enough to retard migration of the polymer through the pores of the fibers, thus preventing loss of activity over time.

A new type of synthetic polymers with applications in paper strength have emerged recently with the development of polyvinyl formamide (PVF) (Pfohl) and polyvinyl amine (PVAm) (Lorencak, Stange *et al.*, 2000; Miao, Leduc *et al.*, 2008). These water-soluble polymers contain primary amino groups, which are able to form hydrogen bonds with hydroxyl groups on the fiber surface, thereby improving bonding between fibers. These products have no residual monomers and do not contain formaldehyde or organically bound chlorine. These additives are applied in the form of solutions or emulsions (10%-40% solids) in doses ranging from 0.1%-0.5% of solid material.

Wet strength

When paper is exposed to water, pulp fibers are wetted and swell quickly, because of the inherently hydrophilic components of the fiber. This swelling results in loss of contacts between fibers leading to a dramatic decrease in paper strength properties. In order to maintain paper strength in the wet state, it is necessary to add wet strength additives (WSA) to the pulp furnish. WSA consist of polymer resins that protect the bonds between cellulose fibers and, in some cases, reinforce adhesion with covalent intra- and interfibrillar chemical bonds. The resin chemical nature determines the way it acts as a WSA (Roberts, 1996).

WSA are added in the pulp preparation stage and therefore are required to be soluble, cationic polymers. Solubility ensures homogeneous dispersion of additives and their effective distribution in the pulp suspension. Their cationic character facilitates adsorption by ion-exchange mechanisms. A high molecular weight polymer is more easily absorbed and can form stronger bonds. These characteristics are very important
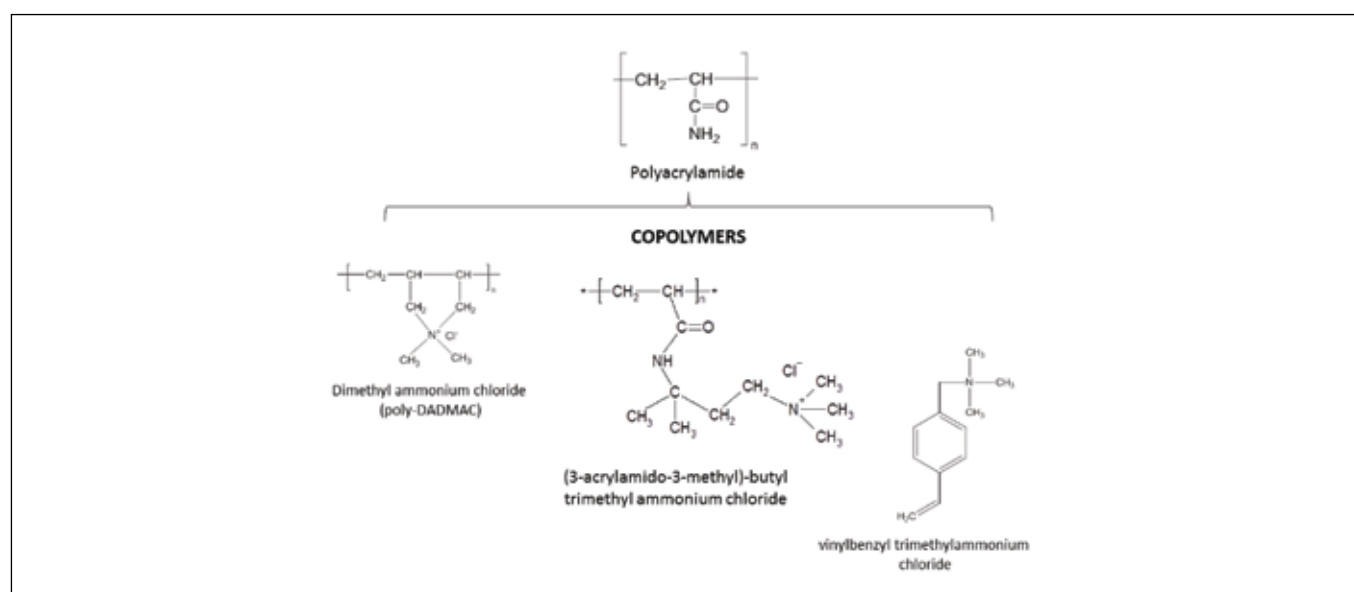

Figure 3. Polyacrylamide and their copolymers used as dry strength agents

because WSA should be adsorbed onto the fibrous surface to form a network that protects the joints and inhibits interfibrillar swelling (Espy, 1995).

The first acid-curing cationic resins used as WSA were condensation products of urea and formaldehyde to which small amounts of a polyamine were added to make them cationic. Methylol groups are dehydrated to form methylene groups and methylene ether bridges between the urea units. This crosslinking protects fiber-binding sites. It is unlikely that resins react with the polysaccharide fraction of fibers, rather the anionic nature of hemicelluloses aids resin retention (Swanson, 1965).

In melamine-formaldehyde resins, methylol groups form bridges between units of melamine similar to those formed in the urea formaldehyde resin, which results in a three-dimensional interwoven structure that protects the weak interfibrillar junctions. In addition, methylol groups can also react with cellulose.

Polyamidoamine epichlorohydrin resins (PAAE) cure in neutral/alkaline medium and are known as azetidinium type (**Figure 4**).

These resins are produced by condensation of a polyamine (e.g. diethylenetriamine) with a dibasic acid or ester to form a polyamine amide (Fischer, 1996; Obokata and Isogai, 2007). Epichlorohydrin reacts with primary and secondary amines to form the respective aminopolyamide epichlorhydrin intermediate. At neutral pH and temperature above room temperature the tertiary aminochlorohydrin moieties self-alkylate to form 3-hydroxyazetidinium groups. These strained rings confer the resin both a cationic character and reactivity, independently of pH. Some of the hydroxyazetidinium
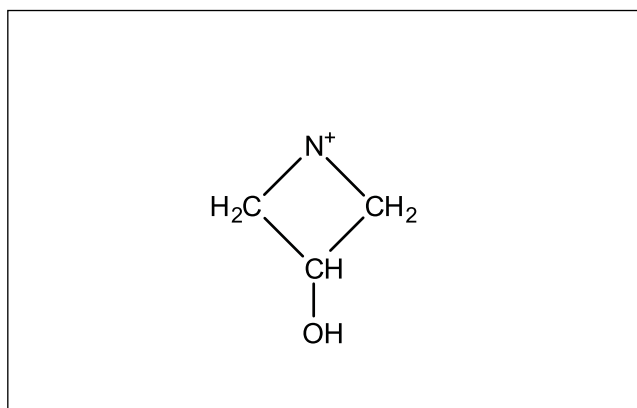

Figure 4. Azetidinium group of cationic character

moieties react within the macromolecule building molecular weight whilst maintaining solubility. These compounds probably react with carboxyl groups present in cellulose through the formation of ester groups (Espy, 1995). Epichlorohydrin can also react with tertiary amines present in the main polymer chain to form a quaternary amine epoxide. This epoxide is more reactive than the azetidinium group, and can be hydrolyzed unless is stabilized with hydrochloric acid to produce chlorohydrins. Chlorohydrins treated with dilute alkali form epoxy groups again, and the reactivity of the resin is completely restored allowing reaction not only with carboxyl groups contained in the pulp, but also with cellulose hydroxyl groups forming ether bonds [28].

The type of resins that contain aldehyde groups cure under acidic conditions and provide "temporary" wet strength due to the formation of acetal and hemiacetal bonds with the cellulose hydroxyl groups (Espy, 1995). The first commercial aldehyde resins were cationic dialdehyde starches; later, polyacrylamides modified with glyoxal entered the market. The temporary wet strength nature of these additives can be seen in papers treated with aldehyde resins and immersed in water over 2 hours. The initial wet strength is reduced to a third, compared to only 10%-20% in resins based on formaldehyde or the polyamino- and polyamide-epichlorhydrin type. Dialdehyde glyoxal promotes the crosslinking of polyacrylamide, resulting in an increase in molecular weight. Moreover, the formyl groups can react with hydroxyl groups of polysaccharides to form hemiacetal bonds. Acetal formation between the formyl and the hydroxyl groups in the main chain of dialdehyde starch can crosslink polysaccharides and bind to cellulose.

A case of wet strength additives for special papers is polyethylenimine or PEI. It has been postulated that PEI acts as a WSA through the mechanism of "*Jack in the box*" (Allan and Reif, 1971). This mechanism postulates that the polymer chains diffuse into the microcavities and pores of the fiber surface at alkaline pH, where the hydrodynamic volume allows them to penetrate. When pH is reduced, PEI chains are caught up physically because of an increase in their hydrodynamic volume when the multiple nitrogen atoms of PEI become protonated. It has been suggested that the mechanism for imparting wet strength is due to ionic interactions between the carboxyl groups of cellulosic fibers and cationic centers of the PEI resin, which is apparently sufficient to resist the action of water. ∎

REFERENCES

1. Allan, G. G.; Reif, W. M. (1971): *Fibre surface modification. Part 6. The Jack-in-the-box effect: a new mechanism for the retention of polyethylenimine and other polyelectrolytes by pulp fibres.* Svensk Papperstid. 74 (2) 25-31Barzyk, D.; Page, D. H.; Ragauskas, A. (1997): *Acidic Group Topochemistry and Fibre-to-Fibre Specific Bond Strength.* J. Pulp Paper Sci. 23 (2) J59-J61

2. Davison, R. W.*: In Theory of dry strength development.* Dry strength additives; Reynolds, W. F., ed; Tappi Press: Atlanta, GA, 1980.

3. de Oliveira, M. H.; Maric, M.; van den Ven, T. G. M. (2008*): The role of fiber entanglement in the strength of wet papers.* Nordic Pulp Paper Res. J. 23 (4) 426-431

4. Eriksson, M. (2006): *The Influence of Molecular Adhesion on Paper Strength.* Department of Fibre and Polymer Technology, School of Chemical Science and Engineering. Stockholm, Sweden, KTH, Royal Institute of Technology. Doctoral Thesis in Fibre Technology.

5. Espy, H. H. (1995): *The mechanism of wet-strenght development in paper: a review.* Tappi J. 78 (4) 90-99

6. Feiler, A. A.; Stiernstedt J.; Theander, K.; Jenkins, P.; Rutland, M. W. (2007): *Effect of capillary condensation on friction force and adhesion.* Langmuir 23 (2) 517-522

7. Fischer, S. A. (1996): *Structure and wet strength activity of PAE resins having azetidinium functionality.* Tappi J. 79 179-185

8. Gardner, D. J.; Oporto, G. S.; Mills, R.; Samir, M. A.S. A. (2008): *Adhesion and Surface Issues in Cellulose and Nanocellulose.* J. Adhes. Sci. Technol. 22 545-567

9. Holik, H.*; Handbook of Paper and Board,* Wiley-VCH: Weinheim, Germany, 2006.

10. Hubbe, M. A. (2006): *Bonding between cellulosic fibers in the absence and presence of dry strength agents-* A review. BioRes. 1 (2) 281-318

11. Linhart, F. (2005): *Some thoughts on the mode of action of paper strength agents.* Wochenbl. Papierfabr. 133 (11/12) 662-672.

12. Lorencak, P.; Stange, A.; Niessner, A.; Esser, A. (2000): *Polyvinylamin- ein neues Polymer zur Papierverfestigung.* Wochenbl. Papierfabr. 128 (1/2) 14-18

13. Lyne, L. M.; Gallay W. (1954): *Fiber properties and fiber-water relationships in relation to the strength and rheology of wet webs.* Tappi J. 37 (12) 581-596

14. McKenzie, A. W. (1984): *The structure and properties of paper. Part XXl: The diffusion theory of adhesion applied to interfibre bonding.* Appita J. 37 (7) 580-583

15. Miao, C.; Leduc, M.; Pelton, R. (2008): *The influence of polyvinylamine microgels on paper strength.* J. Pulp Paper Sci. 34 (1) 69-75.

16. Nissan, A. H. (1962*): General principles of adhesion with particular reference to the hydrogen bond.* Trans. Symp., Fundamentals of papermaking fibres F. Bolam. Oxford, England, Tech. Sect. British Paper Board Mak. Assoc. 119-134

17. Notley, S. M.; Pettersson, B.; Wägberg, L. (2004): *Direct measurement of attractive van der Waals' forces between regenerated cellulose surfaces in an aqueous environment.* J. Am. Chem. Soc. 126 (43) 13930-13931.

18. Obokata, T.; Isogai, A. (2007): *The mechanism of wet strength development of cellulose sheets prepared with PAE resin.* Colloids Surf., A 302 (1-3) 525-531

19. Pelton, R. (2004): *On the design of polymers for increased paper dry strength-* A review. Appita J. 57 (3) 181-190

20. Pfohl, S.*: Water-soluble copolymers containing vinylamine units as wet strength and dry strength agent for paper.* U. S. Pat. 4,978,427 1990.

21. Pollack, G. H.; Figueroa, X.; Zhao, Q. (2009*): Molecules, Water, and Radiant Energy: New clues for the origin of life.* Int. J. Mol. Sci. 10 1419-1429

22. Roberts, J. C.*; The Chemistry of Paper,* Royal Soc. Chem.: Cambridge, U.K., 1996.

23. Scott, W. E.*; Principles of wet end chemistry*, TAPPI Press: Atlanta, GA, 1996.

24. Swanson, J. W.: In Wet Strength in Paper and Paperboard; Weidner, J. P., ed; Tappi Press: New York, 1965.

25. Topgaard, D.; Söderman, O. (2001): *Diffusion of Water Absorbed in Cellulose Fibers* Studied with 1H-NMR. Langmuir 17 (9) 2694-2702

26. Torgnysdotter, A.; Wågberg, L. (2004): *Influence of electrostatic interactions on fibre/fibre joint and paper strength.* Nordic Pulp Paper Res. J. 19 (4) 440-447

27. Voiutskii, S. S. (1963): *Autohesion and adhesion of high polymers.* Polym. Rev. 4 (XIV) 272

28. Wang, X. H.; Jiang, C.: *In Encyclopedia of Surface and Colloid Science;* Somasundaran, P., ed; CRC Press Taylor and Francis Group, Ciudad, 2006.

29. Zheng, J.-m.; Pollack, G. H. (2003): *Long-range forces extending from polymer-gel surfaces.* Phys. Rev. E. 68 31408-31401